

THE UNIVERSITY OF LEICESTER

DEPARTMENT OF CHEMISTRY

STUDIES ON PHOTO-EXCITED COMPLEX FORMATION

by

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A thesis submitted in partial fulfilment of the
requirements for the degree of Doctor of Philosophy
in the Faculty of Science, University of Leicester.

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STATEMENT

The experimental work in this thesis was carried out in the Department of Chemistry of the University of Leicester between October 1978 and September 1980 and in the Department of Chemistry, The City University London, between October 1980 and September 1981. This work has not previously been presented and is not being presented for any other degree.

A handwritten signature in cursive script, reading 'R.A. Beecroft'. The signature is fluid and stylized, with the first letters of the first and last names being capitalized and prominent.

R.A. Beecroft

December 1982

Mum and Dad

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Some of the work contained in this thesis has previously been published, as detailed below:

- (1) The Quenching of Aromatic Hydrocarbon Fluorescence by α,ω -Diaminoalkanes and the Formation of Excited Ternary Complexes.
R.A. Beecroft, R.S. Davidson* and T.D. Whelan,
J.C.S. Chem. Commun., (1978), 911.
- (2) Examples of Competition Between Energy Transfer and Excited Complex Formation in the Reactions of Benzenoid Compounds with Tertiary Amines.
R.A. Beecroft and R.S. Davidson*,
Chem. Phys. Letts., (1981), 77, 77.
- (3) Photo-induced Electron Transfer Reactions- Pitfalls and Opportunities.
R.A. Beecroft, R.S. Davidson*, D. Goodwin and J.E. Pratt,
Pure and Appl. Chem., (1982), 54, 1605.

CONTENTS

<u>CHAPTER ONE - INTRODUCTION.</u>	<u>Page</u>
<u>1.1.</u> <u>Introduction.</u>	1
1.1.(1). Absorption of Radiation.	1
1.1.(2). The Nature of the Absorption Spectrum.	4
1.1.(3). Modes of Decay from Excited States.	5
1.1.(4). Quantum Yields and Lifetimes of Excited State Species.	11
<u>1.2.</u> <u>Intermolecular Exciplexes.</u>	13
1.2.(1). Factors Affecting Intermolecular Exciplex Formation and Stability.	13
1.2.(2). Methods of Exciplex Formation.	19
1.2.(3). The Role of the Exciplex in Photo- chemical Processes.	24
<u>1.3.</u> <u>Intramolecular Excited Complexes.</u>	27
1.3.(1). Introduction.	27
1.3.(2). Intramolecular Excimer Formation.	28
1.3.(3). Intramolecular Exciplexes.	35
1.3.(4). Competition Between Intramolecular Excimer and Exciplex Formation.	39
1.3.(5). Twisted Excited Charge Transfer Complexes.	40
<u>1.4.</u> <u>Multi-Chromophore Excited Complex Formation.</u>	42
<u>1.5.</u> <u>Object of the Work.</u>	45
 <u>CHAPTER TWO - THE FORMATION OF INTRAMOLECULAR FLUORESCENT EXCIPLEXES IN 1-ARYL-2- (AZACYCLOALKYL)ETHANES.</u>	 50
<u>2.1.</u> <u>Introduction.</u>	50
<u>2.2.</u> <u>Naphthyl Derivatives.</u>	50
2.2.(1). U/V Absorption Spectra.	50

	<u>Page</u>
2.2.(2). Fluorescence Spectra.	52
2.2.(3). Triplet-Triplet Absorption Spectra.	67
<u>2.3. Phenyl Derivatives.</u>	77
2.3.(1). U/V Absorption Spectra.	77
2.3.(2). Fluorescence Spectra.	77
<u>2.4. Summary.</u>	84
<u>2.5. Miscellaneous Compounds.</u>	85

CHAPTER THREE - THE INTERACTION OF EXCITED SINGLET
STATE BENZENE WITH TERTIARY ALI-
CYCLIC AMINES.

<u>3.1. Introduction.</u>	88
<u>3.2. Quenching of the Benzenoid Fluorescence.</u>	88
3.2.(1). Experimental.	89
3.2.(2). Results and Discussion.	95
<u>3.3. Sensitisation Experiments.</u>	107
3.3.(1). Experimental.	107
3.3.(2). Results and Discussion.	109
3.3.(3).. Concentration Effects Upon Sensitised Amine Fluorescence.	115
<u>3.4. Variable Temperature Studies.</u>	117
3.4.(1). Introduction.	117
3.4.(2). Experimental.	118
3.4.(3). Results and Discussion.	119
<u>3.5. The Addition of High Concentrations of</u> <u>Neat Benzene to Solutions of Tertiary</u> <u>Aliphatic Amines in Cyclohexane Solution.</u>	121
3.5.(1). Introduction.	121
3.5.(2). Experimental.	122
3.5.(3). Results and Discussion.	123
<u>3.6. Reversible Energy Transfer.</u>	133

	<u>Page</u>
<u>3.7.</u> <u>Sensitisation Experiments in Tetra-</u> <u>hydrofuran Solution.</u>	137
3.7.(1). Introduction.	137
3.7.(2). Results and Discussion.	138
<u>3.8.</u> <u>The Mechanism of Energy Transfer</u>	143
3.8.(1). Radiative Energy Transfer.	144
3.8.(2). Non-Radiative Energy Transfer.	144
 <u>CHAPTER FOUR - THE PHOTOPHYSICAL PROPERTIES OF</u> <u>SATURATED TERTIARY ALICYCLIC AMINES.</u>	
<u>4.1.</u> <u>Introduction.</u>	148
<u>4.2.</u> <u>Ultra-Violet Absorption Spectra.</u>	157
<u>4.3.</u> <u>Fluorescence Measurements.</u>	160
4.3.(1). Experimental.	160
4.3.(2). Results.	161
4.3.(3). Discussion.	163
<u>4.4.</u> <u>Fluorescence Lifetime Measurements.</u>	166
4.4.(1). Experimental.	166
4.4.(2). Results and Discussion.	167
<u>4.5.</u> <u>Nitrogen-15 Nmr Spectroscopy.</u>	171
4.5.(1). Introduction.	171
4.5.(2). Results and Discussion.	174
<u>4.6.</u> <u>Miscellaneous Amines.</u>	176
4.6.(1). N-Alkylated Azacycloalkanes.	176
4.6.(2). N-methyl-1,2,3,4-tetrahydroiso- quinoline.	177
4.6.(3). Amino-alcohols.	178

	<u>Page</u>
<u>CHAPTER FIVE - STUDIES ON THE PHOTOPHYSICAL</u>	
<u>PROPERTIES OF α,ω-DIAMINOALKANES.</u>	
<u>5.1.</u> <u>Introduction.</u>	180
<u>5.2.</u> <u>Fluorescence Measurements.</u>	185
5.2.(1). Experimental.	185
5.2.(2). Results and Discussion.	185
<u>5.3.</u> <u>Quenching of Triplet State Aromatic</u> <u>Hydrocarbons by α,ω-Diaminoalkanes.</u>	189
5.3.(1). Experimental.	189
5.3.(2). Results and Discussion.	189
<u>5.4.</u> <u>Nitrogen-15 Nmr Spectra of</u> <u>α,ω-Diaminoalkanes.</u>	195
 <u>CHAPTER SIX - INTRAMOLECULAR POLYCHROMOPHORIC</u>	
<u>SYSTEMS.</u>	
<u>6.1.</u> <u>Introduction.</u>	198
<u>6.2.</u> <u>1-Naphthyl Diamino Derivatives.</u>	199
6.2.(1). U/V Absorption Spectra.	199
6.2.(2). Fluorescence Measurements.	199
6.2.(3). Triplet-Triplet Absorption Decays.	214
6.2.(4). ^1H Nmr Studies on Selected N-((1-naphthylethyl)oxamethyl)diamino Derivatives.	217
<u>6.3.</u> <u>Phenyl Diamino Derivatives.</u>	219
 <u>CHAPTER SEVEN - EXPERIMENTAL.</u>	
<u>7.1.</u> <u>Instrumentation.</u>	221
<u>7.2.</u> <u>Preparation of 1-Naphthyl Derivatives.</u>	223
<u>7.3.</u> <u>Phenyl Derivatives.</u>	247

	<u>Page</u>
<u>7.4.</u> <u>Preparation of N-Alkylated Amines.</u>	257
<u>7.5.</u> <u>Preparation of α,ω-Diaminoalkanes.</u>	264
<u>7.6.</u> <u>Purification of Materials by Preparative</u> <u>Gas Liquid Chromatography (Prep GLC).</u>	272
<u>7.7.</u> <u>Sources of Materials Used.</u>	272
<u>7.8.</u> <u>Photophysical Measurements.</u>	273
 <u>REFERENCES.</u>	 281
 <u>APPENDIX (I).</u>	 292

CHAPTER ONE

Introduction.

1.1. BASIC PHOTOCHEMISTRY.

The development of increasingly accurate and sophisticated electronic devices over the last thirty years or so, has provided chemists with the opportunity to investigate extremely fast photochemically induced processes. A mechanistic understanding of these processes has enabled the widespread application of photochemistry in industry and doubtless this trend will continue in the future.

1.1.(1). Absorption of Radiation.

It was suggested by de Broglie⁽¹⁾, that both light and matter have simultaneous wave and particulate properties. Thus light can be thought of as a quantised source of energy, absorbed, transmitted and emitted in discrete units known as photons, whose energy is related to the frequency (ν) of the radiation by the expression,

$$\underline{E = h\nu = hc/\lambda} \quad - \text{Eqn. 1.(1).}$$

(where h = Planck's constant, c = velocity of light, ν = frequency and λ = wavelength of the radiation).

Since the total energy (E_t) of a molecule in its electronic ground state can be expressed in terms of the sum of its electronic (E_{el}), vibrational (E_v) and rotational (E_{rot}) energies, the effect of an interaction with a photon will be to perturb these energies. Transitions affecting only E_{rot} can be brought about using far-IR radiation, those involving E_{rot} and E_v by radiation in the near-IR region and finally transitions involving E_{el} and E_v by using radiation in the visible and ultraviolet regions.

In an unexcited aromatic molecule, the electron spins are paired according to the Pauli Exclusion Principle, to give the singlet electronic ground state (S_0). If a π electron is then

excited without change of spin, then the resultant excited electronic state of the molecule is also a singlet state (S_i), where $i = 1, 2, 3, \dots, n$. However, if during excitation the π electron spin inverts, the excited electronic state of the molecule now becomes a triplet state (T_i), where $i = 1, 2, 3, \dots, n$. The terms singlet and triplet refer to the multiplicity of the electronic state and are shown diagrammatically in Figure 1.(1).

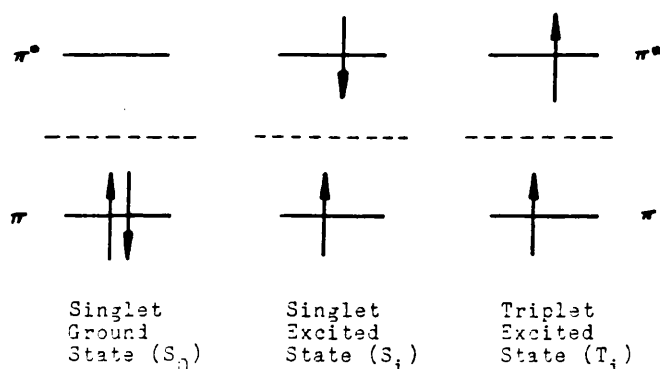


FIGURE 1.(1). Electronic Spins in the S_0 , S_i and T_i States.

Selection rules state that transitions in which there is a change in the total electronic spin quantum number (S) are spin forbidden.

The relative positions of the energy levels and transitions between them in a simple diatomic molecule are illustrated in Figure 1.(2)., using Morse Potential energy curves⁽²⁾. The curves for the electronic ground state (G) and excited state (S) are shown, each point on the curve representing the net energy of nuclear-nuclear, nuclear-electronic and electronic-electronic interactions for a particular bond distance R . Vibrational levels and equilibrium bond lengths R_e^* and R_e are also indicated. Since the transition from the ground state to the excited state is essentially instantaneous (10^{-16} s), in comparison with the time for nuclear motion (10^{-13} s), the transition will initially be to a vibrationally excited level with an identical internuclear distance, on the basis of the

Franck-Condon Principle. The transition is therefore depicted as a vertical line in Figure 1.(2). and is referred to as the Franck-Condon maximum. On completion of the electronic transition, the nuclei then move to a new equilibrium internuclear separation R_e^* .

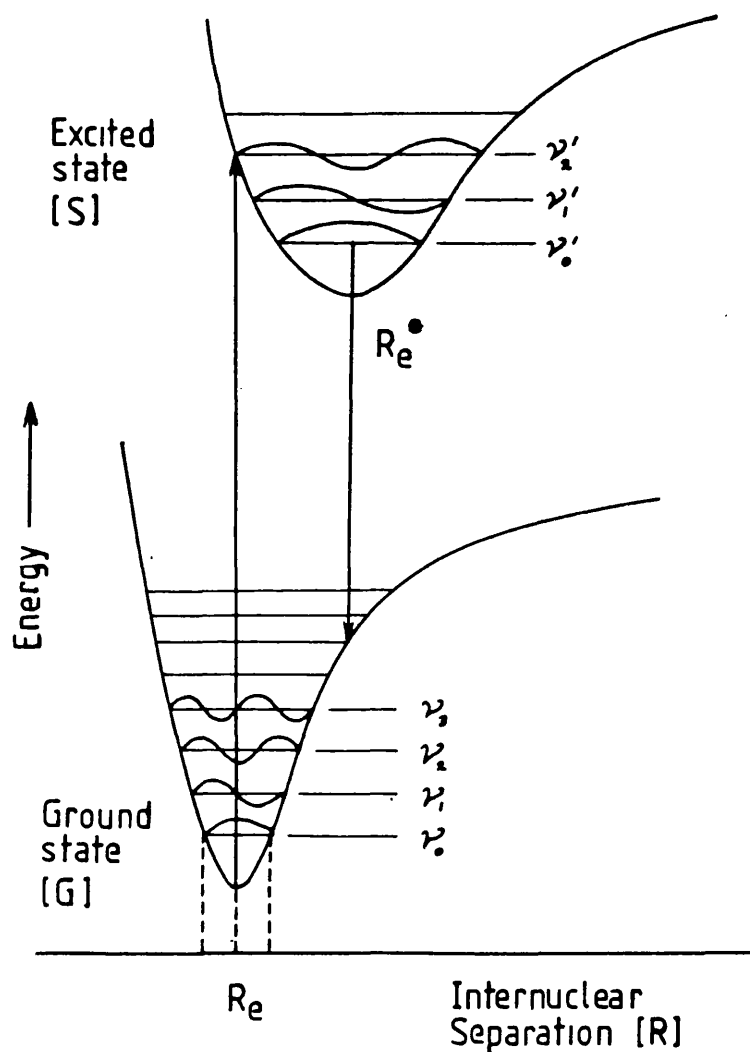


FIGURE 1.(2). Morse Potential Energy Curves for a Simple Diatomic Molecule.

In order to quantify spectroscopic studies, one needs to know the proportion of radiation falling on the sample that is actually absorbed. For most systems, this can be conveniently determined by application of the Beer-Lambert law, shown in Equation 1.(2).

$$\log_{10} \frac{I_0}{I_t} = \epsilon c l = OD \quad - \text{Eqn. 1.(2).}$$

(I_0 = intensity of incident radiation, I_t = intensity of transmitted radiation, ϵ = molar extinction coefficient ($\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$), c = concentration (mol dm^{-3}) and l = path length (cm)).

1.1.(2). The Nature of the Absorption Spectrum.

The absorption of radiation in the u/v or visible region causes excitation of electrons present in either the n (non-bonding) or π (bonding) orbitals of the chromophore involved, and for aromatic hydrocarbons involves transitions to the π^* antibonding orbitals. Figure 1.(3). shows a typical example of the relative energies of the orbitals, which can be affected by solvent interactions, for instance. Increasing the conjugation

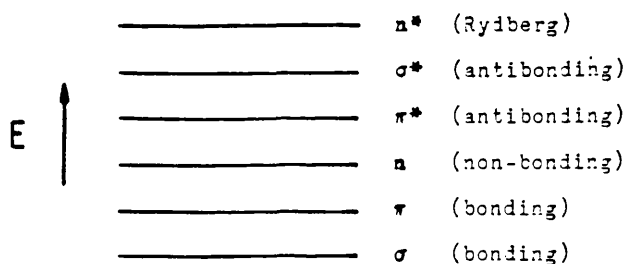


FIGURE 1.(3). Typical Example of the Relative Orbital Energies (drawn uniformly spaced for ease).

of the chromophore or introducing auxochromes like $-\text{OH}$ or $-\text{NH}_2$ cause changes in both the intensities and maxima of the absorptions, as shown by considering the spectra of benzene, naphthalene and anthracene⁽³⁾, which undergo a red-shift.

The absorption spectra of gaseous samples at low pressures, enable the observation of vibrational and rotational fine structure, but the spectra become more diffuse at higher pressures and in neat liquids and solids. The spectra are also influenced by temperature and the nature of the solvent, so that if the excited state has an increased permanent dipole,

the spectrum undergoes a bathochromic or red-shift in polar solvents. The reverse effect causes a hypsochromic or blue-shift.

1.1.(3). Modes of Decay from Excited States.

Once a species has been photochemically excited, into a higher electronic state, there are a number of pathways available to the molecule for dissipation of the energy, as summarised in Figure 1.(4).

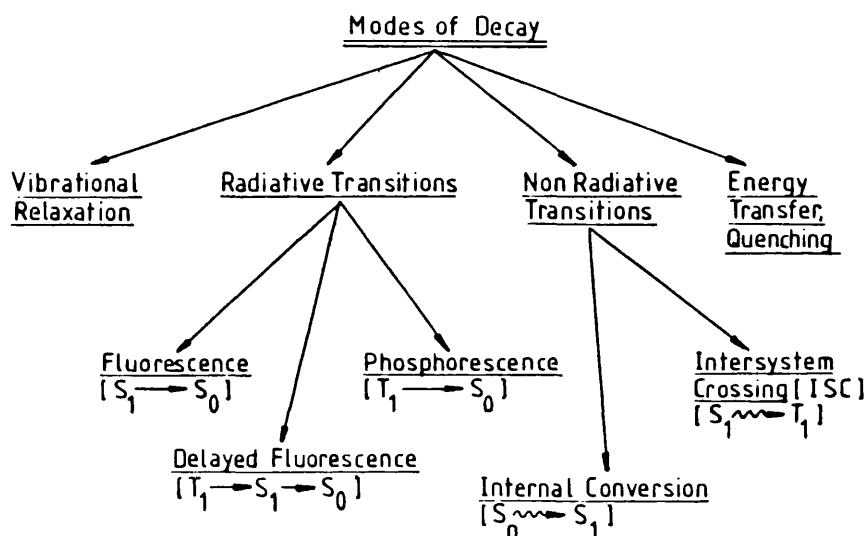


FIGURE 1.(4). Physical Pathways for the Decay of Excited States.

1.1.(3).1. Radiationless Transitions.

There are a number of radiationless transitions available to the excited species, as detailed below:

Vibrational relaxation - involves the loss of excess vibrational energy by molecular collisions to yield the electronically excited species in its lowest vibrational level (ν_0'), with rate constants of the order 10^{13} s^{-1} .

Internal conversion (IC) - the very rapid transitions between isoenergetic vibrational levels of different states of the same multiplicity (e.g. $S_n \rightsquigarrow S_m$ or $T_n \rightsquigarrow T_m$). This accounts for the negligible emission from upper excited states, $k \sim 10^{11} - 10^{14} \text{ s}^{-1}$.

Intersystem crossing (ISC) - this process occurs between iso-energetic levels of different multiplicity and provides the normal route for population of the triplet manifold $S_1 \rightsquigarrow T_1$, competing with radiative transitions from S_1 . ISC is considerably enhanced by the presence of halogen atoms either within the excited species or the solvent, by the so-called heavy atom effect^(4,5). Rate constants are in the range $\sim 10^4$ - 10^{12} s⁻¹.

1.1.(3).2. Radiative Transitions.

In radiative transitions, the excited species returns to the electronic ground state with the emission of a photon.

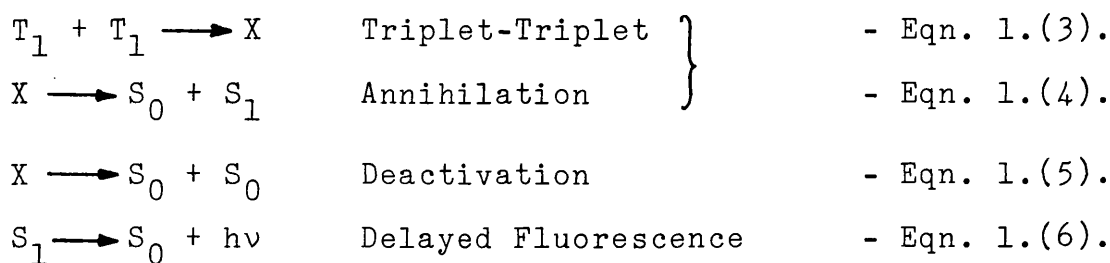
Fluorescence - for transitions between states of the same multiplicity, the process is known as fluorescence and occurs very rapidly ($k_f \sim 10^6$ - 10^9 s⁻¹). Kasha's rule⁽⁶⁾ states that irrespective of the singlet state initially reached upon excitation, fluorescence will occur from the lowest excited π electronic singlet state (S_1). Several exceptions to this rule have been established in which $S_2 \rightarrow S_0$ fluorescence can be observed, involving azulene⁽⁷⁾ and pyrene and selected derivatives⁽⁸⁾. By analogy to absorption, fluorescence is governed by the Franck-Condon Principle, consequently emission occurs before molecular rearrangement, giving a ground state molecule in a vibrationally excited state ν_i , where $i > 0$. Since a whole slew of transitions are possible, the emission appears as bands, often broad and structureless. The wavelength maximum is simply a measure of the most favourable electronic transition, e.g. $\nu_0' \rightarrow \nu_3$, and the absorption and fluorescence spectra are commonly approximate mirror images of each other.

The fluorescence spectra are affected by solvent interactions, solvent pH, temperature and the presence of quenching species. Since the excitation is often accompanied by a change in dipole moment of the species, it will be stabilised to

varying degrees by solvents of different polarity. Elevated temperatures have been found to decrease the fluorescence intensity, attributed to enhanced ISC to the triplet state, as a result of thermal population of higher vibrational levels in the S_1 state⁽⁹⁻¹¹⁾.

Phosphorescence - radiative transitions between states of different multiplicity is known as phosphorescence. The process is spin-forbidden and consequently $T_1 \rightarrow S_0$ or $T_n \rightarrow S_0$ phosphorescence is very uncommon, with rate constants $k_p \sim 10^{-2} - 10^4 s^{-1}$. The long radiative lifetime of triplet states make them very susceptible to quenching by impurities. Although the use of perfluorocarbon solvents⁽¹²⁾ enable phosphorescence to be detected in solution, measurements are usually made on solutions in rigid glasses at 77K. More recently however, examples have appeared in the literature of phosphorescence being observed at room temperature, the triplet state being protected by a protein structure⁽¹³⁾ or the use of aqueous micellar solutions⁽¹⁴⁾. Utilisation of high-powered lasers for excitation has also aided the study of phosphorescence, generating sufficient concentrations of the triplet species.

Delayed fluorescence - this radiative process can be brought about by two mechanisms, (a) triplet-triplet annihilation and (b) thermal activation. The accepted mechanism for (a) is outlined in Scheme 1.(1)., involving the collision of two excited triplet species, to form an intermediate species X. Excimer X



SCHEME 1.(1). Mechanism for Triplet-Triplet Annihilation.

then breaks down to yield an S_1 species which is then responsible for the delayed fluorescence. The alternative mechanism (b) involves thermal activation of the T_1 state through ΔE , followed by reverse ISC to generate the S_1 state, as shown in Figure 1.(5).

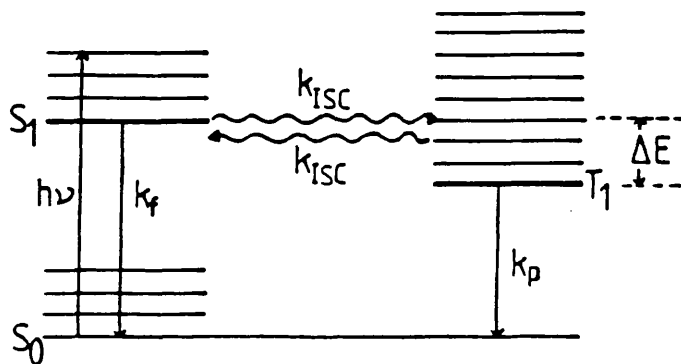


FIGURE 1.(5). Diagram Showing the Energy Levels for the Thermally Activated Delayed Fluorescence.

The various dissipative pathways (excluding delayed fluorescence) can be summarised diagrammatically on a Jablonski Diagram^(15,16), see Figure 1.(6).

1.1.(3).3. The Quenching of Excited States.

Another important method by which the energy of a molecule in an electronically excited state can be lost is by the interaction of the excited species with a ground state atom or molecule, in a quenching process. Considering only the photophysical quenching mechanisms, these can be subdivided into self-quenching or impurity quenching.

Self-quenching - the observation that increasing the concentration of a solute (A) is accompanied by a decrease in the fluorescence intensity, has been attributed to a phenomenon known as self-quenching or concentration quenching. However whilst studying the fluorescence of pyrene in solution, Förster and Kasper^(17,18) noted that the quenching was accompanied by the appearance of a new fluorescence band to

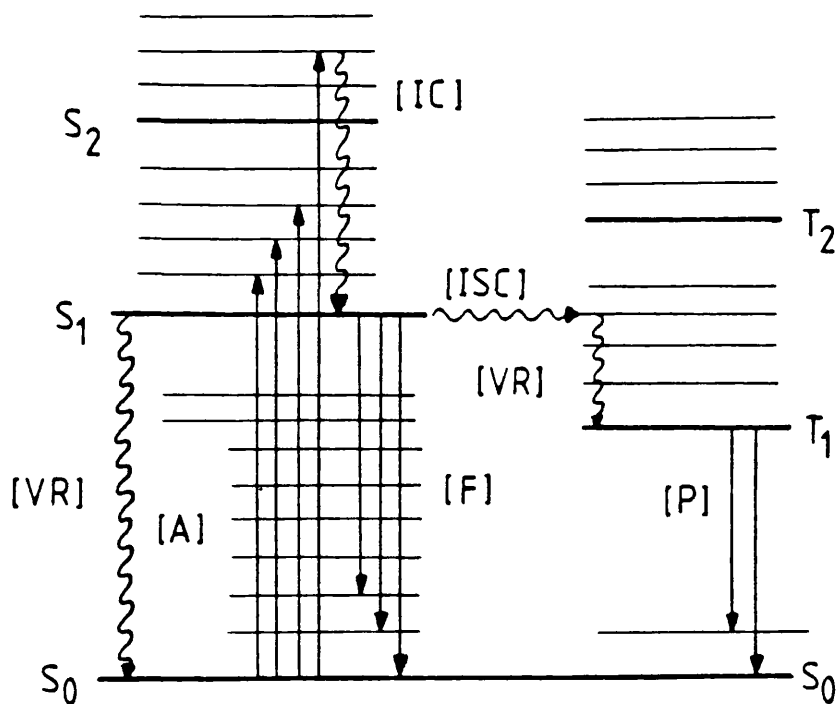
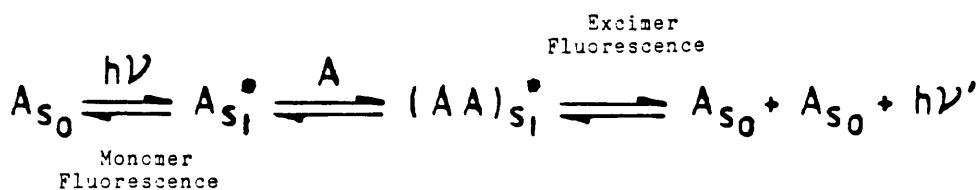


FIGURE 1.(6). Jablonski Diagram.

- A Absorption
- F Fluorescence
- IC Internal conversion
- ISC Intersystem crossing
- P Phosphorescence
- VR Vibrational relaxation

the red of the monomer, due to the formation of an excited state dimer or excimer, as detailed in Scheme 1.(2). Excimer



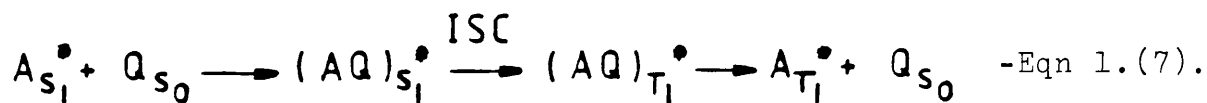
SCHEME 1.(2). Schematic Representation of the Quenching of \$A^*\$ by \$A_{S_0}\$, Leading to Excimer Formation and Fluorescence.

formation has subsequently been found to be quite widespread, particularly amongst the aromatic hydrocarbons.

Impurity quenching - this arises when the excited species A* is quenched by another molecule (Q) and can be caused by (i) exciplex formation, (ii) heavy atom quenching or (iii) energy transfer quenching.

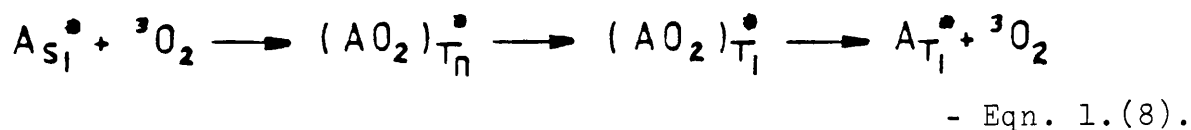
(i) When two species come together to form an exciplex, usually of a 1:1 stoichiometry, the fluorescence of A* is quenched and can be replaced by a broad new structureless emission at longer wavelengths. Since the exciplex possesses some degree of charge transfer character, the stability of the exciplex and therefore its emission shows a variation with solvent polarity. In some cases, for solvents of high dielectric constant like acetonitrile, the emission disappears altogether and this has been shown by flash photolysis experiments to be due to the formation of radical ion pairs⁽¹⁹⁾, derived from both the exciplex and the initially formed encounter complex. A kinetic study on the role of the encounter complex in electron transfer quenching has been made by Rehm and Weller⁽²⁰⁾. Although the exact nature of the entities involved is not clear, it has been established as an important quenching process of the singlet excited state. The exciplex is dealt with in Sections 1.(2). and 1.(3). in more detail.

(ii) Species containing heavy atoms such as halogens, quench molecular fluorescence by the initial formation of a singlet exciplex which then undergoes enhanced ISC to the triplet exciplex, finally giving the components by dissociation as shown in Equation 1.(7). A large proportion of work in this

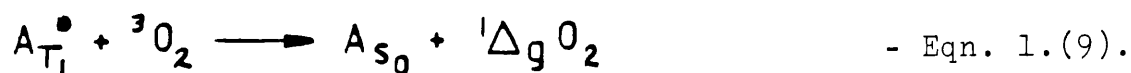


area has been carried out by Wilkinson et al.⁽²¹⁻²³⁾, studying the quenching of aromatic hydrocarbons by xenon and halogen derivatives. Oxygen is also a highly efficient quencher of

excited states⁽²⁴⁾, quenching at diffusion controlled rates. The quenching is thought to proceed via triplet exciplexes as in Equation 1.(8)., ultimately generating singlet oxygen



as in Equation 1.(9). The free radical species nitric oxide



also quenches singlet excited states, presumably enhancing ISC.

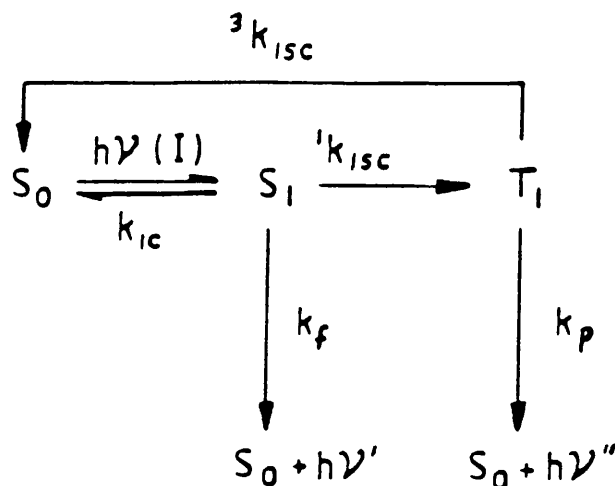
(iii) Electronic energy transfer quenching is dealt with in detail in Chapter 3, but essentially involves an excited donor molecule (D*) returning to the ground state with the simultaneous transfer of the excitation energy to an acceptor molecule A.



1.1.(4). Quantum Yields and Lifetimes of Excited State Species.

1.1.(4).1. Quantum Yield of Fluorescence (ϕ_f).

The general kinetic scheme for the excitation of a ground state molecule and its subsequent decay is detailed in Scheme 1.(3). I represents the rate of absorption of photons



SCHEME 1.(3). Kinetic Scheme for the Photophysical Pathways Associated with an S₁ Excited Species.

and k_f , k_p , k_{ISC} and k_{IC} , the rates of fluorescence, phosphorescence, intersystem crossing and internal conversion respectively. By the application of the steady-state approximation, the rates of formation and destruction of the S_1 state are equal. Defining the rate of absorption (I) as in Equation 1.(11).,

$$I = [S_1] \sum^1 k \quad - \text{Eqn. 1.(11).}$$

(where $\sum^1 k = k_{IC} + k_f + k_{ISC}$), the quantum yield of fluorescence (ϕ_f) is given by Equations 1.(12). and 1.(13).

$$\phi_f = \frac{\text{rate of emission of } S_1}{\text{rate of absorption of photons by } S_0} \quad - \text{Eqn. 1.(12).}$$

$$\text{or } \phi_f = \frac{k_f [S_1]}{I} = \frac{k_f}{\sum^1 k} \quad - \text{Eqn. 1.(13).}$$

1.1.(4).2. Lifetimes of Fluorescence and Phosphorescence.

For an excited species A^* undergoing deactivation processes with rates $k_1, k_2, \dots, k_n$, the concentration of A^* falls exponentially with a rate constant $\sum k$. Defining the lifetime (τ) of A^* as the time taken for $[A^*]$ to fall by $1/e$ of its initial value, then the lifetimes of fluorescence (τ_f) and phosphorescence (τ_p) are given by the expressions in Equation 1.(14).

$$\tau_f = \frac{1}{\sum^1 k}, \quad \tau_p = \frac{1}{\sum^3 k} \quad - \text{Eqn. 1.(14).}$$

Combining Equations 1.(13). and 1.(14). then gives,

$$k_f = \frac{\phi_f}{\tau_f} \quad - \text{Eqn. 1.(15).}$$

1.1.(4).3. Quantum Yield of Phosphorescence (ϕ_p).

With reference to Scheme 1.(3)., the rates of formation

and destruction of the T_1 state are assumed to be equal, therefore

$$\underline{{}^1k_{ISC}[S_1] = \sum {}^3k[T_1]} \quad - \text{Eqn. 1.(16).}$$

(where $\sum {}^3k = k_p + {}^3k_{ISC}$)

Since ϕ_p is defined by Equation 1.(17).,

$$\underline{\phi_p = \frac{k_p[T_1]}{I}} \quad - \text{Eqn. 1.(17).}$$

substitution for I and rearranging gives the expression,

$$\underline{\phi_p = \theta_p \theta_{ISC} = k_p \tau_p \phi_T} \quad - \text{Eqn. 1.(18).}$$

(where θ_p and θ_{ISC} are the quantum efficiencies of phosphorescence and intersystem crossing respectively).

Finally since all the energy supplied to a molecule during excitation, must be lost on returning to the ground state, combining the efficiencies of the various radiationless processes in a term (ϕ_R) gives the expression

$$\underline{\phi_f + \phi_p + \phi_R = 1.} \quad - \text{Eqn. 1.(19).}$$

1.2. INTERMOLECULAR EXCIPLEXES.

1.2.(1). Factors Affecting Intermolecular Exciplex Formation and Stability.

1.2.(1).1. Introduction.

The term EXCIPLEX (or excited complex) is used to describe an electronically excited molecular complex, usually of a 1:1 stoichiometry. A number of complexes fall into this broad category including:

- (1) Excimers - (excited dimers) formed between two identical atoms or molecules.
- (2) Heteroexcimers - formed between two non-identical atoms or molecules.

(3) Excited Charge-Transfer (CT) Complexes - produced upon excitation of ground state associated molecular complexes. For the remainder of this thesis, the term exciplex will be used to indicate a heteroexcimer and the specialised term excimer used when applicable.

In general, the electronic structure of an exciplex formed between two chromophores A and D can be expressed in terms of a wave function of the type detailed in Equation 1.(20).⁽²⁵⁾

$$\psi \approx \frac{c_1\phi(A^*D) + c_2\phi(AD^*) + c_3\phi(A^-D^+) + c_4\phi(A^+D^-) + c_5\phi(AD)}{c_5\phi(AD)} \quad - \text{Eqn. 1.(20).}$$

For the excited CT complexes, the c_5 term becomes significant and accounts for their stability in the ground state. However, if the ground state (g.s.) interactions are unimportant, then the weighting of c_1 and c_2 relative to c_3 and c_4 determines the extent to which the exciton resonance contributes to the exciplex stability relative to charge-transfer interactions. In principle, the S_1 exciplexes should exhibit fluorescence, but since the g.s. collision complex AD will be less tightly bound than (AD^*) or $(A--D)^*$ the emission will occur to a weakly bound or dissociative ground state.

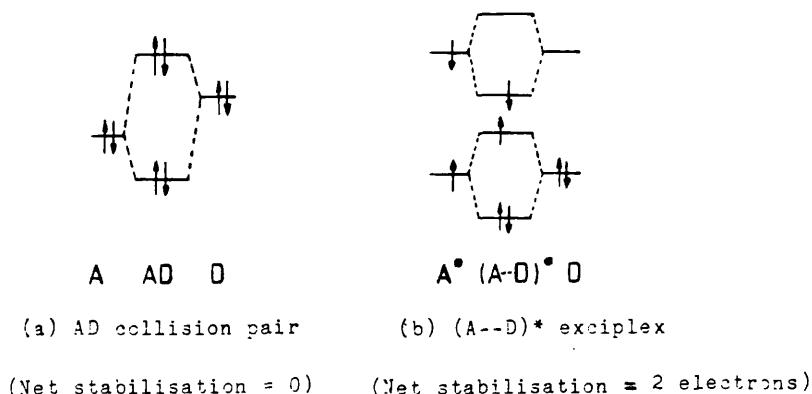


FIGURE 1.(7). Electronic Stabilisation in the Collision Pair (AD) and the Exciplex (A--D)*.

Consideration of molecular orbital (MO) interactions in exciplexes provides a simple explanation of the enhanced stability of the (A--D)* exciplex relative to the g.s. collision pair (AD) as shown in Figure 1.(7).

Another approach is to consider the potential energy surface for the emission of an exciplex (A--D)*, stabilised primarily by charge-transfer interactions, as given in Figure 1.(8). Assuming the ground state attractions of the

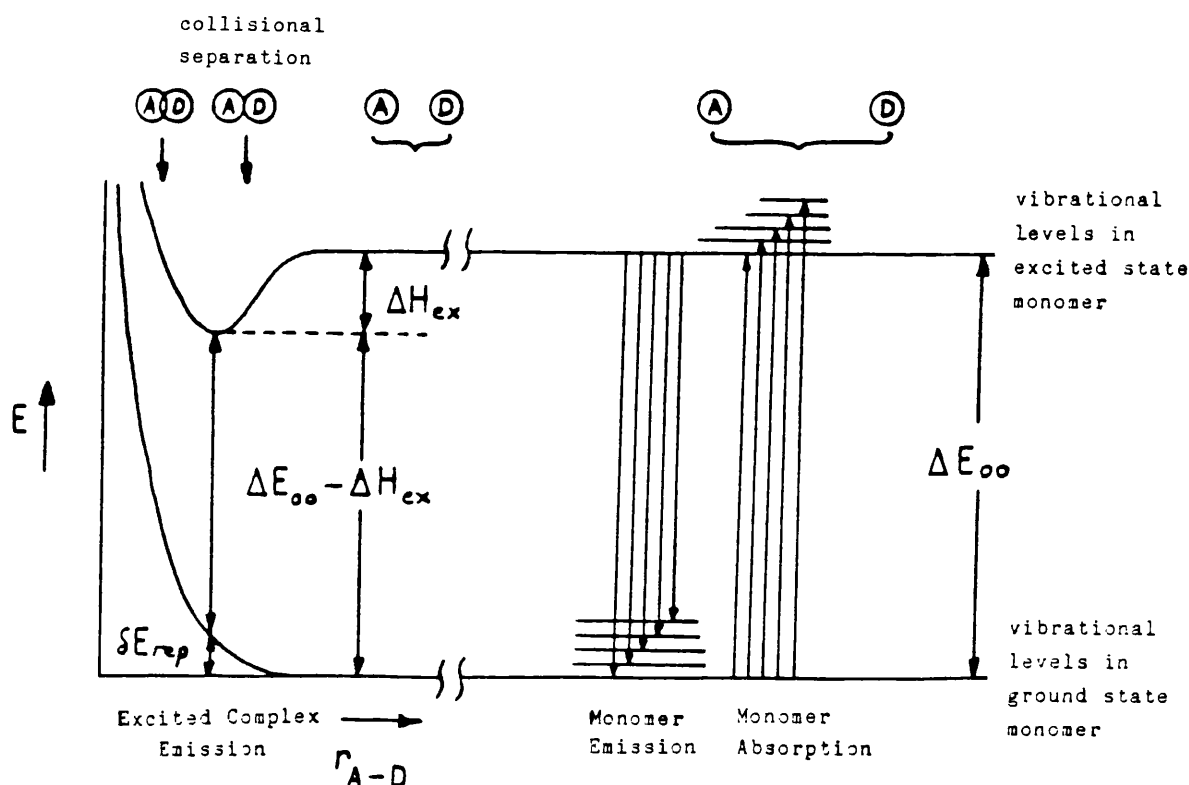


FIGURE 1.(8). Potential Energy Surface for Exciplex Emission in a Donor-Acceptor Exciplex.

donor (D) and acceptor (A) are negligible, then when the two groups are close enough to undergo collisions, the energy of the system will be raised, since the ground state collision complexes are unstable. For the interaction of A* and D on the excited P.E. surface however, although at large separations the emission is that of A*, as the groups approach, the binding energy may increase due to charge transfer or

exciton resonance interactions and cause a minimum to occur in the P.E. curve. Provided this enthalpy decrease is not offset by an entropy increase, an exciplex will form between D and A. Emission from the exciplex will then occur vertically (according to the Franck-Condon Principle) from the P.E. minimum on the excited state to a repulsive point on the g.s. P.E. curve. Since the collision pair rapidly flies apart and therefore has a very short lifetime, the emission spectra of exciplexes and excimers contain no vibrational fine structure. The stability of the exciplex (A--D)* is represented by the difference in energy between $A^* + D$ and (A--D)* and is indicated by ΔH_{ex} in Figure 1.(8).

1.2.(1).2. Thermodynamic Factors Affecting Exciplex Stability.

If the stabilisation of an exciplex arose entirely from charge-transfer interactions between the donor and acceptor moieties, then the energetics of exciplex formation would be governed by the following expression:

$$\underline{E_{(D^+A^-)} = I_D - EA_A - C - \Delta H_S} \quad - \text{Eqn. 1.(21).}$$

where $E_{(D^+A^-)}$ = energy of the pure CT state relative to the g.s. energy of A and D.

I_D = ionisation potential of donor species.

EA_A = electron affinity of acceptor species.

C = Coulombic interaction energy between D^+ and A^-

ΔH_S = Solvation energy of the exciplex.

For a given solvent, ΔH_S can be taken as approximately constant for a series of exciplexes and assuming C , the Coulombic energy gained by bringing the ions D^+ and A^- from infinity to the internuclear distance (r_{AD}) remains essentially constant, the energy of the exciplex (E_{ex}) will be proportional to $(I_D - EA_A)$. Since I_D and EA_A are proportional to

the oxidation potential of the donor and reduction potential of the acceptor, this gives the expression in Equation 1.(22).

$$\underline{E_{\text{ex}} = h\nu_{\text{max}} \propto I_D - EA_A \propto E(D/D^+) - E(A^-/A) \quad - \text{Eqn. 1.(22).}}$$

This relationship has been confirmed by plotting graphs of fluorescence maxima of exciplexes against $E(D/D^+) - E(A^-/A)$ and obtaining excellent linearity^(19,26-28). The presence of both the Coulombic term and the ΔH_S term in Equation 1.(21). suggests that the solvent polarity will affect the exciplex energy and has been clearly demonstrated in a number of aromatic hydrocarbon-amine exciplexes^(26,29,30).

1.2.(1).3. Steric Factors and the Nature of the Participating Groups.

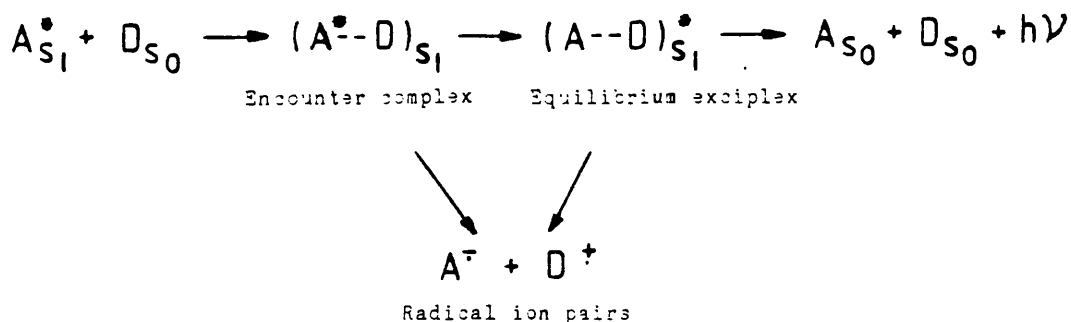
Steric congestion obviously hinders the close approach of the donor and acceptor species and reduces the efficiency of both quenching and exciplex formation. This has been shown by the quenching of 1-cyano-naphthalene by a series of dialkyl sulphides⁽³¹⁾ and exciplex formation between pyrene and N,N-dimethylaniline and its 3,5-ditertiarybutyl derivative⁽³²⁾.

The nature of the amine group has been shown to affect exciplex formation with a number of aromatic hydrocarbons. Generally tertiary amines are found to form exciplexes more readily than secondary and primary amines, a fact largely accounted for by the magnitudes of the ionisation potentials. The possibility of hydrogen abstraction reactions and the formation of molecular aggregates by hydrogen bonding interactions also arises with compounds containing N-H or O-H groups.

1.2.(1).4. The Effect of Solvent upon Equilibrium Exciplex Formation.

In studies carried out on intermolecular exciplex

formation between aromatic hydrocarbons and tertiary amines, it was established that increasing the solvent polarity caused a red shift in the exciplex fluorescence and a decrease in both the quantum yield and lifetime of the exciplex. It was suggested that increasing the solvent polarity increased the tendency for the exciplex to dissociate into radical ion pairs, despite the improvement in the solvating power of the solvent. Furthermore the observation that the lifetime of the pyrene-dimethylaniline exciplex decreased much slower than the fluorescence intensity in increasing the solvent polarity, was explained by the proposal that the radical ion pairs were produced from both the initially formed encounter complex and the fluorescent exciplex as shown in Scheme 1.(4).



SCHEME 1.(4). Generation of Solvated Radical-Ion Pairs from the Encounter Complex and Fluorescent Complex.

The dependency of the exciplex emission upon solvent polarity has been used to calculate the dipole moments of a variety of exciplexes⁽²⁹⁾. In the majority of cases the exciplexes have been shown to have dipole moments indicative of essentially complete electron transfer between the donor and acceptor groups. The independency of the excimeric emission upon solvent polarity indicates that they derive little stability from CT interactions.

1.2.(2). Methods of Exciplex Formation.

1.2.(2).1. Electron Transfer and Solvent Relaxation.

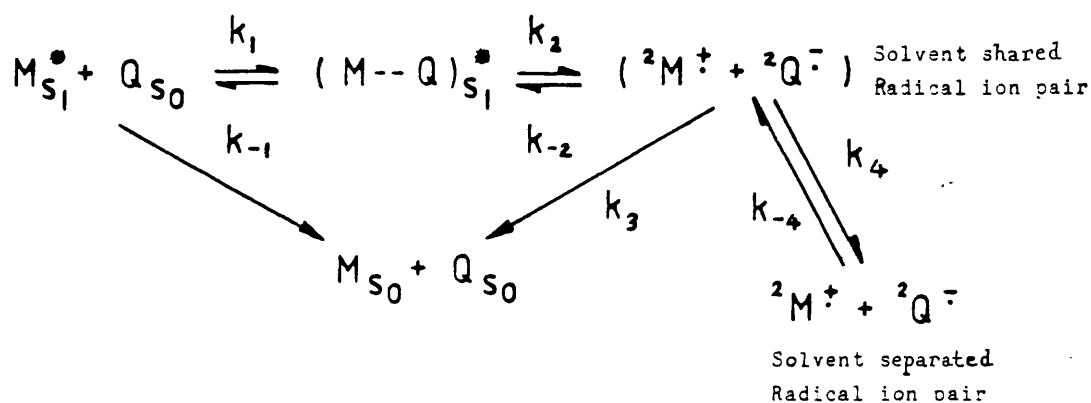
If an intermolecular exciplex is to be generated in solution, it is an essential requirement that after excitation of one of the reaction partners, it collides with the other partner within the lifetime of the excited state. The rate of interaction is clearly determined by the diffusion controlled limits for the solvent being used and indicates that the process is closely linked to solvent reorganisation phenomena. In many cases the need to generate high concentrations of the reaction partners is apparent to favour exciplex formation by ensuring multiple collisions of the two species. A number of methods are available to achieve this, including the generation of the species in micelles or monolayers⁽³³⁾, the utilisation of a quencher molecule with more than one quencher group as with the α,ω -diaminoalkanes⁽³⁴⁾ or linking the two interacting groups together by means of a flexible chain^(35,36).

The formation of a fluorescent exciplex involves the initial creation of a non-relaxed exciplex or encounter complex between the two molecules. The important feature of this excited species being that there has been no time for reorganisation of the surrounding solvent molecules to afford it maximum stabilisation. Although electron transfer can occur at internuclear separations of $\sim 7-8 \text{ \AA}$ ⁽³⁷⁾, the exact extent of charge transfer in these encounter complexes is unclear. Furthermore the non-emissive nature of these complexes means that their involvement in reactions is usually by implication. The observation of triplet species during the quenching of polycyclic aromatic hydrocarbons by added halide ions^(38,39) for example has been explained by the

probable formation of an encounter complex.

In ordinary solvents, at room temperature, the relaxation time is shorter than the lifetime of the emitting species and emission occurs essentially from the fully solvated equilibrium exciplex. However, using time resolved fluorescence spectroscopy and working at low temperatures with high viscosity solvents, the relaxation rate can be slowed down and the exciplex fluorescence then shows a time dependence. Such an effect has been observed by Nakashima et al.⁽⁴⁰⁾ using pyrene (acceptor) and highly viscous super-cooled tri-n-butylamine (donor) at 156K. The involvement of the encounter complex in a non-radiative decay pathway will prevent the formation of the fluorescent species, which can also be impaired by bad steric interactions, a lack of conformational mobility and the need for one of the reaction partners to undergo rehybridisation during electron transfer.

Unlike solvents of low or medium polarity where the main role is that of stabilising the excited species, in highly polar solvents like methanol and acetonitrile, electron transfer to produce a ground state solvent shared ion pair, competes effectively with exciplex formation. Rehm and Weller⁽⁴¹⁾ have carried out systematic investigations into electron transfer reactions in acetonitrile solutions and analysed their results using a scheme originally proposed by Marcus⁽⁴²⁾, as shown in Scheme 1.(5)., to derive the overall rate of fluorescence quenching (k_q). The major deactivation process from the solvent shared ion pair was taken to be the back electron transfer, leading to the neutral ground state ($M + Q$), with rate constant k_3 . A number of theoretical studies have also been carried out into the relationship between the rate constant k_q and the Gibbs Free Energy change



SCHEME 1.(5). Photophysical Processes Involved in the Formation and Decay of Solvent Shared and Solvent Separated Radical-Ion Pairs.

$\Delta G^{(43,44)}$. The ΔG^0 between the equilibrium exciplex $(M--Q)^*$ and the solvent shared radical-ion pair $(^2M^{\dagger} + ^2Q^{\bar{}})$, being calculated using Equation 1.(23).⁽⁴¹⁾

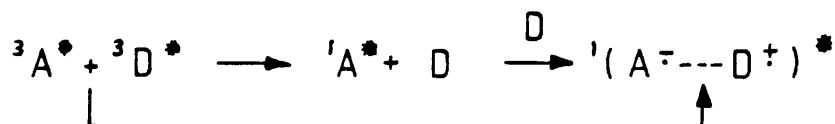
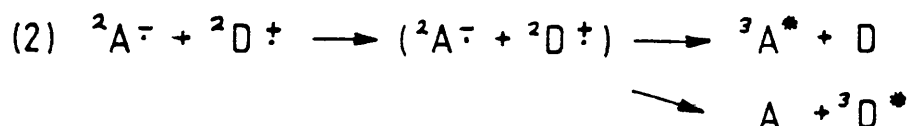
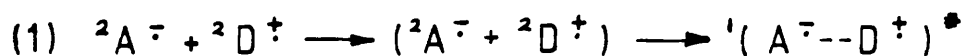
$$\Delta G^0 = E^{\text{ox}} - E^{\text{red}} - \frac{e^2}{\epsilon' a} - \Delta E_{\text{oo}} \quad \text{--- Eqn. 1.(23).}$$

(where E^{ox} = oxidation potential of donor, E^{red} = acceptor reduction potential, $e^2/\epsilon' a$ = Coulombic interaction energy between two radical ions at encounter distance a in a solvent of dielectric constant ϵ' , ΔE_{oo} = electronic excitation energy of fluorescer).

A useful generalisation has emerged from this work namely that for $\Delta G^0 \leq -40 \text{ kJmol}^{-1}$, the quenching is diffusion controlled and for $\Delta G^0 > -40 \text{ kJmol}^{-1}$, an activation energy must be overcome and the rate constants are at least a factor of ten below those for diffusion controlled processes.

1.2.(2).2. Radical-Ion Recombination.

Solvent separated radical-ion pairs can recombine either directly or via the initial formation of the relevant triplet species followed by a mixed triplet-triplet annihilation process to yield the fluorescent exciplex as detailed in



SCHEME 1.(6). Photophysical Processes Leading to the Formation of Fluorescent Exciplexes from Radical-Ion Pairs.

Scheme 1.(6). The radical-ion pair recombination processes are not only restricted to photochemically generated species. Fluorescent exciplexes have been observed upon mixing solutions of chemically produced radical anions and cations⁽⁴⁵⁻⁴⁸⁾ and from the combination of radical species generated electrochemically⁽⁴⁹⁾. The involvement of triplet states in the exciplex formation can be determined by monitoring the effects of an applied magnetic field upon the exciplex yield. Since the degeneracy of the triplet state will be perturbed by an external magnetic field, this will cause a reduction in the triplet lifetime and hence the exciplex yield.

1.2.(2).3. Excited Ground State Aggregates.

The excitation of ground state molecular aggregates provides another means of generating exciplexes, and explains excimer fluorescence from aromatic hydrocarbons at low temperature (77K) in rigid matrices. The use of highly concentrated solutions of the components also favours the formation of the loose g.s. complexes, leading to CT exciplexes upon excitation as in the pyrene-dimethylaniline system⁽⁵⁰⁾.

The exact nature of the molecular interactions in the ground state complexes is uncertain, but is likely to involve Van der Waal's forces, particularly for the excimeric species. It is also apparent that only ground state aggregates of a suitable geometrical configuration can form exciplexes.

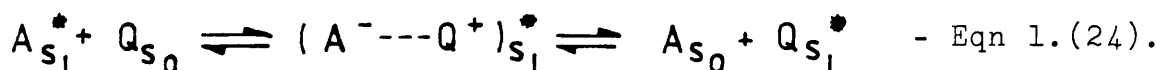
1.2.(3). The Role of the Exciplex in Photochemical Processes.

1.2.(3).1. The Modes of Decay of Excited Complexes.

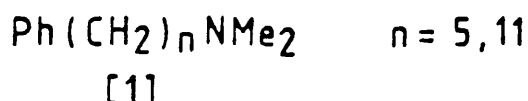
Scheme 1.(7). details some of the photochemical processes which the encounter complex and solvent relaxed exciplex can undergo. The fact that the non-relaxed exciplex is capable of taking part in a chemical reaction, provides a highly efficient non-radiative decay pathway for the excited species and may explain the lack of fluorescence in certain systems. An example of this effect is provided by the interaction of aromatic hydrocarbons with primary and secondary amines. Whilst N-methylindole and related compounds have been shown to form fluorescent exciplexes with aromatic hydrocarbons⁽⁵¹⁾, pyrrole does not do so, but instead undergoes an addition reaction with the hydrocarbon^(52,53). Many other examples of chemical reaction occurring from excited state systems, accompanied by little or no exciplex fluorescence have appeared in the literature^(54,55).

1.2.(3).2. The Role of Exciplexes in Energy Transfer.

In the energy transfer reaction between a singlet excited state species ($A_{S_1}^*$) and a ground state quencher molecule (Q), the process can in principle proceed via the intermediacy of an exciplex as detailed in Equation 1.(24).



The route taken will be dependent upon the relative energies of the species and since these may be affected to different degrees by changing the solvent or temperature for example, the possibility arises that exciplex formation may be observed under one set of conditions and not another. Energy transfer has been observed between benzene and N-methylazacyclopentane in cyclohexane solution at room temperature⁽⁵⁶⁾, but the results of a variable temperature study (discussed in detail in Chapter 3. (4).) did not reveal the intermediacy of an exciplex in this sensitisation process. In another piece of work in which the intramolecular system (1) $n=11$ was studied, energy transfer was seen from the phenyl to the amino group at room temperature in tetrahydrofuran solution⁽⁵⁷⁾. In this



case however, lowering the temperature resulted in the appearance of a new fluorescence band which was attributed to emission from an intramolecular exciplex.

1.2.(3).3. Triplet Formation from Exciplexes.

In solvents of high polarity, where radical ions are favoured, the recombination of both solvent separated and geminate radical ion pairs can lead to the production of triplet state species, as shown in Scheme 1.(6). It has also been suggested that in certain solvents, triplet formation can occur via the intermediacy of an exciplex⁽⁵⁸⁾. Pico-second laser flash photolysis studies on aromatic hydrocarbon-tertiary amine systems in non-polar solvents have shown that the mechanism of triplet formation involves a relaxed exciplex⁽⁵⁹⁾. Whilst in other systems, the involvement of a non-relaxed exciplex has been invoked, notably when quenching aromatic hydrocarbons by primary and secondary amines⁽⁶⁰⁾.

Studies on both the ω -haloalkylnaphthalenes⁽⁶¹⁾ and the ω -phenoxyalkylbromides⁽⁶²⁾, have demonstrated that the influence of the halogeno- group is affected by the length and flexibility of the linking chain. By analogy to the aromatic hydrocarbon-amine systems therefore it may be possible for quenching species containing one or more halogeno- groups to favour ISC in the exciplex. Studies on the quenching of several naphthalene compounds by chloroacetonitrile in acetonitrile solution have revealed the formation of both the naphthalene radical cation and the triplet state hydrocarbon⁽⁶³⁾. There is at present little evidence to support the intermediacy of triplet exciplexes in the formation of triplet species. However, there is phosphorescence evidence to support the existence of triplet excited CT complexes^(64,65) and a thorough study of the cycloaddition reactions of triplets generated via these complexes has been undertaken by Wong and Arnold⁽⁶⁶⁾. In many cases, the energy of the excited charge-transfer complex actually lies below that of the lowest triplet state consequently preventing triplet formation⁽⁶⁷⁾.

1.2.(3).4. Reactions Occurring via Exciplexes.

(a) Intermolecular Cyclo-Addition Reactions.

A number of groups have carried out detailed investigations into the photochemical reactions of a series of alkenes with benzene and related compounds, and some general rules on their mode of reaction have been postulated by Bryce-Smith and co-workers⁽⁶⁸⁾. The intermediacy of an exciplex has been proposed for reactions between components with a large difference in ionisation potentials, leading to the formation of the 1,2- and 1,4-cycloadducts. Exciplex fluorescence has been observed when using relatively polar solvents and the addition of triethylamine found to quench both the fluorescence and

the product formation.

The photocycloaddition of alkenes and dienes to styrenes and stilbenes has recently been reviewed by Lewis⁽⁶⁹⁾. The selectivity of the reactions has been found to increase with solvent polarity and the involvement of exciplexes suggested. The interactions of 9-cyanophenanthrene with a range of styrenes have been widely studied^(70,71) and shown to involve the formation of fluorescent exciplexes prior to the formation of (2 + 2) cycloaddition products and triplet state species.

(b) Reduction Reactions.

The involvement of exciplexes in a number of photo-induced reduction reactions has been extensively dealt with in a review by Davidson⁽⁷²⁾. A large proportion of work in this field has involved the reduction of carbonyl compounds, for example, in the photoreduction of aromatic carbonyl compounds by hydrazines⁽⁷³⁾.

1.3. INTRAMOLECULAR EXCITED COMPLEXES.

1.3.(1). Introduction.

As mentioned previously in Section 1.2., one of the requirements for excited complex formation in fluid solution, is the need for the two reaction partners to collide and interact with each other, within the lifetime of the excited state species. Since the maximum rate of formation is governed by the diffusion controlled rate constant for processes in the solvent being used, one of the ways in which this diffusional restriction can be eased is to link the two interacting groups together by a flexible polymethylene chain^(35,36). This has the effect of generating high local concentrations of the two species and can therefore partially

offset unfavourable free energies for excited complex formation, by creating conditions under which multiple collisions of the partners can occur. The factors affecting the formation and stability of these intramolecular excited complexes have been widely studied and are dealt with in the following sections.

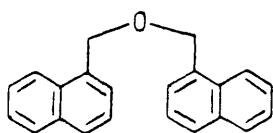
1.3.(2). Intramolecular Excimer Formation.

1.3.(2).1. Conformational Requirements.

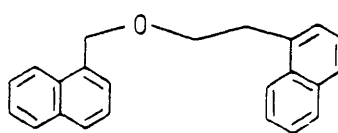
Intramolecular excimers have been the subject of recent reviews by Förster^(74,75) and Birks⁽⁷⁶⁾. The emissions from excimers are broad structureless bands to the red of the monomeric emission and have been observed in neat liquids, solutions and solids. It is also apparent that the requirements for intramolecular excimer formation are stricter than those for the intramolecular heteroexcimers (exciplexes) and that the excimers derive the majority of their stability from exciton resonance rather than Coulombic interactions. Since it is known that aromatic molecules with parallel molecular planes in the crystal lattice form excimers⁽⁷⁷⁾, it is expected that a sandwich arrangement of the two aromatic rings is required for intramolecular excimer formation. The rules governing intramolecular excimer formation in the α,ω -diphenylalkanes were elucidated by Hirayama⁽⁷⁸⁾, who noted that excimer formation was most efficient with three methylene groups interposed between the phenyl rings. The flexible propyl linking chain enabling the molecule to adopt a strain free conformation, with the aromatic rings overlying each other, but without eclipsing interactions occurring in the chain. The binding energy of the excimers has also been found to be important. Whereas with the symmetrical α,ω -dinaphthylalkanes excimer formation occurs only for the propyl system⁽⁷⁹⁾, the

α,ω -dipyrenylalkanes⁽⁸⁰⁾ and pyrenyl systems linked by α,ω -dicarboxyalkanes⁽⁸¹⁾ show excimer formation for a variety of chain lengths, due to the increased binding energy of the pyrenyl groups.

The unfavourable eclipsing interactions between protons in the polymethylene chain can be overcome by the use of an oxygen 'spacer' atom, between the CH_2 groups, as for example in the naphthyl ethers (2) and (3) which both exhibit excimer formation⁽⁸²⁾. Further to this work, it was found that (2)

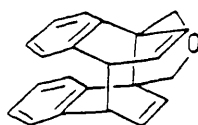


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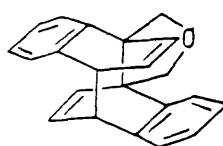


[3]

could be photolysed to yield two products (4) and (5)⁽⁸³⁾. Assuming that the final products bear a close relationship to an intermediate excimer, it indicates that (2) is capable of forming two excimeric species, according to the overlying of the naphthyl rings. The polyethylenoxy grouping has also



[4]



[5]

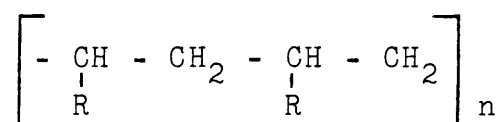
proved to be useful oxygen containing chain for linking aryl groups together⁽⁸²⁾. The dynamics of the flexibility of the chains have been assessed by studying the fluorescence quenching and excimer formation in a number of anthracene derivatives linked together at the 9-position by such a chain⁽⁸⁴⁾. Utilisation of the polyethylenoxy chain has also been found to aid the photodimerisation process^(85,86) in contrast to other anthracene derivatives with a polymethylene chain.

The variation in fluorescence quantum yields of a range

of α,ω -di-(1-naphthyl)alkanes and related compounds in cyclohexane solution has been studied⁽⁸²⁾ and demonstrated that the quenching of the monomeric fluorescence is not necessarily accompanied by excimer formation. The lack of excimer formation was attributed to the inability of the rings to adopt the stable sandwich configuration, the non-relaxed exciplex formed, decaying by a radiationless pathway. A similar study by Halpern et al.⁽⁸⁷⁾ using α,ω -bis-dimethyldiaminoalkanes has also shown that monomeric emission can be quenched even when excimer formation is difficult or impossible to detect.

1.3.(2).2. Excimer Formation in Polymers.

The vinyl polymers of the general formula shown, have



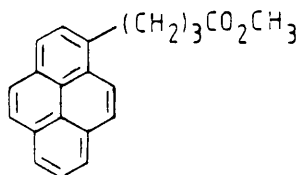
been found to exhibit intramolecular excimer formation when R is an aromatic grouping like phenyl, naphthyl, or carbazoyl, the first and most important example being provided by polystyrene^(78,88,89). Comparison of the fluorescence spectra of polystyrene in a wide range of solvents reveals a long wavelength component in all cases, attributed to the excimer. Since the excimer to monomer ratio is independent of polymer concentration at levels <0.1%, the excimeric emission clearly arises from an intramolecular interaction, probably between neighbouring side groups⁽⁹⁰⁾. The differential quenching of the monomer and excimer emissions by oxygen^(90,91) and CCl_4 ⁽⁹²⁾ however, indicates that the monomeric emission cannot arise solely from breakdown of the excimer. It has also been found that at high polystyrene concentrations (>0.1%) the excimeric fluorescence increases in intensity, attributable to intermolecular excimer formation⁽⁹³⁾.

The formation of intramolecular excimers has also been

noted in biopolymers such as DNA, with its double helical structure containing the hydrogen bonded base pairs adenine (A)-thymine(T) and guanine(G)-cytosine(C). By the comparison of the spectral properties of mono-, di- and poly-nucleotides, it has been established that most dinucleotides show exclusive excimeric fluorescence. Since the fluorescence properties of a copolymer composed of equal amounts of AMP (adenosinemonophosphate) and TMP (thymidinemonophosphate) closely resembles that of DNA, it appears therefore that the DNA fluorescence is due to (AT) excimers⁽⁹⁴⁾.

In proteins, the chances of excimer formation are much smaller than in the nucleic acids, since only three of the common amino acids - tyrosine, tryptophan and phenylalanine - are likely to form excimers. Despite the relatively low concentration of the aromatic amino acids in peptide chains however, it is possible for the tertiary folded structure of the proteins to create local high concentrations and therefore favour excimer formation. Intramolecular excimers have been observed successfully in poly-L-phenylalanine, in helix supporting solvents like tetrahydrofuran. The majority of proteins exhibit only monomeric tyrosine and tryptophan fluorescence.

An interesting piece of work has been carried out on the fluorescence properties of the pyrene ester (6), when incorporated into three polymeric systems⁽⁹⁵⁾ relative to the



[6]

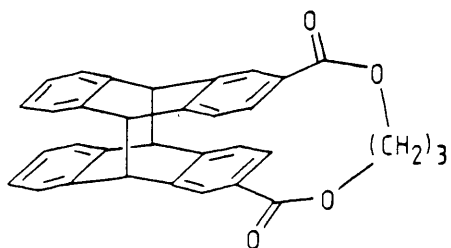
properties in fluid media. The results show that the excimer emission in various polymeric media is blue-shifted by about

40nm relative to that in fluid media. To explain the observed wavelength shift, it has been proposed that the polymeric media prevented the pyrene molecules adopting the ideal sandwich conformation (achieved in fluid media) which was responsible for the characteristic excimer emission at 480nm. Instead the pyrene molecules adopted a less stable conformation, but one nevertheless, which still enabled an excimeric interaction to occur.

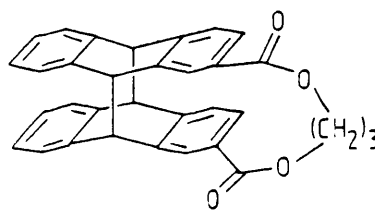
1.3.(2).3. Generation of Excimers in Matrices.

It is well known that the irradiation of dianthracene or photodimers of other anthracene derivatives at 254nm, causes the dimers to revert back to the original molecular pairs. However, if the photodimer is dissolved in a liquid and the solution frozen prior to irradiation, then photolysis leads to the production of a pair of adjacent parallel anthracene molecules held within a rigid matrix⁽⁹⁶⁾. These molecular pairs, known as sandwich dimers, have been prepared for a number of anthracene derivatives^(97,98). One now has a pair of molecules situated close enough to each other that they can exhibit excimer fluorescence upon excitation

Re-examination of the dianthracene photolytic dissociation⁽⁹⁹⁾ has shown the process to be dependent upon both temperature and solvent viscosity and excimer formation to involve the thermal activation of a benzylic like biradical intermediate as shown in Scheme 1.(8). Compounds (7) and (8) also undergo photolytic cleavage upon irradiation in

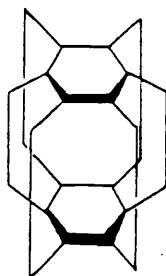


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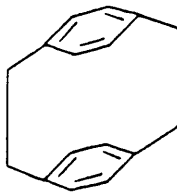


[8]

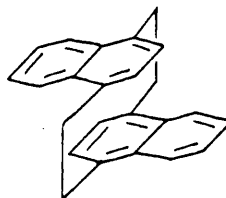
spectroscopic properties of a number of aromatic cyclophanes have been studied, including the benzenoid [2,2] cyclophanes such as (10) and the [2,2] naphthenophane (11)⁽¹⁰²⁾.



[9]

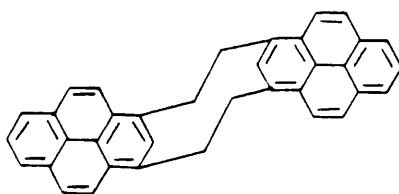


[10]

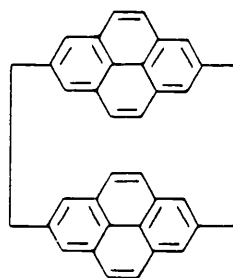


[11]

Both systems exhibited intramolecular excimer formation, but (11) also underwent wavelength and temperature dependent reactions. Studies on the pyrenophanes (12) and (13)⁽¹⁰³⁾, show that in (13), a transannular interaction occurs leading to a new absorption band and a structureless excimeric emission at 560nm, whilst (12) shows characteristic pyrene fluorescence in non-polar solvents and a red-shifted excimer band at 475nm in more polar media. The isomerisation reaction



[12]



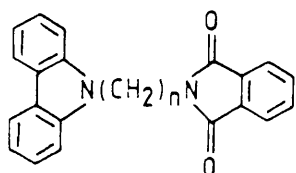
[13]

necessary for (12) to attain the required sandwich configuration is thought to occur via a CT state. Furthermore, this work demonstrates that although intramolecular excimers have highly ordered structures, a compound does not necessarily give rise to a unique excimeric species.

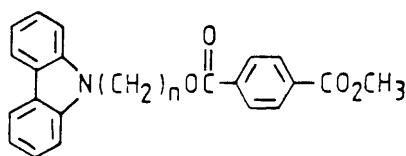
1.3.(3). Intramolecular Exciplexes.

1.3.(3).1. Conformational Requirements for Exciplex Formation.

From the earlier work of Chandross and Thomas⁽¹⁰⁴⁾ and Brimage and Davidson⁽¹⁰⁵⁾ using naphthylalkyl amines, it was established that intramolecular exciplex formation was very efficient, when a di- or tri-methylene chain separated the two interacting groups. The quantum yield of exciplex formation subsequently dropped as the polymethylene chain was lengthened, which presumably reflected the inability of the exciplex binding energy to overcome the energy barriers associated with orientation of the linking chain. By suitably increasing the binding energy of the exciplex however, exciplex emission can be observed using long chain linkages as in (14)⁽¹⁰⁶⁾ and (15)⁽¹⁰⁷⁾ with $n=1-5$ and $n=10$. The mode



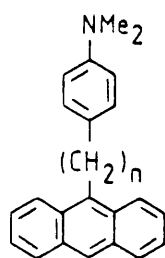
[14]



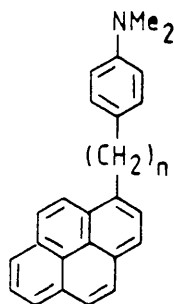
[15]

of fluorescence quenching in (15), was found to be dependent upon the chain length, thus for $n=1$ and 2 , the exciplex was formed via ground state conformations in which the carbazole and ester groups interacted directly (static-quenching), whilst for $n=10$, quenching was by a dynamic process. The use of heteroatoms or groups which relieve the eclipsing interactions in the chain, such as oxygen, also enable longer linkages to be used in exciplex formation⁽¹⁰⁸⁾.

Studies on intramolecular exciplex formation between aromatic hydrocarbons and aromatic amines were first reported by Okada et al.⁽¹⁰⁹⁾ and Ide et al.⁽¹¹⁰⁾ using (16) and (17)



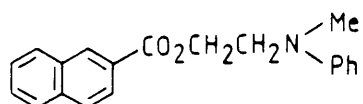
[16]



[17]

It was found that in non-polar solvents, no exciplex emission was observed for $n=1$, due to the inability of the amino group to interact directly with the π system of the anthracenyl or pyrenyl unit. However in more polar solvents, exciplex formation occurred for $n=1$, 2 and 3, indicating the invalidity of the 'n=3 rule' proposed for intramolecular excimers. Subsequent nanosecond laser flash photolysis experiments revealed that the absorption spectra of the exciplexes were the summation of contributions from the aromatic hydrocarbon radical anion and the amine radical cation⁽¹¹¹⁾. It was also shown that the exciplexes of (16) and (17) with $n=2$ and 3 do not necessarily have to adopt the sandwich conformation⁽¹¹²⁾ and that the initially formed complex has a loose structure which undergoes reorientation⁽¹¹³⁾ to give the sandwich structure.

An interesting example of exciplex formation is provided by the naphthenoate ester (18), since the extent of exciplex formation shows a dependency upon whether the amino- or naphthoate grouping is excited⁽¹¹⁴⁾. Time resolved fluores-



[18]

cence studies showed that after excitation of the amine, fluorescence was observed from both the amine and the exciplex for a few nanoseconds, but that this had changed to naphthalene fluorescence within 10ns⁽¹¹⁵⁾. It was suggested that the exciplex was produced by static quenching and acted as an intermediate in energy transfer from the amine to the naphthoate unit.

Davidson and Trethewey⁽¹¹⁶⁾ have carried out a detailed study on the fluorescence behaviour of a series of ω -^{aryl}N,N-diethylaminoalkanes. The observation that the quantum yield of exciplex formation was highly dependent upon chain length whereas the quenching efficiency of the naphthalene fluorescence remained high throughout, was explained by proposing different conformational requirements for the two processes, with quenching occurring over larger distances.

1.3.(3).2. Steric Effects.

The presence of bulky substituents in molecules can cause quite considerable hindrance to intramolecular exciplex formation. For example the addition of an N-methyl substituent to 3-(N-p-tolyl)amino-1-(9-anthraceno)propane, was found to reduce the dipole moment of the exciplex from 15 to 12.2 Debye, indicating a reduction in the charge-transfer character of the excited species⁽¹¹⁷⁾. Presumably the additional methyl group causes a perturbation of the sandwich conformation adopted by the non-methylated compound. Steric effects have also been demonstrated by considering the changes in the entropy of formation of intramolecular excimers⁽¹¹⁸⁾

1.3.(3).3. Solvent Effects upon Exciplex Formation.

The earlier work of Weller and co-workers on the formation of intermolecular exciplexes between aromatic hydrocarbons and tertiary amines, demonstrated the effects of

solvent polarity on exciplex fluorescence. The tendency for the exciplex to dissociate into radical ions in polar solvents was proposed, to account for the observed decrease in quantum yield and lifetime of the exciplex upon increasing the solvent polarity. Work on a series of aromatic hydrocarbon-amine intramolecular exciplexes however,^(105,108) has shown that exciplex fluorescence can be observed in highly polar solvents and in some cases the fluorescence lifetime of the exciplex actually shows an increase. In these situations it appears that the dissociation of the solvent-relaxed exciplex into radical ion pairs is not as important and electron transfer may occur from the non-equilibrium exciplex.

The ability of intramolecular exciplexes to fluoresce in such a wide range of solvents and the variation in λ_{max} values of the emission has been utilised in studying a number of solvation phenomena. The emission of the naphthyl-alkyl amines for instance, which exhibit quite strong fluorescence in non-polar solvents, is dramatically affected by the addition of only small amounts of a polar solvent^(119, 120). From time-resolved fluorescence measurements, it can be seen that the non-polar environment of the initially formed exciplex, is gradually modified during the lifetime of the excited species due to the diffusion of the small polar molecules to the exciplex and subsequent solvation. It is this modification of the solvation shell which causes the wavelength maxima to be red-shifted and the shape of the fluorescence band to change. This observation helps to highlight the dangers of utilising mixed solvent systems when studying exciplex phenomena or in the determination of reaction mechanisms.

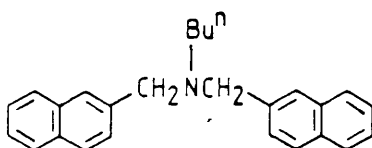
The solvent dependency of exciplex emission has also

been used to calculate the dipole moments of a variety of excited complexes. Intramolecular exciplexes which essentially have pure charge transfer character, are typically found to have dipole moments of 12-15 Debye.

In marked contrast however, the emission from the majority of inter- and intra-molecular excimers has been shown to be almost completely independent of solvent polarity, indicating that they derive little if any stabilisation from charge transfer interactions in the excited state⁽¹²¹⁾.

1.3.(4). Competition Between Intramolecular Excimer and Exciplex Formation.

N-(n-butyl)-N,N-di-(2-naphthylmethyl)amine (19), provides an interesting example of a compound which exhibits both intramolecular excimer and exciplex formation⁽¹²²⁾. In



[19]

cyclohexane solution, compound (19) appeared to show a broad emission due to a mixture of excimer and exciplex fluorescence. Whereas in degassed solution, the emission closely resembled that of 1,3-di-(2-naphthyl)propane and was therefore attributed mainly to the excimer, in aerated solution the emission underwent a blue-shift of around 20nm. Since the excimeric species will be of longer lifetime and therefore quenched by oxygen to a greater degree, the emission was ascribed mostly to the exciplex under these conditions. In benzene solution the single broad emission was again interpreted as being due to a mixture of excimer and benzene solvated exciplex emission. Finally in the polar solvent methanol, it appeared that emission was due only to the

exciplex. Further evidence to confirm that the emissive species in methanol was the exciplex was provided by the addition of small concentrations of ethanoic acid, which quaternised the nitrogen and led to the reappearance of a fluorescent excimer.

1.3.(5). Twisted Excited Charge Transfer Complexes.

The possibility of intramolecular exciplex formation also arises when the two groups are bonded directly to one another by a sigma (σ) bond as in the case of 9,9'-bianthryl. Bad steric interactions prevent the compound adopting a structure in which the two ring systems are coplanar and in non polar solvents the fluorescence resembles that of anthracene. However as the solvent polarity is increased, a new structureless emission band is observed⁽¹²³⁾ which laser flash photolysis experiments have shown is due to the presence of the anthracene radical anion and cation⁽¹²⁴⁾. More recent picosecond laser flash photolysis experiments⁽¹²⁵⁾ have shown that the rise time of the exciplex fluorescence was ~ 20 ps in acetonitrile solution, which may reflect a need for the compound to undergo rotation about the 9,9' bond prior to charge transfer (bringing the two systems nearer to coplanarity). Some of the earliest work on twisted CT complexes was carried out on 4-dimethylaminobenzonitrile, a compound in which the amino group is forced to tilt slightly out of the plane of the benzene ring, as shown in Figure 1.(9). As the solvent polarity was increased, a new structureless emission appeared, attributed to the formation of a twisted intramolecular charge transfer state in the more polar solvents. The effects of angular distortion can also be assessed by comparing the spectroscopic properties of com-

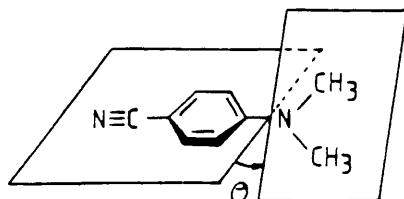
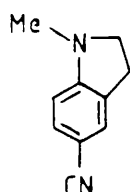
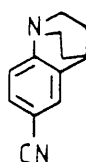


FIGURE 1.(9). Diagrammatic Representation of the Twisted Structure in 4-Dimethylaminobenzonitrile.

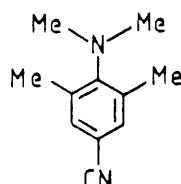
pounds in which the amino group is either held in the same plane or forced out of plane of the benzene ring and cannot rotate as in compounds (20) and (21) respectively^(126,127).



[20]

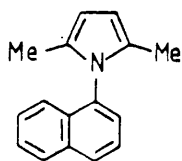


[21]

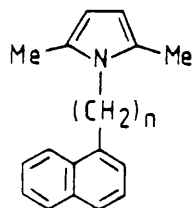


[22]

In compound (22) the steric interactions between the ortho methyl groups and the dimethylamino group prevent the adoption of a conformation in which the benzene ring and the amine are coplanar. When using solvents of medium polarity, (21) and (22) exhibit a red-shifted structureless emission, whereas (20) failed to fluoresce at all. This clearly demonstrated that the formation of an excited charge-transfer state was not dependent upon the benzene and amino groups achieving coplanarity in the excited state. A more recent study on the formation of excited twisted CT complexes has been carried out on compound (23) in comparison with compound (24; $n=1,2$)⁽¹²⁸⁾. The strong steric hindrance between the methyl groups of the pyrrole ring and the H_1 and H_8 atoms on the naphthalene ring, prevent (23) adopting a



[23]



[24]

coplanar structure. Despite this (23) gave a broad structureless emission which was red-shifted with increase in solvent polarity accompanied by a reduction in quantum yield. The similarity in the results to those of (24; $n=1,2$) indicated that all three compounds were capable of forming fluorescent excited charge transfer complexes whilst adopting very different conformations in the excited state.

1.4. MULTI-CHROMOPHORE EXCITED COMPLEX FORMATION.

An increasing number of examples have appeared in the literature of excited complexes involving the interaction of more than two chromophores. In studies on the quenching of aromatic hydrocarbon fluorescence by tertiary amines⁽¹²⁹⁾, it was found that an optimal concentration of amine was reached for exciplex formation. Exceeding this level, resulted in a diminution of the exciplex fluorescence intensity and the appearance of a red-shifted band, attributed to the formation of an intermolecular excited ternary complex (exterplex) between two molecules of the amine and one of the hydrocarbon.

Extensive work has been carried out on the interaction of 1,4-dicyanobenzene (DCB) with aromatic hydrocarbons. Beens and Weller⁽¹³⁰⁾ found that the initially formed 1:1 exciplex between naphthalene and DCB was quenched by the hydrocarbon to give an exterplex emitting at longer wavelength. On the

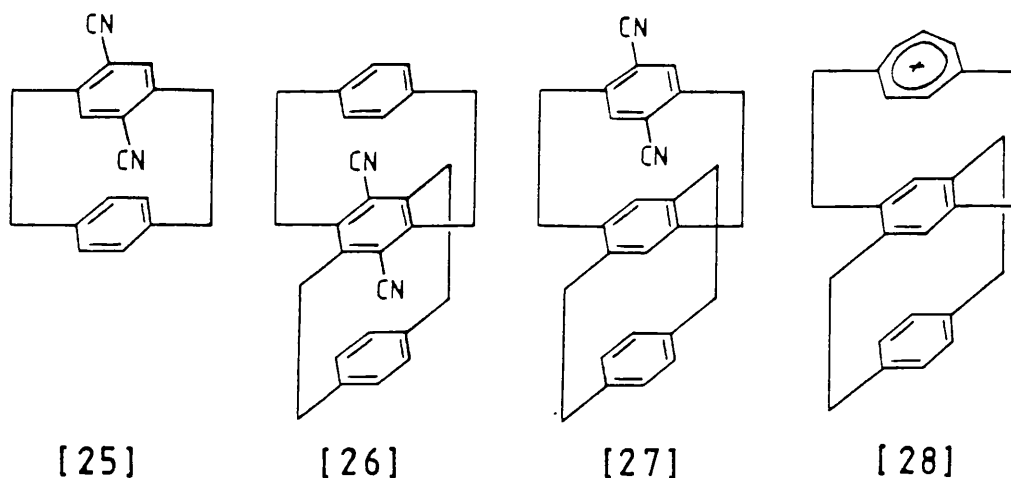
basis of the solvent dependency of the exterplex emission it was assigned a DDA structure, which was subsequently verified by theoretical calculations⁽¹³¹⁾. The quenching of the excimeric emission from 1,3-di-(2-naphthyl)propane by DCB has also been shown to involve a triple complex⁽¹³²⁾ favoured by the fact that the two naphthalene units are held together by a polymethylene chain. Davidson and Whelan⁽¹³³⁾ went on to study the interaction of DCB with a series of dinaphthyl derivatives in degassed chloroform solution. Finding that exterplex formation occurred in the di-(naphthylmethyl)ethers, but was inefficient for 1,4-di-(2-naphthyl)butane, they concluded that fluorescent exterplex formation was only efficient when the dinaphthyl compound could itself form an intramolecular fluorescent excimer.

The efficiency with which N,N-dimethylaniline quenches anthracene photodimerisation shows a dependency upon the anthracene concentration. It has been proposed⁽¹³⁴⁾ that with high anthracene concentrations, the hydrocarbon is able to interact with the initially formed anthracene - N,N-dimethylaniline exciplex, to give a triple complex, which subsequently collapses to yield the photodimer.

The observation that the use of high amine concentrations in the quenching of aromatic hydrocarbon fluorescence, led to exterplex formation⁽¹²⁹⁾, was investigated further by studying the quenching of naphthalene fluorescence by the α,ω -diaminoalkanes⁽³⁴⁾. It was found that for those diamines efficient at fluorescent excimer formation, the quenching of the hydrocarbon fluorescence was accompanied by exterplex emission. Also, fluorescence quantum yields for the exterplexes were low due to the increased likelihood of non-radiative decay from these systems. The very efficient quenching of

fluorescence from Rose Bengal by the α,ω -diaminoalkanes has also been attributed to the involvement of ternary complexes (135).

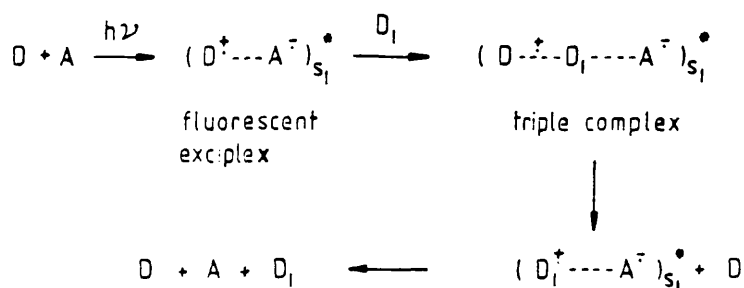
Another category of compounds which very effectively enable the study of bi- and tri-chromophore interactions is the cyclophanes. In a recent piece of work by Mataga and co-workers⁽¹³⁶⁾ the fluorescence properties of the cyano-substituted aryl cyclophanes (25), (26) and (27) were examined.



Whilst (25) corresponded to a bichromophoric DA complex, (26) and (27) were able to form the so-called 'triple-decker' complexes of the DAD and DDA arrangement respectively. Furthermore, in (26) the emission was virtually independent of solvent polarity, providing confirmation of the zero dipole moment in symmetrical DAD type exterplexes. Cyclophanes have also been synthesised which show charge transfer absorption bands as in compound (28)⁽¹³⁷⁾. A number of cycloaddition reactions, including those of phenanthrene with dimethylfumarate⁽¹³⁸⁾ and 9-cyanophenanthrene with dimethylacetylenedicarboxylate⁽¹³⁹⁾ have been found to be quenched by the addition of either electron donor or electron acceptor species. In order to explain these observations, the formation of triple complexes between the added electron donor or acceptor and the exciplex which leads to cycloadduct for-

mation has been proposed.

Following on from this work Caldwell, Creed et al.⁽¹⁴⁰⁾ observed a very interesting result when studying the reaction of 3,10-dicyanophenanthrene and trans-anethole. They found that the exciplex formed between these compounds was quenched by the addition of N,N-diethylaniline, resulting in the formation of a new exciplex between the phenanthrene and the amine. It was proposed that the aniline displaced the anethole from the initially formed anethole-phenanthrene exciplex, via an intermediate triple complex and denoted the reaction as an Exciplex Substitution Reaction (S_{EX}) as shown in Scheme 1.(9). The role of S_{EX} reactions and the formation of



SCHEME 1.(9). Representation of the Exciplex Substitution Reaction (S_{EX}) Involving an Intermediate Exterplex.

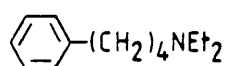
triple complexes has subsequently been studied by invoking the use of Frontier Molecular Orbital Theory⁽¹⁴¹⁾.

1.5. Object of the Work.

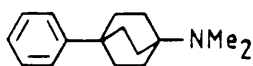
1.5.(1). Introduction.

The conformational requirements for the formation of intramolecular fluorescent excimers and exciplexes have been the subject of extensive investigations and shown to be far stricter than those for quenching of the parent aromatic hydrocarbon fluorescence.

In an elegant piece of work by Davidson et al.⁽¹⁴²⁾, the effect of separating the amine and aromatic hydrocarbon by a rigid bicyclo-[2,2,2]-octane spacer unit was investigated, to see whether the fluorescence quenching process could be stopped and to monitor the effects upon exciplex formation and electron transfer. Comparing the photophysical properties of compounds (29) and (30) revealed that unlike the flexible compound (29), (30) was unable to form an exciplex in non-polar solvents but gave an emission characteristic of the

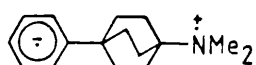


[29]



[30]

amine instead. Since >95% of the incident radiation was entering the phenyl group this result was clearly indicative of energy transfer occurring from the phenyl to the amino group. The observed decrease in fluorescence quantum yield with increasing solvent polarity was interpreted on the basis of laser flash photolysis results, to be due to electron transfer in polar solvents like acetonitrile to generate the



[31]

zwitterionic species (31). Furthermore, in methanol solution a long lived transient was observed which was identified as a solvated electron. These results clearly demonstrated therefore, that conformational mobility was not an essential feature either in energy transfer or electron transfer processes, between donor and acceptor groups within a molecule.

1.5.(2). Hybridisation and Structural Effects upon
Exciplex Formation.

Further to this work on the conformational requirements for intramolecular exciplex formation, the effects of enclosing the nitrogen atom in a saturated cyclic system were investigated. A series of N-(2-arylethyl)azacycloalkanes were therefore synthesised varying the ring substituent from an azacyclopentyl to an azacyclotridecyl unit, to determine whether or not this affected the electron donating properties of the amino grouping and hence the yield of fluorescent exciplex formation.

The ability of tertiary amines to quench aromatic hydrocarbon fluorescence has already been shown to vary according to the hybridisation of the amino group. Planar sp^2 hybridised amines, such as aromatic amines, being more efficient at quenching than the sp^3 hybridised amines. In the case of the saturated aliphatic amines, the amine must become planar in order to form a fluorescent exciplex, thereby expending energy during rehybridisation.

The analogous intermolecular interactions between singlet excited state benzene and a series of N-methylated saturated alicyclic amines were also investigated and the results of these studies are dealt with in Chapter (3). The quenching of naphthalene fluorescence by tertiary aliphatic amines has previously been shown to occur at rates well below the diffusion controlled limit^(34,143,144). Furthermore by carrying out variable temperature studies on the quenching of 2-methylnaphthalene (2MN) by triethylamine (TEA) and N-methylazacyclohexane (NMACH), De Schryver and his colleagues found that both the enthalpy and entropy of complex formation were more negative in the 2MN-TEA system, indicating

that it formed a more ordered and tightly bound complex.

More recently, the influence of the ground state starting conformations upon the rate of intramolecular exciplex formation has been studied in a series of ω -phenyl- α -N,N-dimethylaminoalkanes⁽¹⁴⁵⁾. Although exciplex emission was observed for $n=2,3$ and 4 , a detailed analysis of the fluorescence decay curves, indicated that only certain ground state conformations can readily form the exciplex. The slow-decaying component was therefore attributed to molecules in which the C-N bond had an unfavourable orientation for exciplex formation.

1.5.(3). ^{15}N NMR Spectroscopy.

Another technique which was utilised to investigate the behaviour of the nitrogen atom in the alicyclic systems, was Nitrogen-15 Nmr spectroscopy. Spectra were recorded for a series of amines ranging from the five to the thirteen membered ring derivatives, to determine whether any information could be derived about the electron density around the nitrogen atom in these systems. A number of α,ω -diaminoalkanes were also studied by this technique, in which the linking chain was varied from two up to twelve methylene units in length, to see if this affected the nitrogen chemical shift, relative to the parent N-methylated amine. The 1,2-diaminoethanes and the 1,3-diaminopropanes for example, were known to form excimeric species in cyclohexane solution. The data obtained are discussed in Chapters (4) and (5).

1.5.(4). The Formation of Multi-Chromophore Intramolecular Exciplexes.

As discussed previously in Section 1.4., the formation of exciplexes involving the interaction of more than two

groups has not been widely investigated. Furthermore with the exception of the trichromophoric cyclophanes^(136,137) the examples of ternary complexes reported in the literature have involved the interaction of an excimer or exciplex with another ground state molecule by an intermolecular process. One of the objects of the work undertaken in this thesis therefore was to investigate the formation of intramolecular excited complexes involving more than two interacting chromophores. Attempts were made to synthesise a number of compounds containing an aromatic hydrocarbon unit (the acceptor species) and two or more amino groups (the donor species) and the results of this work are discussed in Chapter (6).

CHAPTER TWO

The Formation of Intra- Molecular Fluorescent Exciplexes in 1-Aryl-2- (Azacycloalkyl) Ethanes.

2.1. INTRODUCTION

The formation of intramolecular fluorescent exciplexes between aromatic hydrocarbons and both aromatic and aliphatic amines, has been extensively studied and is well documented in the literature. Since exciplex formation occurs most efficiently, when the two interacting chromophores are separated by a di- or trimethylene chain, compounds for use in this present investigation, were synthesised with a dimethylene linkage. The experimental procedures are detailed in Chapter (7) Sections 7.2. and 7.3.

Previous work involving aliphatic amines, had utilised compounds containing a terminal dialkyl amino group, (NR_2 ; where $\text{R} = \text{Me}; \text{Et}$), but little solution phase work had been reported on the use of saturated alicyclic amines. A number of azacyclo-alkyl derivatives were therefore prepared of the general formula shown below,



varying the size of the ring from a 5 to a 13 membered ring, to determine whether this affected the ability of the amino group to quench the aromatic hydrocarbon fluorescence, or reduce the quantum yield of fluorescent exciplex formation (ϕ_{f_E}). Studies on the efficiency of intramolecular exciplex formation, were carried out using two aromatic hydrocarbons. The results for the 1- or α -naphthyl series of derivatives are detailed in Section 2.2., whilst those for the phenyl series are dealt with in Section 2.3.

2.2. 1-NAPHTHYL DERIVATIVES.

2.2.(1). U/V Absorption Spectra.

Solutions used for fluorescence measurements were made

up to an OD = 0.1 at 310nm, the excitation wavelength and in each case, the ultra-violet absorption spectrum of the solution was recorded. The absence of any new absorption bands in the u/v spectra of the 1-naphthyl derivatives, relative to the spectrum of 1-methylnaphthalene, indicated the lack of charge transfer interactions between the aromatic hydrocarbon and the amino group in the ground state. However, certain changes in the intensity of the absorption spectra were apparent, and a representative sample of the spectra for the 1-naphthyl derivatives in cyclohexane solution, are shown in Figure 2.(1).

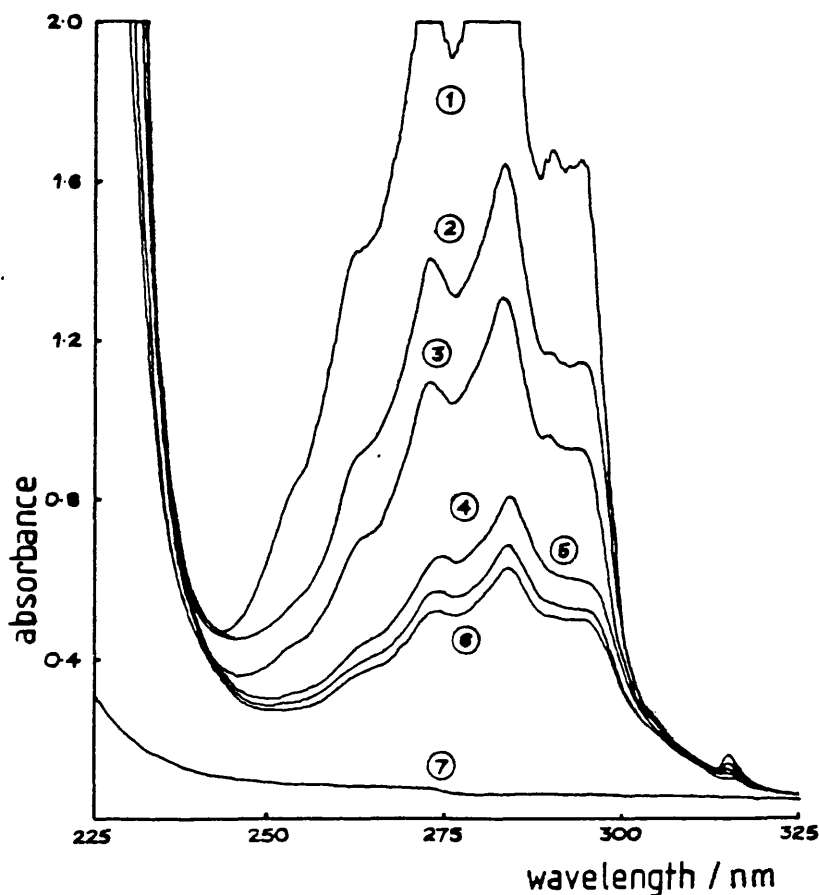


FIGURE 2.(1). U/V Absorption Spectra of the following
1-Naphthyl Derivatives in Cyclohexane
Solution (OD 0.1 @ 310nm): (1) 1-MeNp,
1-Np(CH₂)₂N(CH₂)₂n (2) n=4, (3) n=5,
(4) n=6, (5) n=7, (6) n=8, (7) Cyclohexane
Solvent Blank.

Although the absorption maxima remained the same as those for 1-methylnaphthalene (bands at 262nm, 272nm, 282nm, 290nm, 293nm and 315nm), the absorption spectra of the N-(2-(1'-naphthyl)ethyl)azacycloalkanes were weaker. Furthermore, the decrease in intensity of the absorption with respect to the 1-methylnaphthalene, was observed to increase with increase in ring size of the azacycloalkane, from the 5 up to the 9 membered ring. Also, for a given 1-naphthyl derivative, the absorption decreased in intensity on going from the non-polar solvent cyclohexane, to tetrahydrofuran (fairly polar) and finally to a polar solvent like acetonitrile. The loss of fine structure in the u/v absorption spectrum, particularly on moving to the larger ring derivatives, suggests that the amine is making a considerable contribution to the absorption, i.e. the amine chromophore is competing with the aromatic hydrocarbon chromophore for the absorption of the incident radiation.

2.2.(2). Fluorescence Spectra.

The fluorescence spectra of the 1-naphthyl derivatives were recorded for both aerated and degassed solutions, using an excitation wavelength of 310nm. Details of the degassing procedures used are given in Chapter (7), Section 7.8.

2.2.(2).1. N-(2-(1'-naphthyl)ethyl)azacycloalkanes.

The fluorescence spectra of the 2-(1'-naphthyl)ethyl derivatives were recorded in cyclohexane, benzene, tetrahydrofuran (THF) and acetonitrile solutions and the wavelength maxima ($\lambda_{\max}$) for the emissions are summarised in Table 2.(1). To enable the calculation of the quantum yields of fluorescent exciplex formation (ϕ_{f_E}) and the quantum yields of residual naphthalene monomer fluorescence (ϕ_{f_M}),

COMPOUND	$\lambda_{\max}(\text{nm})$			
	SOLVENT			
			THF	MeCN
1-Np(CH ₂) ₂ N(CH ₂) ₄	374	417	447	500
1-Np(CH ₂) ₂ N(CH ₂) ₅	360	405	438	488
1-Np(CH ₂) ₂ N(CH ₂) ₆	374	413	440	493
1-Np(CH ₂) ₂ N(CH ₂) ₇	374	413	443	490
1-Np(CH ₂) ₂ N(CH ₂) ₈	370	408	432	470
1-Np(CH ₂) ₂ N(CH ₂) ₁₂	370	405	430	467

TABLE 2.(1). Fluorescence $\lambda_{\max}$ Values (nm) for a Series of N-(2-(1'-naphthyl)ethyl)azacycloalkanes in Degassed Cyclohexane, Benzene, Tetrahydrofuran and Acetonitrile Solutions.

the spectra were all recorded relative to a fluorescence standard, 1-methyl naphthalene, of known absolute quantum yield of fluorescence ($\phi_{f_s} = 0.21$)⁽¹⁴⁶⁾. The values of ϕ_{f_E} and ϕ_{f_M} for the 2-(1'-naphthyl)ethyl- derivatives in degassed solutions are summarised in Table 2.(2).

2.2.(2).2. N-(1'-naphthylmethyl)azacycloalkanes.

A number of compounds were also prepared in which the 1-naphthyl and the azacycloalkyl units were separated by a single methylene group. The wavelength maxima ($\lambda_{\max}$) for the fluorescence spectra observed are given in Table 2.(3). The emission was found to be much weaker for this series of derivatives and in all cases it was necessary to open up the slits on the excitation and emission monochromators (slits 8/8), in order to observe the emission and obtain a more accurate estimate of the $\lambda_{\max}$ values for the signal.

COMPOUND	SOLVENT					
			THF		MeCN	
	ϕ_{fM} ϕ_{fE}	ϕ_{fM} ϕ_{fE}	ϕ_{fM}	ϕ_{fE}	ϕ_{fM}	ϕ_{fE}
1-Np(CH ₂) ₂ N(CH ₂) ₄	- 0.252	0.011 0.124	0.024	0.043	0.008	0.019
1-Np(CH ₂) ₂ N(CH ₂) ₅	0.010 0.236	0.002 0.101	0.025	0.063	0.004	0.029
1-Np(CH ₂) ₂ N(CH ₂) ₆	- 0.261	0.005 0.128	0.173	0.090	0.007	0.039
1-Np(CH ₂) ₂ N(CH ₂) ₇	- 0.313	0.004 0.155	0.082	0.098	0.003	0.049
1-Np(CH ₂) ₂ N(CH ₂) ₈	- 0.400	- 0.189	-	0.190	0.003	0.086
1-Np(CH ₂) ₂ N(CH ₂) ₁₂	- 0.415	- 0.224	0.014	0.143	0.002	0.073

TABLE 2.(2). Quantum Yields of Residual Naphthalene Monomer Fluorescence (ϕ_{fM}) and Fluorescent Exciplex Formation (ϕ_{fE}) for a Series of 1-Np(CH₂)₂N(CH₂)_n Derivatives in , , THF and MeCN Solutions.

COMPOUND	$\lambda_{\max}$ (nm)		
	SOLVENT		
			MeCN
1-NpCH ₂ N(CH ₂) ₄	360	415	495
1-NpCH ₂ N(CH ₂) ₅	360	415	495
1-NpCH ₂ N(CH ₂) ₆	360	415	500
1-NpCH ₂ N(CH ₂) ₇	360	415	490
1-NpCH ₂ N(CH ₂) ₁₂	365	415	470

Table 2.(3). Fluorescence $\lambda_{\max}$ Values (nm) for selected N-(1'-naphthylmethyl)azacycloalkanes in Degassed Cyclohexane, Benzene and Acetonitrile Solutions.

The measurement of quantum yields of fluorescent exciplex formation (ϕ_{f_E}) and residual naphthalene monomer fluorescence (ϕ_{f_M}), was therefore impractical for any of the derivatives, since yields were clearly <0.001 . A structureless emission band maximising at around 350-360nm was noted in both benzene and acetonitrile solutions, which was attributed to fluorescence from the naphthalene monomer. The azacyclotridecane derivative however, appeared to show only exciplex emission when the spectra were recorded in cyclohexane and benzene solutions.

A representative selection of the fluorescence spectra obtained for the 1-naphthylethyl- derivatives, in cyclohexane benzene, tetrahydrofuran and acetonitrile solutions are shown in Figures 2.(2). to 2.(7). For comparative purposes, the fluorescence spectra of 1-methyl naphthalene in cyclohexane solution and both 1-Np(CH₂)₂NEt₂ and 1-Np(CH₂)₂NMePh in various solvents⁽¹⁴⁷⁾ are included.

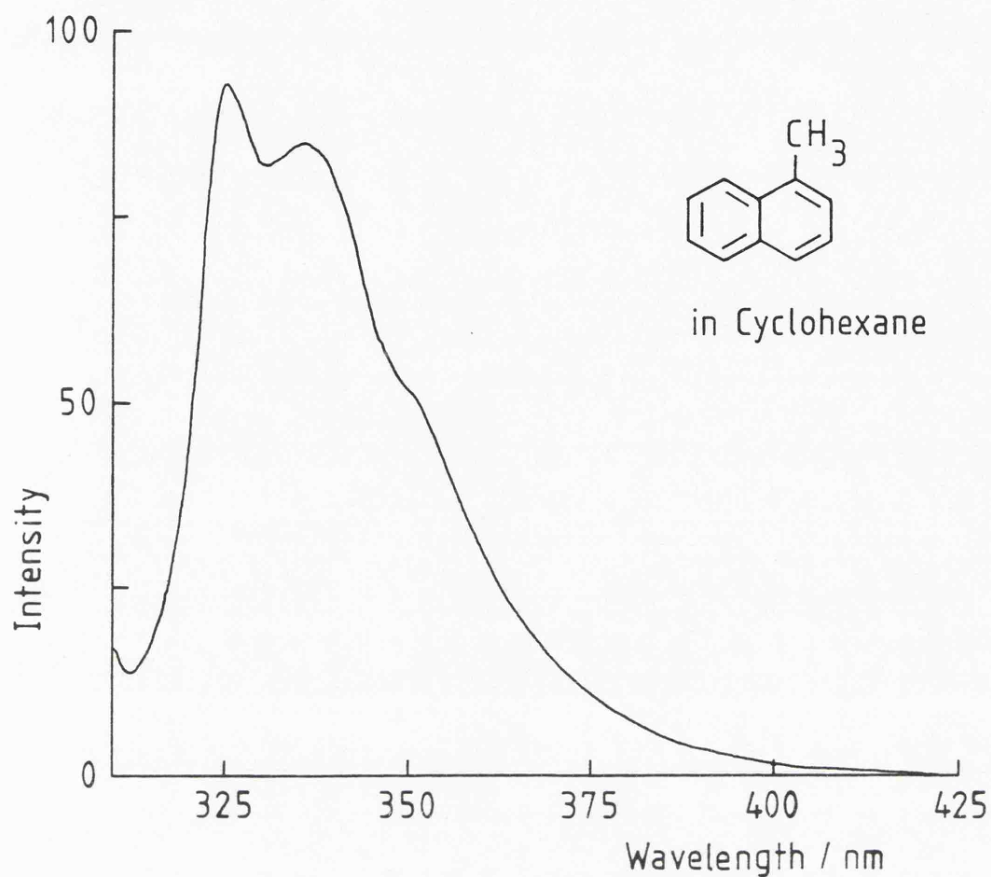


FIGURE 2.(2a). Fluorescence Spectrum of 1-MeNp in
Degassed Cyclohexane Solution.

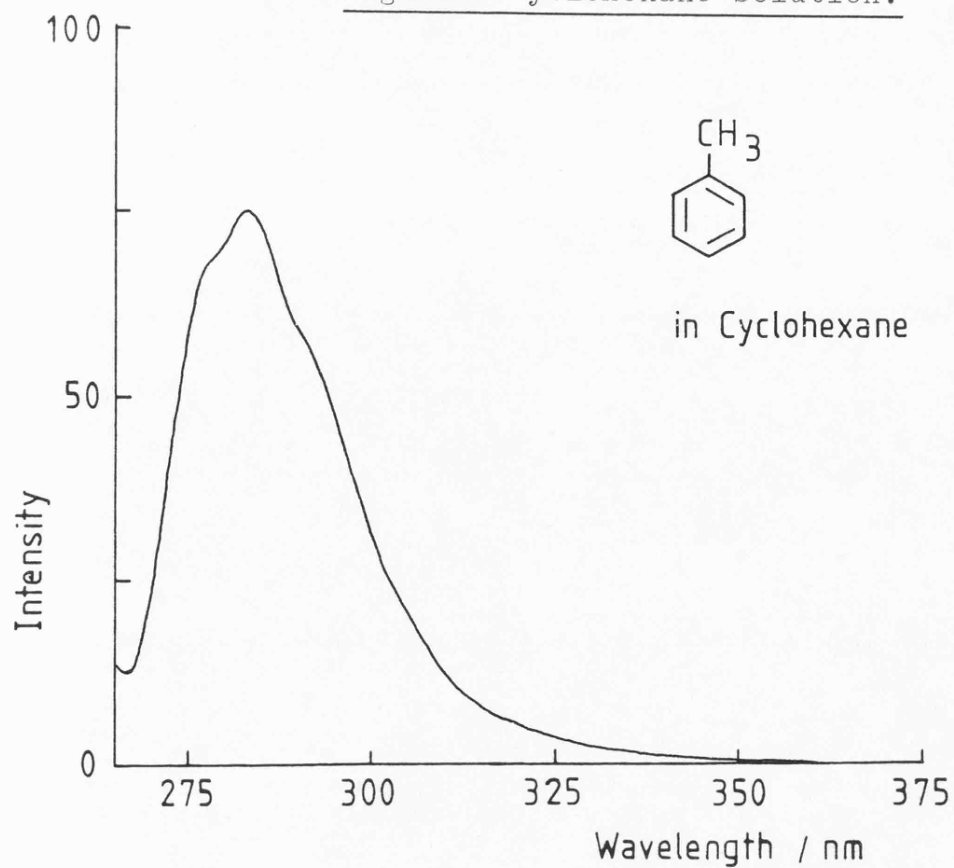


FIGURE 2.(2b). Fluorescence Spectrum of Toluene in
Degassed Cyclohexane Solution.

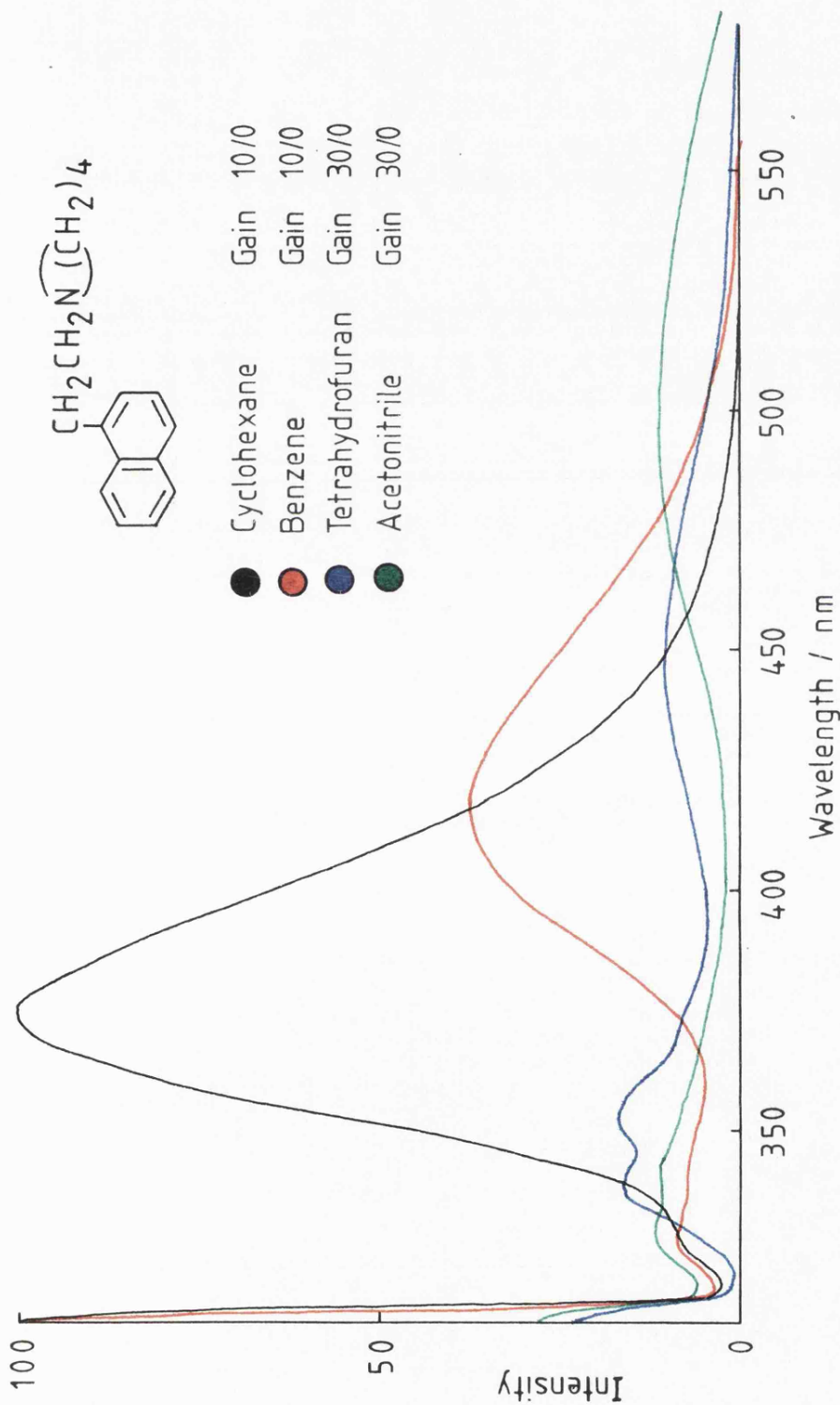


FIGURE 2.(3). Fluorescence Spectra of 1-NpCH₂CH₂N(CH₂)₄ in Degassed Cyclohexane, Benzene, THF and Acetonitrile Solutions at 20°C.

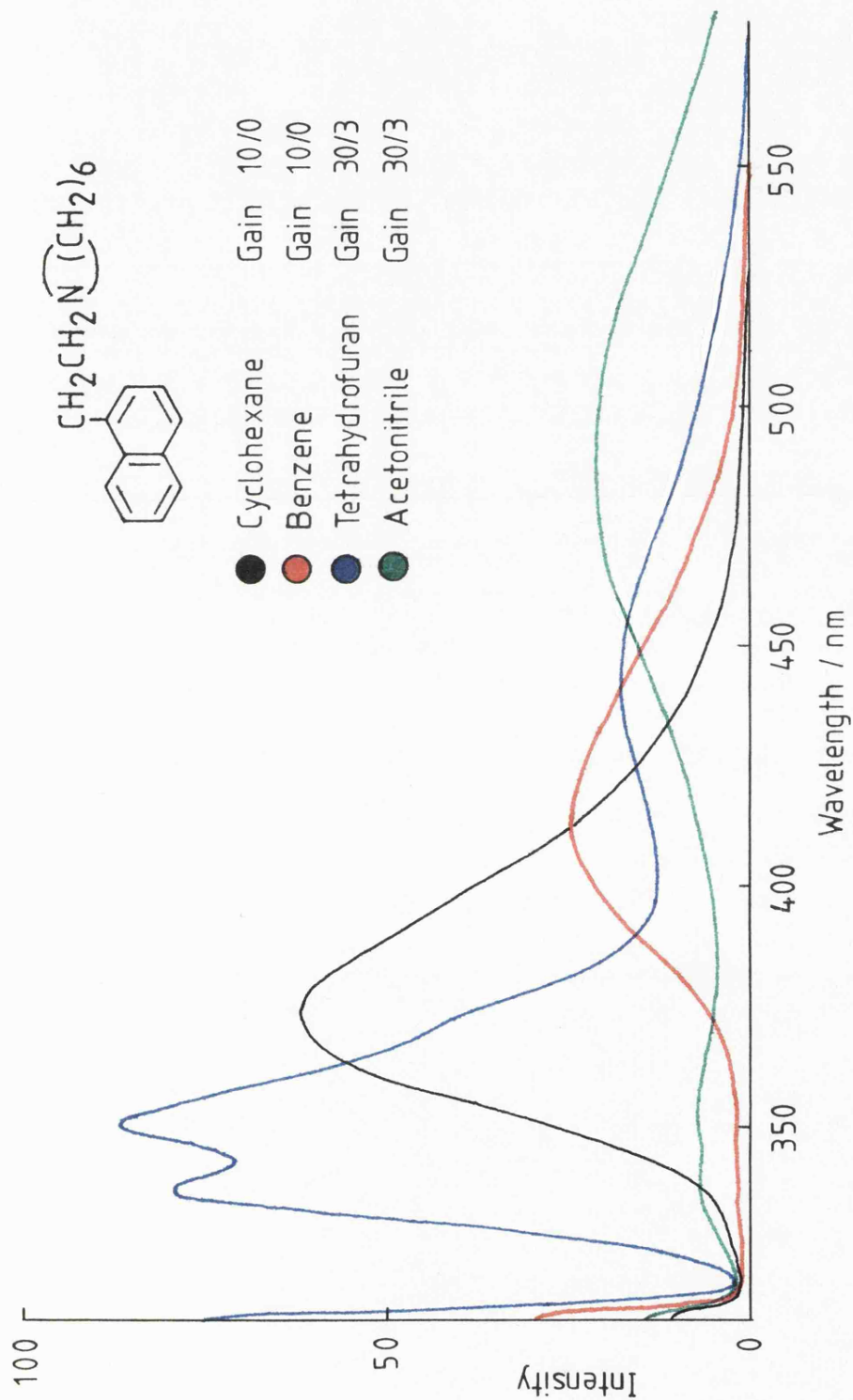


FIGURE 2.(4). Fluorescence Spectra of 1-NpCH₂CH₂N(CH₂)₆ in Degassed Cyclohexane, Benzene, THF and Acetonitrile Solutions at 20°C.

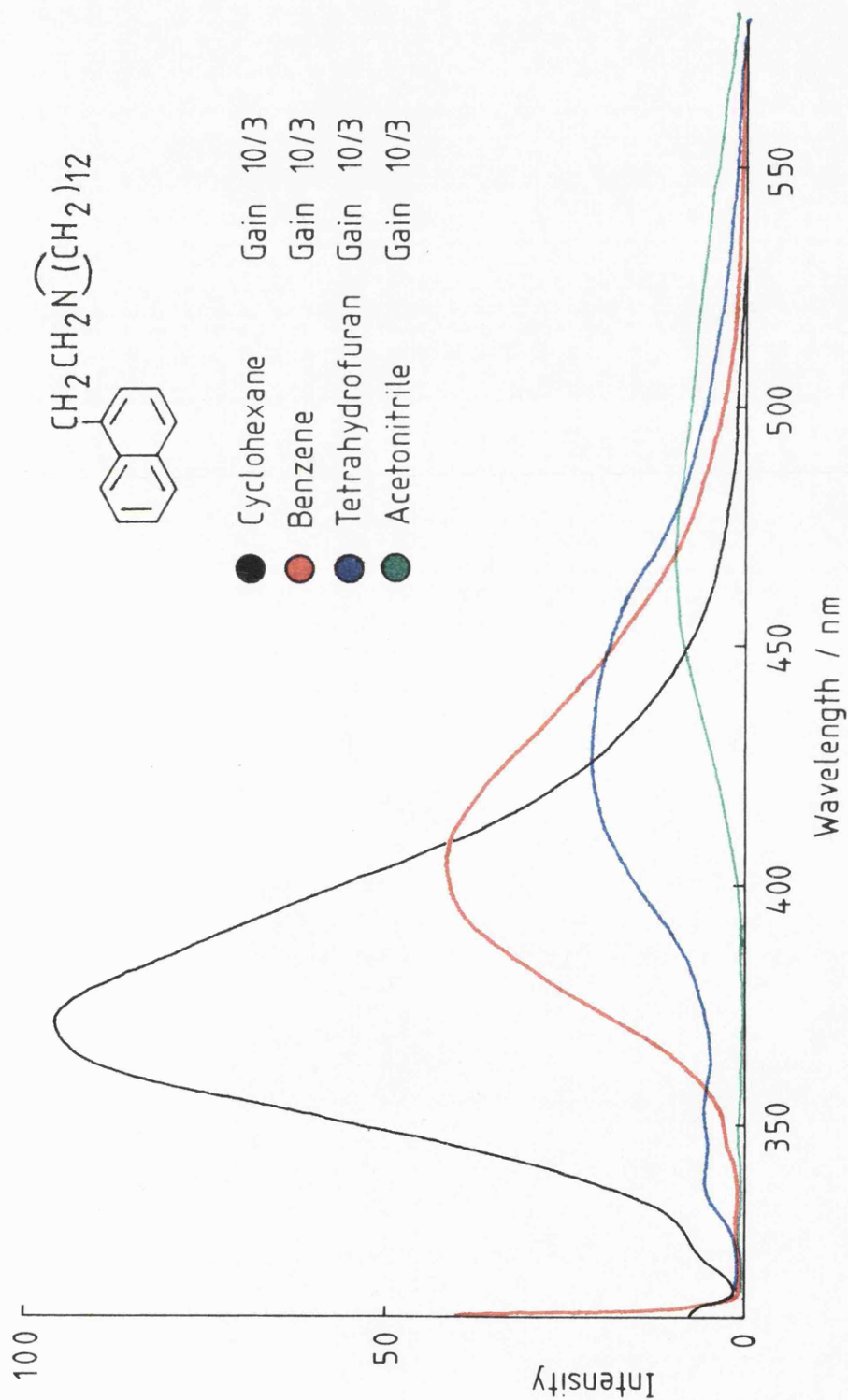


FIGURE 2.(5). Fluorescence Spectra of 1-NpCH₂CH₂N(CH₂)₁₂ in Degassed Cyclohexane, Benzene, THF and Acetonitrile Solutions at 20°C.

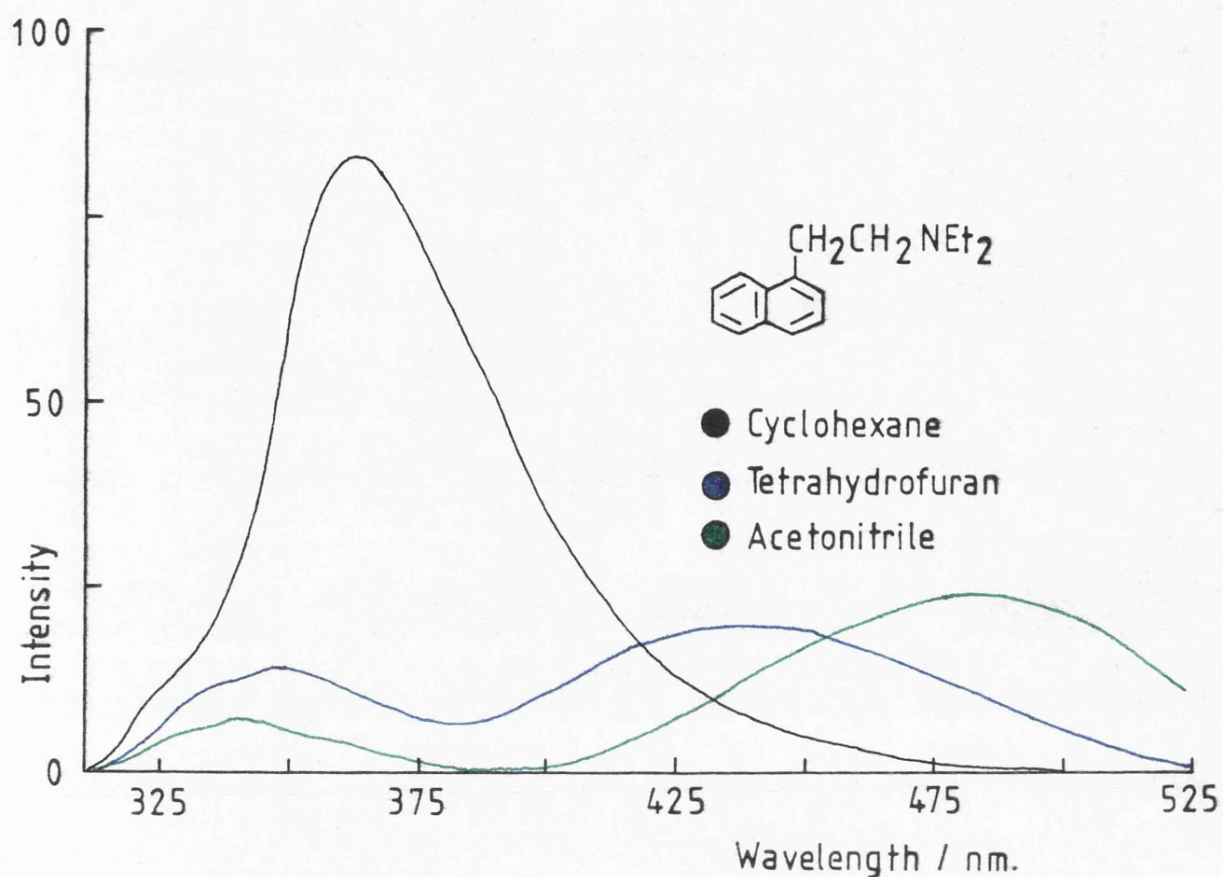


FIGURE 2.(6). Fluorescence Spectra of 1-NpCH₂CH₂NEt₂ in Degassed Cyclohexane, THF and MeCN Solutions.

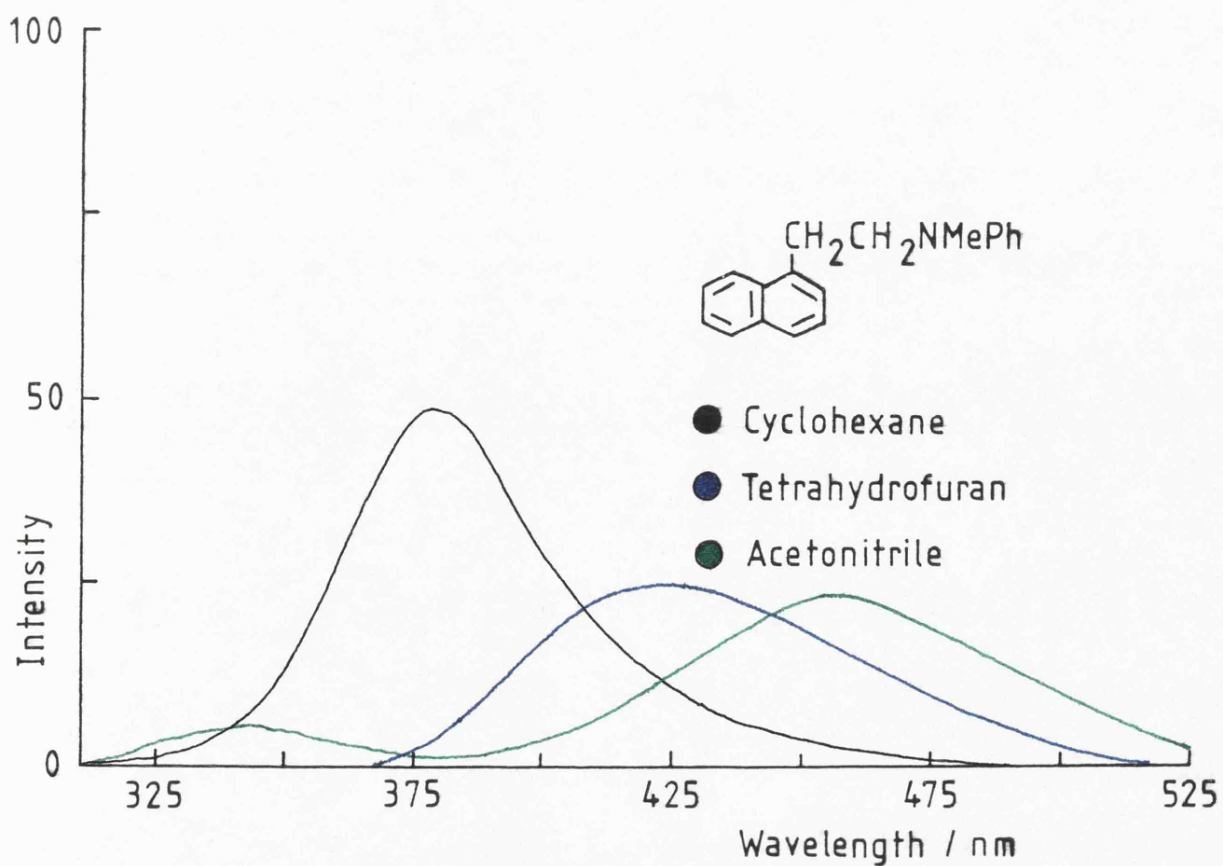


FIGURE 2.(7). Fluorescence Spectra of 1-NpCH₂CH₂NMePh in Degassed Cyclohexane, THF and MeCN Solutions.

2.2.(2).3. Discussion.

Although it can be seen from the fluorescence results, that the quenching of the naphthalene emission by the amino-groups was very efficient in the N-(1'-naphthylmethyl)-azacycloalkanes, the quenching did not lead to the formation of a fluorescent exciplex, to any appreciable extent (only detectable using wide slit widths on the monochromators). Furthermore, for a given solvent, the weak exciplex emission which was observed for these derivatives, showed very little variation in maximal wavelength with change in ring size of the azacycloalkyl group.

In the N-(2-(1'-naphthyl)ethyl)azacycloalkanes however, the quenching of the monomeric emission was accompanied by the relatively efficient formation of a fluorescent exciplex, which could be observed in a wide range of solvents of different polarity. These findings were consistent with the earlier work of Chandross and Thomas⁽¹⁰⁴⁾ and Davidson and Trethewey⁽¹⁴⁸⁾, using compounds of the type $\text{Ar}(\text{CH}_2)_n\text{NR}_2$, where Ar = phenyl or naphthyl and R = methyl or ethyl. A more pronounced trend in the λ_{max} values for the exciplex emission was observed in the 1-naphthylethyl series of compounds, as detailed below.

Cyclohexane - With the exception of the azacyclohexyl derivative, which showed some weak residual naphthalene emission ($\phi_{\text{fM}} = 0.01$), the compounds exclusively gave exciplex emission in this solvent. Overall, little variation was observed in the λ_{max} of fluorescence apart from a very slight shift to shorter wavelength (a hypsochromic or blue-shift) of $\sim 5\text{nm}$, on increasing the ring size from the 5 to the 13 membered ring. However, quite a pronounced blue-shift in the fluorescence spectrum was observed for the aza-cyclohexyl derivative, whose

$\lambda_{\max}$ value was 360nm as opposed to 374nm for both the azacyclopentyl and -heptyl derivatives. A similar deviation was also noted in the quantum yields of fluorescent exciplex formation (ϕ_{f_E}). Whilst the general trend observed was for the quantum yield to increase with increasing ring size, from 0.252 (azacyclopentyl ring) to 0.415 (azacyclotridecane derivative), a decrease in ϕ_{f_E} was found for the 6 membered ring derivative, as shown in Table 2.(2).

Benzene - On moving to the moderately polar solvent benzene, a fairly weak naphthalene monomer emission was exhibited by several of the compounds (ϕ_{f_M} values in the range 0.002 to 0.011) upto and including the azacyclooctyl derivative. All of the compounds showed a characteristic exciplex emission, which was red-shifted relative to the exciplex emission in cyclohexane solution. Once again, the azacyclohexyl derivative showed slight deviations from the rest of the series. As can be seen from Tables 2.(1). and 2.(2)., there was a gradual blue-shift in the fluorescence $\lambda_{\max}$ values and increase in quantum yield (ϕ_{f_E}), on increasing the ring size. However, the $\lambda_{\max}$ value for the azacyclohexyl derivative was low (405nm) in comparison with the 5 and 7 membered ring derivatives, and gave the lowest quantum yield ($\phi_{f_E} = 0.101$).

Tetrahydrofuran - In this solvent, the quenching of the naphthalene fluorescence was found to be less efficient, and a considerable amount of the fluorescence observed, could be attributed to the monomeric species, the quantum yields of which varied quite appreciably, as shown in Table 2.(2). The azacycloheptyl derivative, appeared to be particularly inefficient at quenching the naphthalene fluorescence in tetrahydrofuran solution ($\phi_{f_M} = 0.172$), but did nevertheless form a fluorescent exciplex. At the other extreme, the azacyclononyl derivative quenched the naphthalene fluorescence

so efficiently, that it gave exclusively exciplex emission.

Exciplexes were observed for all of the derivatives, with the wavelengths of maximal emission to the red of those observed in less polar solvents. A blue-shift in the fluorescence maxima was noted, with increase in ring size, from 447nm to 430nm. The azacyclohexyl derivative, deviated only slightly from the trend in λ_{max} values shown by the other compounds in the series.

Acetonitrile - In the highly polar solvent acetonitrile, emission from both the naphthalene monomer and the exciplex was observed, for all the azacycloalkane derivatives. The quantum yields of fluorescence from the monomer were low, (ranging from 0.002 to 0.008), showing little variation with ring size of the amino group. The emission from the exciplex was also found to be fairly weak but increased in intensity down the series (to larger ring size) though the ϕ_{f_E} value for the azacyclononyl derivative was higher than that of the azacyclotridecane derivative. The λ_{max} values underwent a blue-shift as the ring size was increased, and this was particularly pronounced for the larger ring systems, which maximised at ~470nm in comparison with ~490nm for the medium sized ring derivatives.

Clearly, increasing the solvent polarity has caused a red-shift in the exciplex fluorescence, accompanied by a reduction in the quantum yield of exciplex formation (ϕ_{f_E}), consistent with the results of work previously carried out on aromatic hydrocarbon-amine exciplexes. The red-shift in the fluorescence with increasing solvent polarity, has been attributed to the increasing solvating power of the solvent, stabilising the excited charge-transfer species by favourable dipole-dipole interactions. However, working in opposition

to this effect, is the increasing tendency for complete electron transfer to occur in polar solvents such as acetonitrile, leading to dissociation of either the encounter complex or the relaxed exciplex into solvent separated radical ions. It is the availability of this additional non-radiative decay pathway from the excited state, which accounts for the observed reduction in the quantum yield of exciplex formation.

On the basis of the spectroscopic data summarised in Tables 2.(1). and 2.(2)., it would appear that the efficiency of intramolecular exciplex formation, increases with increase in the ring size of the amino group, and this trend is particularly pronounced in cyclohexane solution. However one very apparent deviation from this trend occurs with the azacyclohexyl derivative. For this compound, the exciplex formed, emits at a shorter wavelength and gives a lower quantum yield than anticipated. Whilst the quantum yield of fluorescence (ϕ_{fE}), indicates the favourability of exciplex formation, it does not alone indicate which of the exciplexes is energetically most stable. As mentioned in Chapter (1), the stability of the exciplex is dependent upon a number of parameters, including the ionisation potential of the donor, the electron affinity of the acceptor, the Coulombic interaction between the charged entities and the heat of solvation of the charge-transfer species. Therefore, in order to accurately assess the complex stability, it is necessary to monitor the temperature dependency of the monomer and exciplex emission. Since the nature of the amine is being varied in this series, it would appear that the differences in exciplex yield observed, might simply be due to the differences in ionisation potential and hybridisation of the amino group.

In two recent pieces of work by De Schryver and his colleagues, using ω -phenyl- α -N,N-dimethylaminoalkanes⁽¹⁴⁵⁾ and N-(2-(2'-naphthyl)ethyl)azacyclohexane⁽¹⁴⁹⁾, the authors suggested on the basis of their kinetic studies, that the photophysical processes occurring in the excited state, were controlled by ground state conformational factors. They proposed that it was necessary for the nitrogen lone pair to be able to interact with the aromatic hydrocarbon, in order to form an intramolecular complex and that this was only possible for certain favourable conformations. From a consideration of the energy barriers to nitrogen inversion and C-N bond rotation, it was concluded that conformational changes were not expected to occur within the lifetime of the excited state aromatic hydrocarbon. Since one would anticipate the azacycloalkane derivatives to adopt different ground state conformations, these differences should be reflected in the efficiencies of intramolecular fluorescent exciplex formation. The efficiency of fluorescent exciplex formation can only really be accurately assessed by consideration of the rate constants for the processes. However since it was not possible to obtain values for these rate constants from fluorescent lifetime measurements, we were forced to use the quantum yield data to assess the efficiency. The reasons for this are twofold. In the intramolecular systems, it is still necessary for the interacting groups to migrate towards one another, therefore one cannot treat the exciplex formation process as being truly unimolecular. Furthermore, these compounds adopt a number of conformations in solution, each of which will have its own rate constant for fluorescent exciplex formation.

In Table 2.(4) ., the quantum yields of fluorescent exciplex formation (ϕ_{f_E}) and the fluorescence $\lambda_{\max}$ values are given, for the related compounds 1-Np(CH₂)₂NEt₂⁽¹⁴⁷⁾ and 1-Np(CH₂)₂NMePh⁽¹⁴⁷⁾.

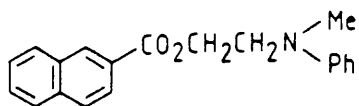
COMPOUND	SOLVENT					
		THF		MeCN		
	$\lambda_{\max}$	ϕ_{f_E}	$\lambda_{\max}$	ϕ_{f_E}	$\lambda_{\max}$	ϕ_{f_E}
1-Np(CH ₂) ₂ NEt ₂	365	0.41	433	0.10	482	0.04
1-Np(CH ₂) ₂ NMePh	377	0.21	425	0.17	465	0.10

TABLE 2.(4). Fluorescence Wavelength Maxima and Quantum Yield of Fluorescent Exciplex Formation of 1-Np(CH₂)₂NEt₂ and 1-Np(CH₂)₂NMePh, in Degassed Cyclohexane, Tetrahydrofuran and Acetonitrile Solutions.

If one compares the ϕ_{f_E} values for the diethylamino-derivative, with those of its nearest alicyclic analogue the azacyclopentyl derivative, then it would appear that the acyclic compound is more efficient at fluorescent exciplex formation. Despite this fact however, once formed, the differences in energy between the exciplexes in their S₁ states and their respective S₀ dissociative ground states, appear to be similar, as reflected by the fluorescence $\lambda_{\max}$ values. In non-polar solvents, both the acyclic and alicyclic aliphatic amino derivatives appear to be more efficient at fluorescent exciplex formation than the N-methylanilino-derivative, but this order is reversed on moving to solvents of greater polarity. This suggests that the non-radiative decay pathways become more important for the aliphatic amino

derivatives in polar solvents. The observed increase in quantum yield of fluorescent exciplex formation with increase in ring size of the amino group, cannot be explained in terms of conformational effects in the ring, since the amines vary only slightly in their hybridisation at nitrogen. It is possible that this increase is due to the amino group competing increasingly effectively with the aromatic hydrocarbon chromophore, for the incident excitation radiation. If the amine group is excited into its S_1 manifold, then it will already be in the planar conformation thought to be a requirement for interaction with the excited aromatic chromophore. The absorption of the acyclic and alicyclic tertiary aliphatic amines, will be discussed in detail in Chapter (4), and also the nature of the amine in its excited state.

A precedent for this interpretation of the dual chromophoric excitation enhancing exciplex formation, was provided by the work of Costa and Davidson⁽¹¹⁴⁾, using the naphthoate ester (18) shown below. The authors found that the quantum yield of fluorescent exciplex formation, could be altered quite considerably by selective excitation of either the amino or the naphthalene chromophore.



[18]

2.2.(3). Triplet-Triplet Absorption Spectra.

The triplet-triplet absorption spectra of the naphthalene chromophore in the N-(2(1'-naphthyl)ethyl)azacycloalkanes, were recorded by the technique of nanosecond laser flash photolysis, using cyclohexane, tetrahydrofuran and acetonitrile as solvents. Details of the instrumentation used for

measuring the triplet-triplet absorption decays are given in Chapter (7) Section 7.8.(3). Solutions of the azacycloalkyl derivatives (OD 1.0 @ 249nm, the excitation wavelength) were degassed by repeated 'freeze-pump-thaw-shake-cycles', prior to excitation using single pulses from a KrF excimer laser (260mJ, ~25ns duration).

The absorption spectrum of the naphthalene triplet was measured by noting the change in intensity of the signal with the wavelength at which the absorption was being monitored. Having established the monitoring wavelength at which the absorption was a maximum, (418nm for the 1-methylnaphthalene standard solution), this was kept at the same value for all subsequent decay measurements. The decays of the triplet-triplet absorption spectra with time, were recorded on a Tektronix storage oscilloscope and the traces photographed. A thoroughly degassed solution of 1-methylnaphthalene in cyclohexane ($\phi_{T_S} = 0.48^{(146)}$), was used as the standard for the determination of the quantum yields of triplet formation (ϕ_T) of the azacycloalkyl derivatives, which are summarised in Table 2.(5). The assumption was made in evaluation of the quantum yields of triplet formation, that the ϕ_{T_S} value for 1-methylnaphthalene was invariant with solvent.

Analysis of the decays of the triplet-triplet absorption spectra, according to the graphical procedures detailed in Appendix (I), enabled the evaluation of both the lifetime (τ_T) and the rate of decay (k_T) of the naphthalene triplet, in each case.

Cyclohexane solution - first order decay analyses of the data were found to give linear relationships, enabling the calculation of k_T and τ_T for each of the azacycloalkane derivatives.

<u>COMPOUND</u>	ϕ_T		
	<u>SOLVENT</u>		
		THF	MeCN
1-Np(CH ₂) ₂ N(CH ₂) ₄	0.30	0.29	0.29
1-Np(CH ₂) ₂ N(CH ₂) ₅	0.23	0.27	0.43
1-Np(CH ₂) ₂ N(CH ₂) ₆	0.30	0.25	0.33
1-Np(CH ₂) ₂ N(CH ₂) ₇	0.24	0.21	0.32
1-Np(CH ₂) ₂ N(CH ₂) ₈	0.22	0.24	0.31
1-Np(CH ₂) ₂ N(CH ₂) ₁₂	0.28	0.21	0.38

TABLE 2.(5). Quantum Yields of Triplet Formation (ϕ_T) of
the N-(2-(1'-naphthyl)ethyl)azacycloalkanes,
Recorded in Degassed Cyclohexane, Tetrahydro-
furan and Acetonitrile Solutions, 1-MeNp
 $\phi_{TS} = 0.48.$

Tetrahydrofuran solution - analysis of the spectra in terms of a first-order decay, appeared to give a two component linear relationship, as shown diagrammatically in Figure 2.(8). We interpreted this, as being due to a combination of two first order decays, consequently two rate constants (k_1 and k_2) and the corresponding triplet lifetimes (τ_1 and τ_2) were evaluated in each case. However, it should be noted that an alternative explanation for the observed decay of the triplet naphthalene species in tetrahydrofuran solution, is that it is comprised of both a first and a second order decay component. Second order decay analyses of the data, gave non-linear relationships for these compounds in tetrahydrofuran solution.

Acetonitrile solution - in this solvent, curved relation-

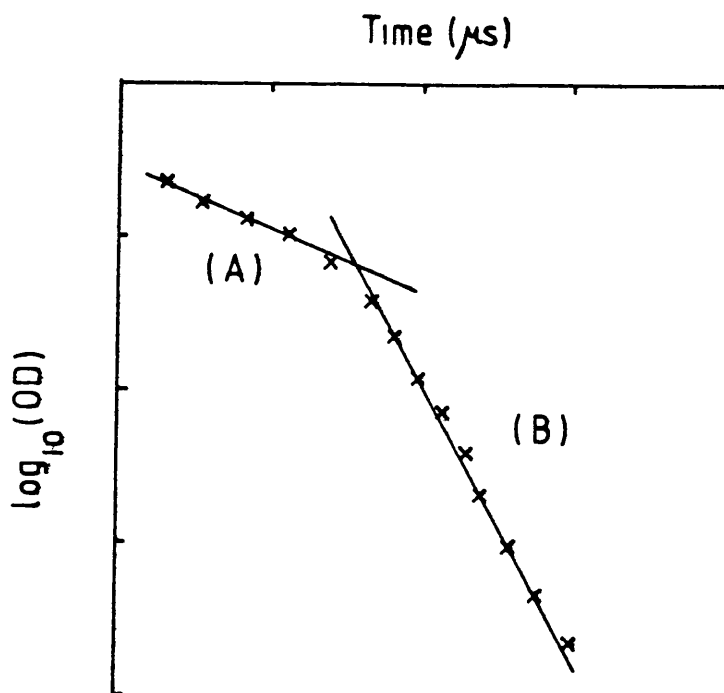


FIGURE 2.(8). Diagrammatic Representation of a Typical Plot of $\log_{10}(\text{OD})$ versus Time (μs) for the Azacycloalkane Derivatives in Tetrahydrofuran Solution. Rate Constant k_1 Derived from Slope of Part(B), and k_2 Derived from Slope of Part(A).

ships were obtained for the first order plots of $\log_{10}(\text{OD})$ versus time but, linearity was obtained from the second order decay analyses. This indicated that the primary decay pathway for the triplet species involved a bimolecular process in acetonitrile solution.

The triplet lifetimes and rate constants for the decay of the naphthalene triplet in azacycloalkane derivatives, are summarised in Table 2.(6). In evaluating the rate constants for the second order decays, the triplet-triplet molar extinction coefficient of naphthalene, was taken as $\epsilon = 22600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (recorded in cyclohexane solution at 20°C)⁽¹⁵⁰⁾.

Discussion

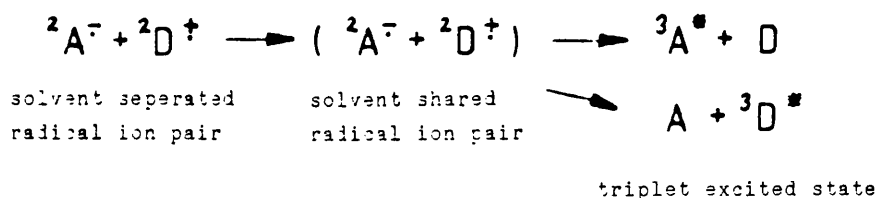
As can be seen from the data summarised in Table 2.(5)., the quantum yield of triplet formation (ϕ_T), shows little

COMPOUND	SOLVENT					
			THF		MeCN	
	$k_1 \times 10^6$ (s ⁻¹)	$\tau_1 \times 10^{-6}$ (s)	$k_1 \times 10^6$ (s ⁻¹)	$\tau_1 \times 10^{-6}$ (s)	$k_2 \times 10^6$ (s ⁻¹)	$\tau_2 \times 10^{-6}$ (s)
1-Np(CH ₂) ₂ N(CH ₂) ₄	0.124	8.04	0.234	4.27	0.521	1.92
1-Np(CH ₂) ₂ N(CH ₂) ₅	0.129	7.75	0.262	3.82	0.512	1.95
1-Np(CH ₂) ₂ N(CH ₂) ₆	0.171	5.85	0.224	4.47	0.423	2.37
1-Np(CH ₂) ₂ N(CH ₂) ₇	0.106	9.42	0.173	5.78	0.382	2.62
1-Np(CH ₂) ₂ N(CH ₂) ₈	0.113	8.84	0.216	4.64	0.407	2.46
1-Np(CH ₂) ₂ N(CH ₂) ₁₂	0.131	7.66	0.218	4.60	0.444	2.25
						$k_3 \times 10^{10}$ (s ⁻¹)

TABLE 2.(6). The Triplet State Lifetimes and Rate Constants for the Decay of the Naphthalene Triplet, in a Series of N-(2-(1'-naphthyl)ethyl)azacycloalkyl Derivatives Recorded in Cyclohexane, Tetrahydrofuran and Acetonitrile Solutions.

variation with the solvent used. Since in contrast to this, the quantum yield of fluorescent exciplex formation (ϕ_{fE}), drops off markedly on moving from non-polar to highly polar solvents, clearly the triplet naphthalene species cannot be produced solely from the fluorescent exciplex. Furthermore, the exciplex must lie at an energetically higher level than the naphthalene triplet state.

This suggests that the mechanism for the formation of the triplet state, varies with the solvent used. In non-polar solvents where stabilisation of radical ions is very poor, the triplet will be produced almost entirely from either the non-relaxed encounter complex or the fluorescent exciplex. However, upon increasing the solvent polarity, the radical-ion pairs will be stabilised by favourable interactions with the solvent molecules, and provide an additional pathway to the formation of the triplet species, as shown in Scheme 2.(1).



SCHEME 2.(1). Formation of Triplet State Species from Solvent Separated Radical-Ion Pairs.

In both cyclohexane and tetrahydrofuran solutions, the quantum yield of triplet formation, appeared to decrease slightly with increase in ring size of the amino group, (the opposite of the trend observed in the ϕ_{fE} values). This trend was not however repeated in acetonitrile solution, where the larger ring compounds gave higher ϕ_T values. Since we believe that radical ions play an important part in the formation of the triplet naphthalene in this solvent, the trend may well

reflect the different ionisation potentials of the amines concerned.

The relative lack of variation in the triplet yield of a given azacycloalkyl derivative with the solvent polarity, was in marked contrast to the results obtained for systems containing greater than two interacting groups in the excited state, which will be dealt with in greater detail in Chapter (6).

Table 2.(7) ., summarises the quantum yields of exciplex formation (ϕ_{f_E}) and triplet formation (ϕ_T), for each of the azacycloalkane derivatives studied. The summations of the two terms ($\phi_{f_E} + \phi_T$), have also been evaluated. Although there are slight irregularities in the values shown in the table, it would appear that in general, the ($\phi_{f_E} + \phi_T$) term, increases with increase in ring size of the azacycloalkyl group.

Kinetic analysis - from our analysis of the decays of the triplet-triplet absorption spectra, it is apparent that the mode of decay, varies with the solvent system used. Let us consider the rate of decay of the triplet naphthalene species in these systems, to be given by the expression shown in Equation 2.(1).

$$\frac{-d[\text{Triplet}]}{dt} = k_1[\text{Triplet}] + k_2[\text{Triplet}][\text{Amine}] + k_3[\text{Triplet}]^2 \quad - \text{Eqn. 2.(1).}$$

where the k_1 , k_2 and k_3 terms in the equation, represent the unimolecular, pseudo-unimolecular and bimolecular rate constants for the triplet decay, respectively.

In cyclohexane solution, where first-order decay analyses for the decay of the triplet naphthalene species gave linear relationships, it appeared that $k_1 > k_2[\text{Amine}]$ or $k_3[\text{Triplet}]$ and therefore that the decay occurred by a unimolecular

COMPOUND	SOLVENT									
						THF		MeCN		
	ϕ_{fE}	ϕ_T	$\phi_{fE} + \phi_T$	ϕ_{fE}	ϕ_T	ϕ_{fE}	ϕ_T	ϕ_{fE}	ϕ_T	$\phi_{fE} + \phi_T$
1-Np(CH ₂) ₂ N(CH ₂) ₄	0.252	0.30	0.552	0.043	0.29	0.333	0.019	0.29	0.309	
1-Np(CH ₂) ₂ N(CH ₂) ₅	0.236	0.23	0.466	0.062	0.27	0.332	0.029	0.43	0.459	
1-Np(CH ₂) ₂ N(CH ₂) ₆	0.261	0.30	0.561	0.090	0.25	0.340	0.039	0.33	0.369	
1-Np(CH ₂) ₂ N(CH ₂) ₇	0.313	0.24	0.553	0.098	0.21	0.308	0.049	0.32	0.369	
1-Np(CH ₂) ₂ N(CH ₂) ₈	0.400	0.22	0.620	0.173	0.24	0.413	0.086	0.31	0.396	
1-Np(CH ₂) ₂ N(CH ₂) ₁₂	0.415	0.28	0.695	0.143	0.21	0.353	0.073	0.38	0.453	

TABLE 2.(7). Quantum Yields of Fluorescent Exciplex Formation (ϕ_{fE}), Triplet Formation (ϕ_T) and the Summation of the Two Terms ($\phi_{fE} + \phi_T$) for the N-(2-(1'-naphthyl)ethyl)azacycloalkanes in Cyclohexane, Tetrahydrofuran and Acetonitrile Degassed Solutions at 20°C.

process. Little variation was observed in the magnitude of the rate constant (k_1) for the process - which remained in the range $\sim 1.1-1.3 \times 10^5 \text{ s}^{-1}$ throughout the series of azacycloalkyl derivatives studied. Triplet lifetimes were found to be slightly longer than that of the standard, 1-methylnaphthalene.

In tetrahydrofuran solution, the triplet naphthalene decays gave non-linear plots for both the first order and second order analyses, as shown in Figure 2.(8). It appeared on the basis of these results therefore, that the decay was made up of a pure unimolecular decay component (the k_1 term) and a pseudo-unimolecular decay component (the k_2 term). Hence in Equation 2.(1).,

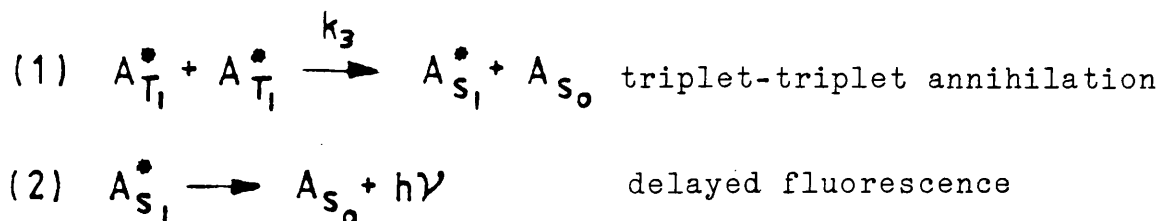
$$\frac{-d[\text{Triplet}]}{dt} = k_1[\text{Triplet}] + k_2[\text{Triplet}][\text{Amine}] \quad \text{--- Eqn. 2.(2).}$$

Since the triplet hydrocarbon is generated in the close vicinity of an amino group in these derivatives, we believe that a quenching interaction is possible between the two species, thereby increasing the rate of decay of the naphthalene triplet state and reducing its lifetime. Consequently we propose that the pseudo-unimolecular k_2 term in the equation, is first order with respect to both the concentration of the triplet hydrocarbon and the concentration of the amine (azacycloalkyl derivative). The magnitudes of both of the rate constants k_1 and k_2 were higher in tetrahydrofuran solution, than those evaluated for k_1 in cyclohexane solution, with corresponding reductions in the lifetimes of the triplet hydrocarbon, as shown in Table 2.(6).

Finally, when the triplet-triplet absorption spectra of the azacycloalkyl derivatives were recorded in acetonitrile solution, linear relationships were obtained from plots of

(1/OD) versus time, indicating that the triplet naphthalene was decaying via a second order (bimolecular) process. Hence it appeared that on moving to highly polar solvents like acetonitrile, $k_3[\text{Triplet}] \gg k_1$ or $k_2[\text{Amine}]$ and therefore the decay occurred primarily by triplet-triplet annihilation.

The general scheme for this process is shown below:



SCHEME 2.(2). Mechanistic Scheme for the Triplet-Triplet Annihilation Process, Leading to p-type Delayed Fluorescence.

As can be seen, the mechanism results in the production of a molecule of A in its excited singlet state, which can then undergo a radiative process on returning to the ground state, producing the so-called p-type delayed fluorescence. The lifetime of this fluorescence is however similar to that of the triplet, because excitation has at some stage resided temporarily in the triplet state A. The rate constants for the triplet-triplet annihilation process for the azacycloalkyl derivatives in acetonitrile solution, were found, as is generally the case, to be close to that for diffusion controlled reactions ($\sim 4-9 \times 10^{10} \text{ s}^{-1}$), see Table 2.(6).

Since the compounds used in this work, contained an intramolecular amino group to act as a donor, the possibility arose, that in addition to generating the excited singlet state naphthalene species, the singlet exciplex could also be produced by the triplet-triplet annihilation process. The latter being formed either by an intra- or an intermolecular interaction between the singlet excited state aromatic hydro-

carbon and the amine. Another possible route to exciplex formation also exists however, since during the annihilation process, two excited triplet state species must approach close to one another, the initially formed excited singlet state naphthalene will be generated in an artificially high local concentration of the amine, such that the interaction of the naphthalene with two amino groups is favoured. Although we have no direct evidence to support the existence of a ternary complex, recent work has shown that the fluorescence quenching in these systems is very efficient. The provision of this decay pathway from the singlet naphthalene, could explain why the decay of the excited triplet naphthalene is so rapid in polar solvents like acetonitrile.

2.3. PHENYL DERIVATIVES.

2.3.(1). U/V Absorption Spectra.

Fluorescence studies on the phenyl derivatives, were carried out on solutions of OD = 0.1, at the excitation wavelength of 265nm. By recording the u/v absorption spectrum of each solution, the existence of any ground state charge transfer absorption bands could be detected. All solutions were found to give only weak absorption spectra, and therefore it was difficult to discern any changes in the absorption either with change in solvent or variation in ring size of the amino grouping. There was no evidence of any ground state interactions between the aromatic hydrocarbon and the amino group.

2.3.(2). Fluorescence Spectra.

The fluorescence spectra were recorded for both aerated and degassed solutions of the N-(2-phenylethyl)azacycloalkanes, using cyclohexane, tetrahydrofuran and acetonitrile

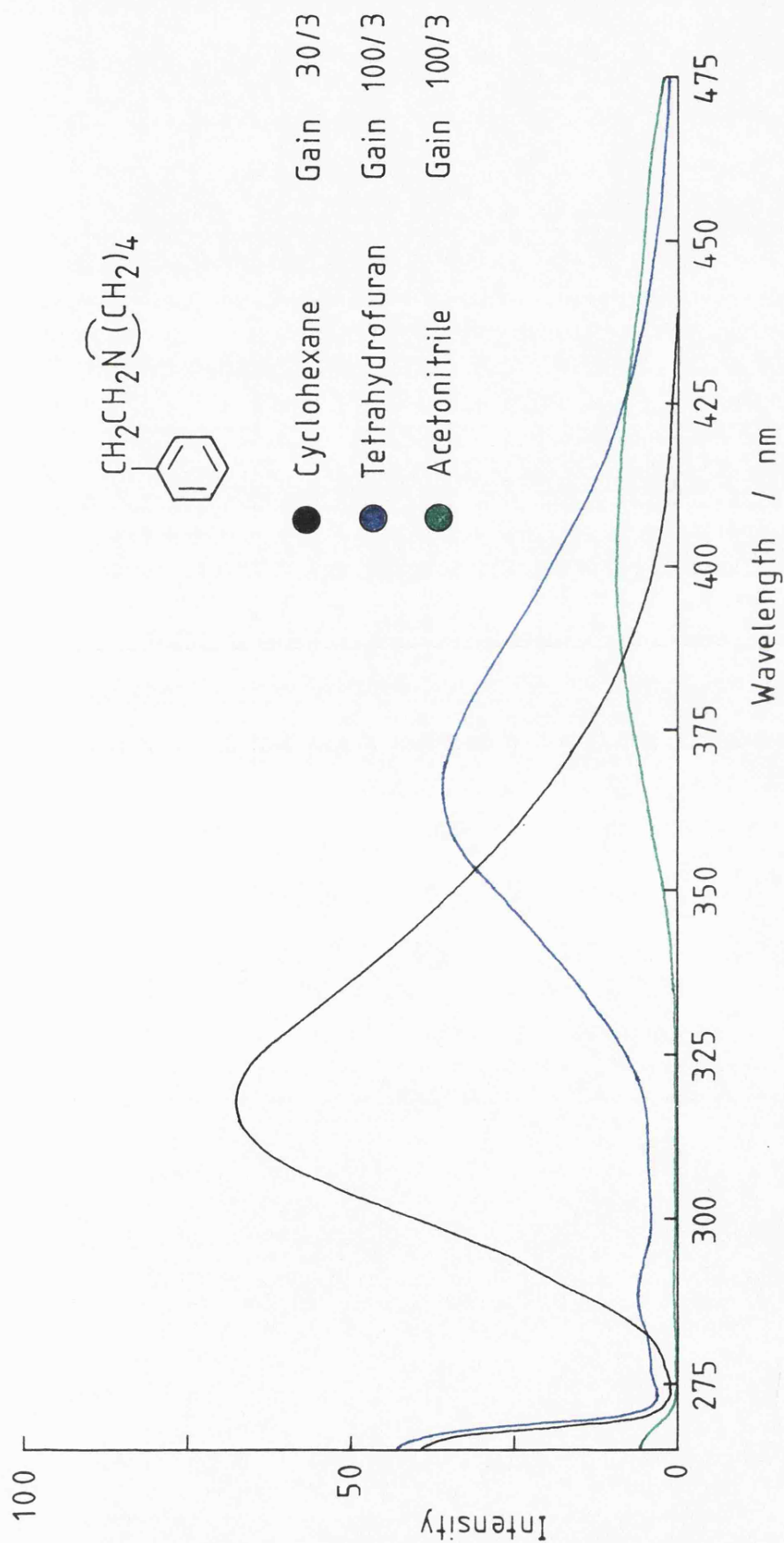


FIGURE 2.(9). Fluorescence Spectra of $\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_4$ in Degassed Cyclohexane, Tetrahydrofuran and Acetonitrile Solutions at 20°C .

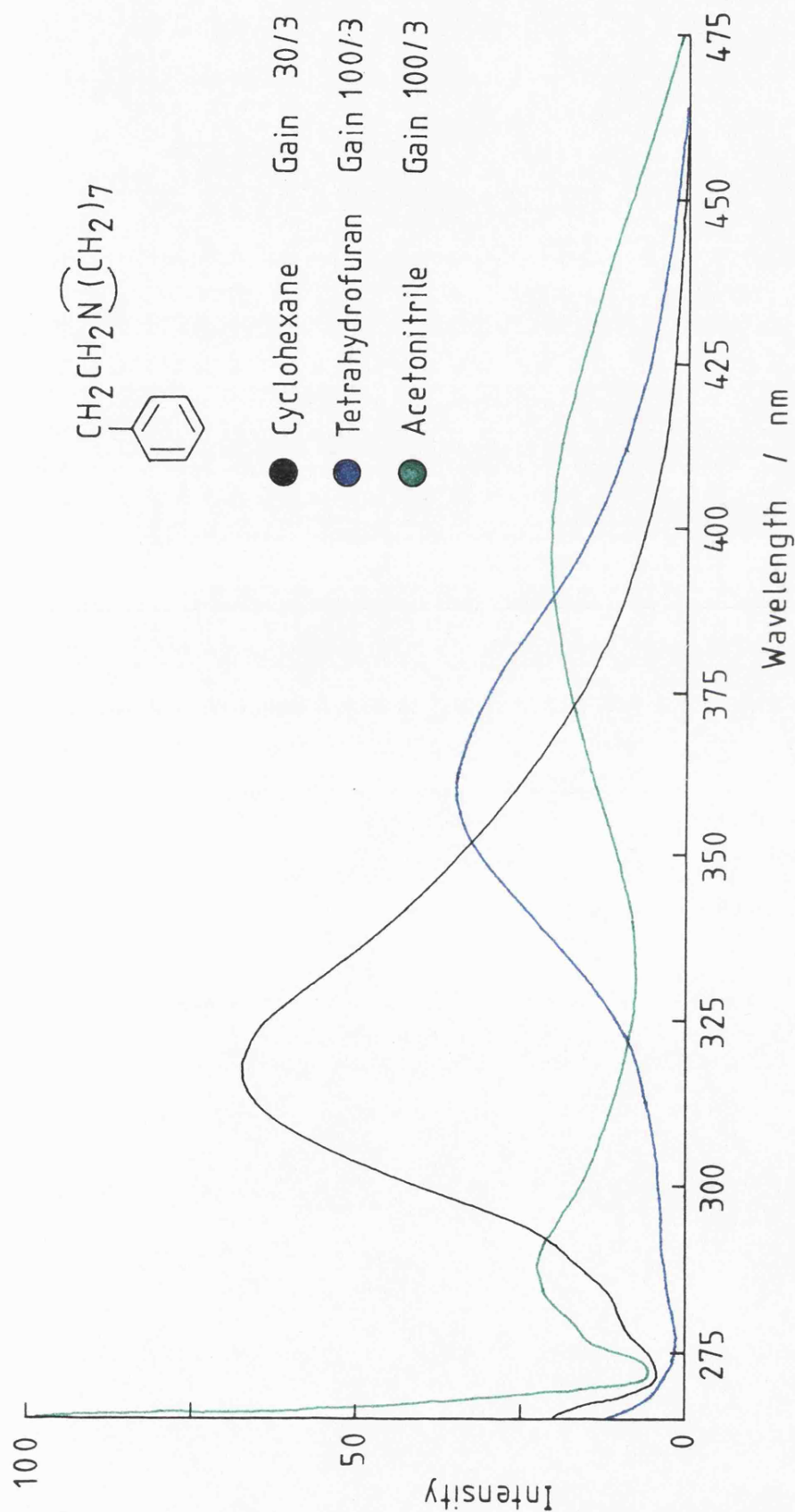


FIGURE 2.(10). Fluorescence Spectra of $\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_7$ in Degassed Cyclohexane, Tetrahydrofuran and Acetonitrile Solutions at 20°C .

as the solvents and excitation at 265nm. The fluorescence $\lambda_{\max}$ values for the emissions are summarised in Table 2.(8). Quantum yields of fluorescent exciplex formation for the azacycloalkyl derivatives were evaluated relative to toluene a standard of known absolute quantum yield of fluorescence ($\phi_{f_S} = 0.14^{(151)}$). The quantum yields of unquenched phenyl monomer emission and exciplex formation are detailed in Table 2.(9).

The fluorescence spectrum of toluene in cyclohexane solution and a representative sample of the spectra of the N-(2-phenylethyl)azacycloalkanes, in solvents of differing polarity, are shown in Figures 2.(2b) 2.(9) and 2.(10)., respectively.

Discussion

As can be seen from the data contained in Tables 2.(8). and 2.(9)., the fluorescence spectra of the N-(2-phenylethyl)azacycloalkanes, follow the typical trends shown by other aromatic hydrocarbon - amine systems, namely a shift in the $\lambda_{\max}$ values for the emission to longer wavelength with increase in solvent polarity, accompanied by a corresponding diminution in the quantum yield of fluorescent exciplex formation (ϕ_{f_E}).

If one now considers the effect of varying the alicyclic amine upon the emission, in cyclohexane solution, there is overall only a small blue-shift in the $\lambda_{\max}$ value, with increase in ring size of $\sim 5\text{nm}$. The exception to this trend however, is provided by the azacyclohexyl derivative, which shows a pronounced blue-shift in its fluorescence spectrum relative to the azacyclopentyl and-heptyl derivatives. The same trend was also shown by the N-(2-(1'-naphthyl)ethyl)azacycloalkanes, which we suggest arises from the different abilities of the

<u>COMPOUND</u>	λ_{max} (nm)		
	<u>SOLVENT</u>		
		THF	MeCN
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_4$	318	365	400
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_5$	305	359	387
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_6$	320	360	400
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_7$	318	362	395
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_8$	316	358	387
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_{12}$	313	357	367

TABLE 2.(8). Wavelengths of Maximal Emission for a Series of N-(2-phenylethyl)azacycloalkanes, in Degassed Cyclohexane, Tetrahydrofuran and Acetonitrile Solutions at 20°C.

amine chromophores to compete with the aromatic hydrocarbon for absorption of the excitation radiation. The broad structureless emission, was attributed to the intramolecular exciplex in all cases, indicating total quenching of the monomeric aromatic hydrocarbon fluorescence. Apart from the azacyclopentyl derivative, whose quantum yield of exciplex formation was 0.11, there was little variation in the ϕ_{f_E} values with ring size of the amine, which were all around 0.16 in magnitude.

In tetrahydrofuran solution, the quenching of the aromatic hydrocarbon fluorescence was accompanied by the formation of a fluorescent exciplex in each case. Wavelength maxima for these emissions, were not noticeably dependent upon the ring size of the amino substituent in the compounds. Quantum yields for exciplex formation were found to be quite

COMPOUND			SOLVENT THF		MeCN	
	ϕ_{fM}	ϕ_{fE}	ϕ_{fM}	ϕ_{fE}	ϕ_{fM}	ϕ_{fE}
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_4$	-	0.106	0.002	0.037	0.002	0.013
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_5$	-	0.164	-	0.033	0.003	0.015
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_6$	-	0.153	0.004	0.050	0.015	0.034
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_7$	-	0.166	-	-	0.009	0.020
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_8$	-	0.158	-	-	0.011	0.034
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_{12}$	-	0.153	0.001	0.112	0.002	0.031

TABLE 2.(9). Quantum Yields of Residual Phenyl Monomeric Emission (ϕ_{fM}) and Fluorescent ExciplexFormation (ϕ_{fE}) for the above Series of N-(2-Phenylethyl)azacycloalkanes, in

Degassed Cyclohexane, Tetrahydrofuran and Acetonitrile Solutions at 20°C.

low (~ 0.03) and a small amount of monomeric emission was also present in the spectra.

Finally in acetonitrile solution, weak emission was observed from both the aromatic hydrocarbon and the fluorescent exciplex (as shown by the magnitudes of the quantum yields ϕ_{f_M} and ϕ_{f_E}). Once again, the azacyclohexyl derivative showed a marked blue shift in the wavelength maximum of the fluorescence relative to the azacyclo-pentyl and -heptyl derivatives (400nm $\rightarrow$ 387nm). Furthermore, there was a blue shift in the λ_{max} values with increase in ring size of the amino chromophore, as shown in Table 2.(8).

The fluorescence spectra of the azacyclo-pentyl and -hexyl derivatives were also recorded in n-hexane solution, to compare them with those obtained in cyclohexane solution. Although the λ_{max} values for the emission spectra were the same, the quantum yields of fluorescent exciplex formation were changed quite markedly, as shown in Table 2.(10).

<u>COMPOUND</u>	ϕ_{f_E}	
	<u>SOLVENT</u>	
	Cyclohexane	n-hexane
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_4$	0.106	0.069
$\text{PhCH}_2\text{CH}_2\text{N}(\text{CH}_2)_5$	0.164	0.113

TABLE 2.(10). Quantum Yields of Fluorescent Exciplex Formation (ϕ_{f_E}) of the N-(2-phenylethyl)-azacyclopentyl and -hexyl Derivatives Recorded in Degassed Cyclohexane and n-hexane Solutions at 20°C.

Since one would expect little difference, if any, in the polarity of the two solvent systems, the reduction in the

quantum yield of fluorescent exciplex formation, on going from cyclohexane to n-hexane solution, may simply reflect the ability of the solvent molecules to solvate the excited state species.

2.4. SUMMARY.

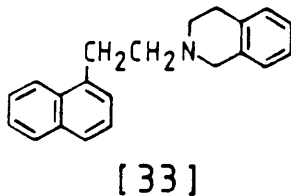
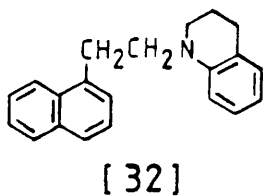
From our studies on the fluorescence properties of a series of N-(2-(1'-naphthyl)ethyl)- and N-(2-phenylethyl)-azacycloalkane systems, it would appear that the intramolecular quenching of aromatic hydrocarbon fluorescence by the azacycloalkane derivatives, is extremely efficient, leading to fluorescent exciplex formation in solvents of widely differing polarity. Consistent with the results of earlier work on aromatic hydrocarbon-amine systems, using saturated acyclic amines^(79,148), the exciplex emission exhibited a red-shift with increase in solvent polarity, accompanied by a decrease in the quantum yield of fluorescent exciplex formation. In cyclohexane solution, the effect of ring size of the amino group upon the quantum yield of fluorescent exciplex formation, was found to be far more pronounced in the 1-naphthyl series than for the phenyl derivatives. Quantum yields were found to increase with increase in ring size of the azacycloalkyl group - varying from 0.252 for the azacyclopentyl derivative to 0.415 for the azacyclotridecyl derivative. We believe that this effect is due largely to the relative ability of the amino group to compete with the naphthalene chromophore, for the absorption of the incident excitation energy. Figure 2.(1). showed quite clearly the change in the u/v absorption spectra of the azacycloalkyl derivatives in cyclohexane solution at 20°C. By excitation of the amine

chromophore into its singlet excited state (S_1), it can then adopt the planar configuration about the nitrogen atom thought to be a requirement for interaction with the excited state aromatic hydrocarbon.

Our studies on the triplet-triplet absorption spectra of the 1-naphthyl derivatives, indicated that the mode of naphthalene triplet decay was dependent upon the solvent used. In non-polar solvents, the triplet state appeared to decay by a unimolecular mechanism, whilst in highly polar solvents like acetonitrile, the decay followed a purely bimolecular pathway.

2. 5 . MISCELLANEOUS COMPOUNDS.

Further to our investigation into the formation of intramolecular fluorescent exciplexes, between aromatic hydrocarbons and saturated alicyclic amines, the effect of applying further conformational constraints on the mobility of the amine was briefly studied. The N-(2-(1'-naphthyl)-ethyl)- derivatives of both 1,2,3,4-tetrahydroquinoline (32) and 1,2,3,4-tetrahydroisoquinoline (33) were prepared and their fluorescence properties examined. The emission spectra



were recorded for degassed solutions of the compounds using cyclohexane, benzene and acetonitrile as the solvents. The fluorescence data obtained are summarised in Tables 2.(11). and 2.(12).

Dealing with the results obtained for the 1,2,3,4-tetrahydroquinoline derivative (32) first, the interaction of the

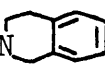
COMPOUND	$\lambda_{\max}$ (nm)		
	SOLVENT		
			MeCN
1-NpCH ₂ CH ₂ N 	390	418	495
1-NpCH ₂ CH ₂ N 	355	400	465

TABLE 2.(11). Fluorecence $\lambda_{\max}$ Values for Compounds (32) and (33) Recorded in Cyclohexane, Benzene and Acetonitrile Solutions at 20°C.

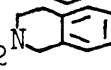
COMPOUND	SOLVENT					
					MeCN	
	ϕ_{f_M}	ϕ_{f_E}	ϕ_{f_M}	ϕ_{f_E}	ϕ_{f_M}	ϕ_{f_E}
1-NpCH ₂ CH ₂ N 	-	0.22	-	0.17	0.011	0.06
1-NpCH ₂ CH ₂ N 	0.003	0.02	0.001	0.10	0.004	0.04

TABLE 2.(12). Quantum Yields of Fluorescence for Residual Naphthalene Monomer (ϕ_{f_M}) and Exciplex Formation (ϕ_{f_E}), for the Compounds (32) and (33), in Degassed Cyclohexane, Benzene and Acetonitrile Solutions at 20°C.

excited naphthalene chromophore and the amino species led to the formation of a fluorescent intramolecular exciplex in all the solvents studied. The shift in the wavelength maximum of the emission to longer wavelengths with increasing solvent polarity (390nm in cyclohexane solution to 495nm in acetonitrile solution), was accompanied by a decrease in the quantum yield of fluorescent exciplex formation (ϕ_{f_E}). In acetonitrile solution, a weak emission from the naphthalene

monomer was also observed. Due to the structural similarities between compound (32) and 1-NpCH₂CH₂NMePh, the fluorescence properties of the two compounds were compared, those of the anilino derivative being detailed in Table 2.(4). Despite differences in the fluorescence λ_{max} values, it appeared that an interaction was taking place between the nitrogen atom and the phenyl group of the tetrahydroquinoline unit, during intramolecular exciplex formation, in a similar way to that occurring in the anilino group.

In the case of the 1,2,3,4-tetrahydroisoquinoline derivative (33) however, the quantum yield of fluorescent exciplex formation in cyclohexane solution was found to be particularly low at 0.02, compared with values of 0.22 for (32) and 0.41 for that of the closely related compound 1-NpCH₂CH₂NEt₂⁽¹⁴⁷⁾. We believe that this result may be attributable to the formation of a ternary intramolecular complex between the naphthyl, phenyl and amino groups in the compound, since these complexes are known to emit very poorly in cyclohexane solution.

Although the exciplex formed by (32) clearly emitted at longer wavelengths than that of (33), both compounds exhibited the same wavelength shift in the emission of the exciplex, on changing the solvent from cyclohexane to acetonitrile ($\sim 100\text{nm}$). Our calculations on the stabilisation of the exciplex with increase in solvent polarity, revealed that the complex formed by (33), was in fact stabilised to a greater extent.

CHAPTER THREE

The Interaction of Excited
Singlet State Benzene With
Tertiary Alicyclic Amines.

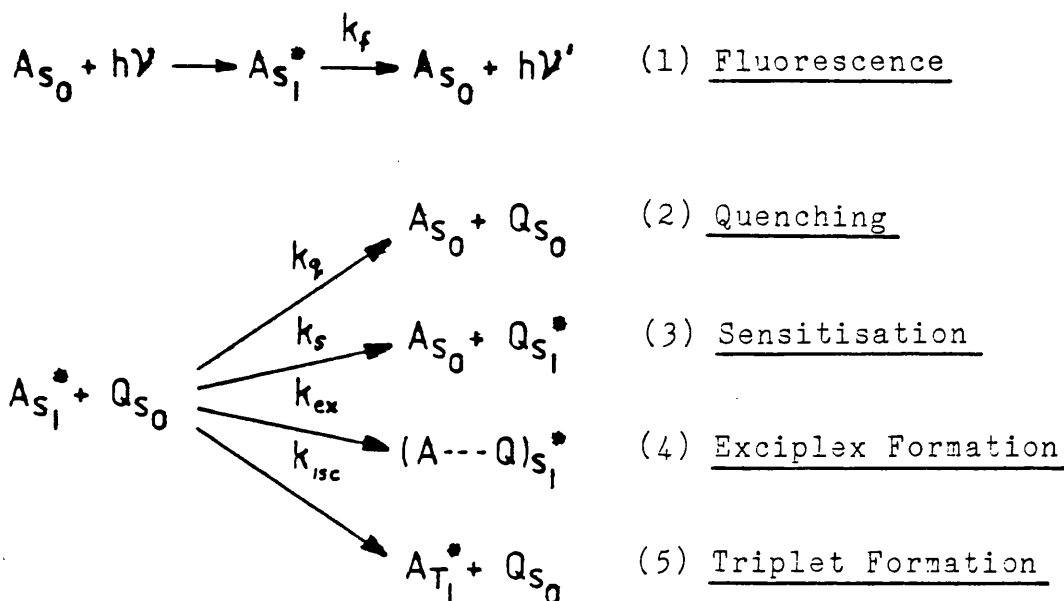
3.1. INTRODUCTION.

Our studies on the fluorescence properties of a series of N-(2-(1'-naphthyl)ethyl)azacycloalkanes and their phenyl analogues, had indicated that the aromatic hydrocarbon fluorescence was efficiently quenched by an intramolecular interaction with the azacycloalkyl group, leading to the formation of a fluorescent intramolecular exciplex. The next stage was to investigate the interaction of the excited aromatic hydrocarbon and the amino group in the absence of the linking polymethylene chain, in a range of solvents of different polarity. Would the hydrocarbon fluorescence be quenched as efficiently by the N-methylated azacycloalkanes, and would this intermolecular quenching process lead to exciplex formation? In this present piece of work, attention was restricted to the use of benzene as the aromatic hydrocarbon.

3.2. QUENCHING OF THE BENZENOID FLUORESCENCE.

As was briefly outlined in Chapter (1) Section 1.1., there are a number of possible processes, both photochemical and photophysical, which an excited species may undergo, following photochemical excitation into the first singlet excited state. If the excited species encounters a ground state quencher molecule or atom (Q), present in the solution, several interactions can then occur between the two species, including fluorescence quenching, sensitisation of fluorescence from the quencher molecule, the formation of an intermolecular fluorescent exciplex or the formation of a triplet excited state species, as detailed in Scheme 3.(1).

Using benzene as the excited species and either an



SCHEME 3.(1). Schematic Representation of Some of the
Decay Pathways Open to an Excited Singlet
State Species, $A_{S_1}^*$.

N-methylated azacycloalkane or triethylamine as the quenching agent, a series of experiments were carried out in cyclohexane and acetonitrile solutions, to investigate the efficiency with which the benzenoid fluorescence was quenched by the tertiary amine systems.

3.2.(1). Experimental.

For each solvent system, stock solutions of the aromatic hydrocarbon (benzene; OD 1.0 @ 265nm) and the tertiary aliphatic amines ($1 \times 10^{-1} \text{ moldm}^{-3}$) were prepared. From these a series of solutions were then made up (5cm^3 total volume) with a constant volume of the benzene stock solution (0.5cm^3) and varying the amount of amine solution added, giving an effective amine concentration in the range 2×10^{-3} to $6 \times 10^{-2} \text{ moldm}^{-3}$. A representative sample of the solutions prepared are given in Table 3.(1).

Volume Benzene Solution (cm ³)	Volume Amine Solution (cm ³)	[Amine] X 10 ⁻³ (moldm ⁻³)
0.5	0	0
0.5	0.1	2
0.5	0.2	4
0.5	0.3	6
0.5	0.4	8
0.5	0.5	10
0.5	1.0	20
0.5	1.5	30
0.5	2.0	40
0.5	3.0	60

TABLE 3.(1). Representative Sample of Solutions Prepared
for Use in the Quenching of Benzene
Fluorescence by Tertiary Amines, in Cyclo-
hexane and Acetonitrile.

The u/v absorption spectra of the solutions were recorded, so that the effect of increasing the amount of amine present upon the optical density of the solution could be monitored. The u/v absorption spectra of the tertiary amines were found to show a marked dependence upon structure, which will be discussed in more detail in Chapter (4), and therefore, for a given concentration of amine, the effect upon the solution optical density varied considerably. For this reason, it was necessary to work with relatively low concentrations of amine so that the optical density of the solutions remained essentially constant, throughout the experiment. Where the amine was found to still absorb a considerable amount of the incident light, at the excitation wavelength of 265nm, even at low concentration, the partitioning of the excitation radiation between the two absorbing chromophores, could be estimated by application of the Beer-Lambert Law.

In order to do this, the molar extinction coefficients of the two components (ϵ_1 and ϵ_2) had to be known at the excitation wavelength and these were evaluated by accurately measuring the optical densities of the stock solutions of both components, at known concentrations.

From the Beer-Lambert Law, the optical density of the mixed benzene-amine solution could be given by Equation 3.(1).

$$\underline{OD = \epsilon_1 c_1 l + \epsilon_2 c_2 l} \quad - \text{Eqn. 3.(1).}$$

where OD = optical density

ϵ_1 = molar extinction coefficient benzene at 265nm

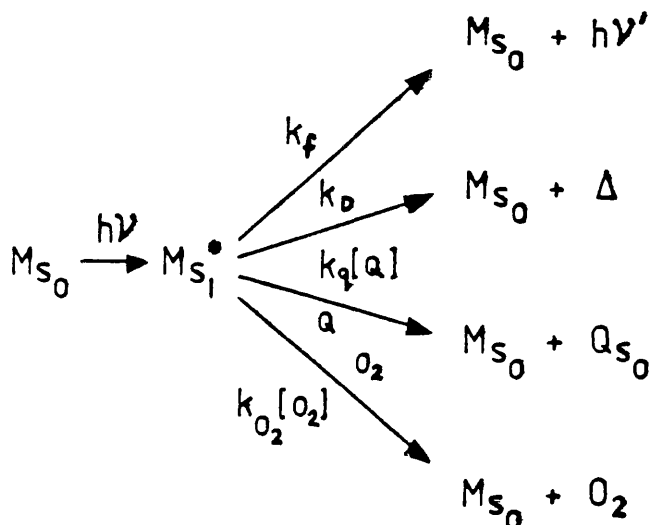
ϵ_2 = molar extinction coefficient amine at 265nm

c_1, c_2 = concentrations of benzene and amine respectively

l = pathlength

It was found during this work, that the N-methylazacyclopentyl, -heptyl and -octyl systems considerably affected the solution optical density, when the concentration of amine was in excess of $\sim 2 \times 10^{-2} \text{ mol dm}^{-3}$. The azacyclohexyl derivative however did not dramatically affect the optical density of the solutions in the concentration range studied. Of the other amine systems used for the quenching experiments, N,N'-dimethyl-1,4-diazacyclohexane (N,N'-dimethylpiperazine) also caused quite significant changes in the optical density of the solutions at 265nm, when used at concentrations above $\sim 1 \times 10^{-2} \text{ mol dm}^{-3}$. Fluorescence measurements were made on both aerated and degassed solutions and from them, the kinetics of the fluorescence quenching of the aromatic hydrocarbon by the tertiary amines were evaluated, using the procedure detailed below.

Consider the simple reaction pathways shown in Scheme 3.(2)., where an excited species (M^*) fluoresces, decays



SCHEME 3.(2). Reaction Scheme for the Decay of an Excited Species (M^*), Used in a Simplified Treatment of the Kinetics of Fluorescence Quenching.

non-radiatively or is quenched either by molecular oxygen or a quencher group (Q), with rate constants k_f , k_D , k_{O_2} and k_q , respectively. Applying the steady-state approximation to the concentration of M^* gives;

$$I = [M^*](k_f + k_D + k_q[Q] + k_{O_2}[O_2]) \quad - \text{Eqn. 3.(2).}$$

therefore the quantum yield of fluorescence (ϕ_f) is given by Equation 3.(3).

$$\phi_f = \frac{k_f[M^*]}{I} = \frac{k_f}{k_f + k_D + k_q[Q] + k_{O_2}[O_2]} \quad - \text{Eqn. 3.(3).}$$

in aerated solution, in the absence of a quencher,

$$\phi_f^0 = \frac{k_f}{k_f + k_D + k_{O_2}[O_2]} \quad - \text{Eqn. 3.(4).}$$

hence combining Equations 3.(3). and 3.(4)., and simplifying

$$\begin{aligned} \frac{\phi_f^0}{\phi_f} &= \frac{k_f + k_D + k_q[Q] + k_{O_2}[O_2]}{k_f + k_D + k_{O_2}[O_2]} \\ &= 1 + \frac{k_q[Q]}{k_f + k_D + k_{O_2}[O_2]} \end{aligned}$$

and therefore

$$\frac{\phi_f^0}{\phi_f} = 1 + k_q \tau [Q] \quad - \text{Eqn. 3.(5).}$$

where τ is the lifetime of the excited species M^* in the absence of quencher and presence of molecular oxygen at a concentration dependent upon the solvent used. Hence in aerated solution, τ is given by the expression in Equation 3.(6).

$$\tau_{\text{Aerated}} = \frac{1}{k_f + k_D + k_{O_2} [O_2]} \quad - \text{Eqn. 3.(6).}$$

The relationship detailed in Equation 3.(5). is known as the Stern-Volmer Equation⁽¹⁵²⁾, which shows that under ideal conditions, a plot of (ϕ_f^0/ϕ_f) versus the concentration of quencher gives a straight line of gradient = $k_q \tau$, and intercept of unity. Knowing the fluorescence lifetime of the singlet excited state of benzene in aerated n-hexane solution at 20°C⁽¹⁵³⁾, enabled the rate constant for the fluorescence quenching process (k_q) to be evaluated.

In degassed solution, the oxygen term in Equation 3.(6). can be ignored, and therefore the lifetime (τ) is given by the expression

$$\tau_{\text{Degassed}} = \frac{1}{k_f + k_D} \quad - \text{Eqn. 3.(7).}$$

The fluorescence lifetime of benzene in degassed cyclo-hexane solution, has been independently evaluated by a number of workers^(151,153-155).

A further problem also arose however, in the steady state measurements of the quenching of the benzene fluorescence by the tertiary amines, caused by the fact that the absorption spectra of the two compounds, overlap at wave-

lengths appropriate for excitation of the benzene chromophore. It therefore became necessary to make corrections to the observed fluorescence intensities to account for this, using the method of Beddard and Davidson⁽¹⁵⁶⁾, as detailed below.

Consider the fluorescence from the centre (O) of a cuvette, illuminated at position X by a light source of intensity I and observed at right angles at position Y, as shown in Figure 3.(1).

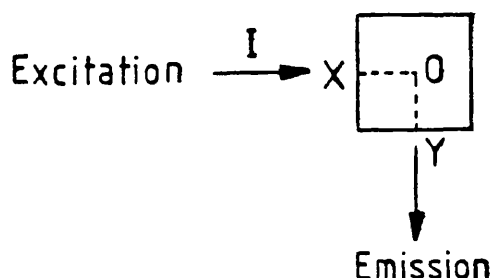


FIGURE 3.(1). Diagram Showing the Light Pathway through the Fluorescence Cell.

In the absence of a quencher species (Q), let the transmittance of the solution over XO and OY be x and y, respectively. Then the fluorescence intensity at position Y is given by the expression

$$\underline{F_o = I \times y \phi_{f0}} \quad - \text{Eqn. 3.(8).}$$

(where ϕ_{f0} is the quantum yield of fluorescence of the unquenched species). If the transmittance of a solution of pure quencher over the distance XO and OY is then given by α and β respectively, the new observed fluorescence intensity of the quenched benzene solution is

$$\underline{F_{obs} = I \times y \alpha \beta \phi_f} \quad - \text{Eqn. 3.(9).}$$

From Equations 3.(8). and 3.(9)., the observed Stern-Volmer quenching (F_o/F_{obs}) is given by;

$$\frac{F_o}{F_{obs}} = \frac{1}{\alpha\beta} \frac{\phi_{f0}}{\phi_f} \quad - \text{Eqn. 3.(10).}$$

However, since $\log_{10}(1/\text{transmittance}) = OD$, then $\alpha^{-1} = \text{antilog}_{10}(OD_{XO})$ and $\beta^{-1} = \text{antilog}_{10}(OD_{OY})$ and therefore the corrected Stern-Volmer quenching becomes;

$$\frac{\phi_{f0}}{\phi_f} = \frac{F_o}{F_{obs}} ((\text{antilog}_{10} OD_{XO})(\text{antilog}_{10} OD_{OY}))^{-1} \quad - \text{Eqn. 3.(11).}$$

In our work, the situation was simplified by the fact that the amines do not absorb any of the benzenoid emission, and consequently the $(\text{antilog}_{10} OD_{OY})$ term could be ignored, giving

$$\frac{\phi_{f0}}{\phi_f} = \frac{F_o}{F_{obs}} (\text{antilog}_{10} OD_{XO})^{-1} \quad - \text{Eqn. 3.(12).}$$

In order to calculate the OD of the amine in each solution, for substitution into Equation 3.(12)., it was first necessary to calculate the molar extinction coefficient (ϵ) of the particular amine, at the excitation wavelength. The (ϕ_{f0}/ϕ_f) values could then be evaluated, and the Stern-Volmer plots drawn, to derive the rate constants for the fluorescence quenching (k_q).

3.2.(2). Results and Discussion.

The results obtained from our studies on the quenching of benzenoid fluorescence by the tertiary aliphatic amines, will be dealt with in two sections, according to the solvent used.

3.2.(2).1. Acetonitrile Solutions.

The intensity of the benzene fluorescence, monitored at 277.5 and 285nm, was found to decrease as the concentration of the amine quencher was increased. From the Stern-Volmer

plots, (corrected for the absorption of the excitation light by the amine, where applicable), the relative efficiencies of the tertiary amines at quenching the benzene fluorescence could be evaluated, by comparing the quenching rate constants (k_q).

The magnitudes of the rate constants, for the amines in aerated acetonitrile solutions at 20°C, are summarised in Table 3.(2). The lifetime of the singlet excited state benzene

<u>AMINE</u>	$k_q \times 10^{10}$ ($M^{-1}s^{-1}$)	<u>AMINE</u>	$k_q \times 10^{10}$ ($M^{-1}s^{-1}$)
MeN(CH ₂) ₇	0.65	NEt ₃	1.44
MeN(CH ₂) ₆	0.62	MeN(CH ₂) ₄ NMe	1.09
MeN(CH ₂) ₅	1.10	MeN(CH ₂) ₄ O	0.53
MeN(CH ₂) ₄	1.81		

TABLE 3.(2). The Rate Constants (k_q), for the Quenching of Excited Singlet State Benzene Fluorescence by a Series of Tertiary Aliphatic Amines in Aerated Acetonitrile Solutions at 20°C.

in this solvent, was taken to be the same as that in aerated cyclohexane solution ($\tau_{DS} = 5.7ns$)⁽¹⁵³⁾. The results indicated that the quenching of the aromatic hydrocarbon fluorescence by the tertiary alicyclic amines occurred at rates approaching the limits for a diffusion controlled process ($k_{diff} = 2.7 \times 10^{10} \text{ mol}^{-1}\text{dm}^3\text{s}^{-1}$ in acetonitrile solution⁽¹⁵⁷⁾). The k_q values for the azacycloalkane derivatives appeared to show a dependency upon the ring size - the rate constants decreasing with increase in the number of methylene units in the ring. This may simply reflect the increasing steric

hindrance to the approach of the amine to the excited aromatic hydrocarbon.

Of the other tertiary amines studied, the acyclic amine triethylamine quenched the fluorescence from the benzene chromophore with comparable efficiency to N-methylazacyclopentane. The diamino- compound, N,N'-dimethyl-1,4-diazacyclohexane was found to behave in a similar way to its mono-amino- analogue, the quenching rates being almost identical. This result was somewhat surprising however, since on purely statistical grounds, one might have expected the N,N'-dimethyl-1,4-diazacyclohexane quencher, with its two nitrogen atoms per molecule, to quench the benzene fluorescence more efficiently than the azacyclohexyl derivative by a factor of two. This suggested that the collision complex formed between the benzene and the diamine was not sufficiently long-lived for the second amino group to be able to interact and enhance the quenching.

The substitution of an oxygen atom into the ring system, appeared to reduce the effectiveness of the amine at quenching the benzenoid emission. Hence N-methyl-1-aza-4-oxacyclohexane (N-methylmorpholine) gave a smaller quenching rate constant, than either of the other six membered ring derivatives used. Presumably the highly electronegative oxygen atom, is tending to withdraw electron density from the nitrogen atom in the molecule.

Unfortunately, our degassing procedure did not appear to be very successful in these experiments, consequently we were unable to evaluate the quenching rate constants for the tertiary amines in degassed acetonitrile solutions. Although purging the solutions with a stream of dry nitrogen for several minutes, caused an enhancement of the fluorescence

intensity our calculations indicated that the gradients of the Stern-Volmer plots, which equalled $k_q \tau$, were not significantly higher than those of the aerated solutions. On the basis of the literature values for the lifetime of singlet excited state benzene in aerated and degassed n-hexane solution of 5.7 and 26ns respectively⁽¹⁵³⁾, for thoroughly degassed solutions, we had anticipated at least a fourfold increase in the gradients of the Stern-Volmer plots. A similar problem with the apparently inefficient removal of oxygen from the solutions during degassing with nitrogen, was also encountered in both our quenching and sensitisation experiments in cyclohexane solution, which are dealt with in the following sections.

3.2.(2).2. Cyclohexane Solution.

The effect of added amine upon the benzene fluorescence, was found to be highly dependent upon the amine being used, when quenching experiments were carried out in the non-polar solvent cyclohexane.

(1) N-methylazacyclopentane - when N-methylazacyclopentane (N-methylpyrrolidine) was used as the quenching agent, the presence of even a small amount of the amine ($2 \times 10^{-3} \text{ mol dm}^{-3}$) was sufficient to bring about a significant quenching of the benzenoid fluorescence.

Consequential to this highly efficient interaction between the two species however, was the appearance of a strong emission, to the red of the benzene fluorescence, due to the N-methyl^{aza}cyclopentane. The intensity of the emission, was observed to increase with increasing concentration of the amine up to a certain limiting value - after which the addition of further portions of the amine solution had no more effect upon the intensity of the fluorescence

band. For the N-methylazacyclopentane, this limiting value was reached at an amine concentration of $\sim 5 \times 10^{-2} \text{ mol dm}^{-3}$. Figure 3.(2)., shows a representative selection of the fluorescence spectra obtained from the quenching experiment using N-methylazacyclopentane.

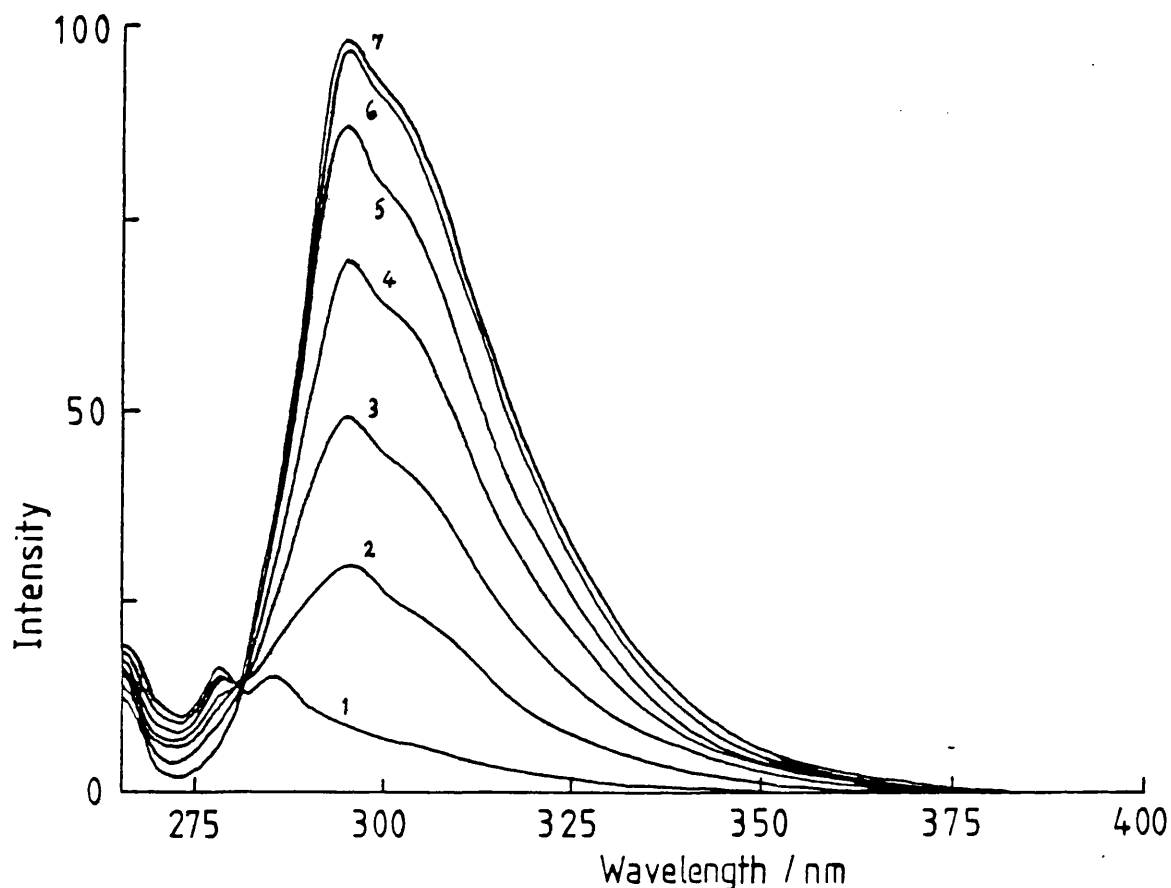


FIGURE 3.(2). Fluorescence Spectra of Aerated Cyclohexane Solutions of Benzene (OD 0.1 at 265nm) Containing Varying Amounts of N-methylazacyclopentane Solution ($\lambda_{\text{exc}} = 265\text{nm}$) at 20°C . (1) 0.0M, (2) $2 \times 10^{-3}\text{M}$, (3) $4 \times 10^{-3}\text{M}$, (4) $8 \times 10^{-3}\text{M}$, (5) $1 \times 10^{-2}\text{M}$, (6) $2 \times 10^{-2}\text{M}$, (7) $4 \times 10^{-2}\text{M}$.

As with the quenching experiments carried out in acetonitrile solution, a correction factor had to be introduced, to account for the overlap in the absorption spectra of the benzene and the amine at the excitation wavelength of 265nm. From the Stern-Volmer plot of (ϕ_f / ϕ_{f0}) versus the concentration of N-methylazacyclopentane added, the quenching

rate constant (k_q) was calculated.

(2) N,N'-dimethyl-1,4-diazacyclohexane - the quenching of the benzenoid fluorescence, accompanied by the appearance of a strong new emission band attributable to the excited amino species, was also clearly seen when using N,N'-dimethyl-1,4-diazacyclohexane as the quenching agent. The emission maximum of the amine at a wavelength of around 315nm, made it easily distinguishable from the characteristic benzene fluorescence maximising at 272, 278 and 285nm, as shown in Figure 3.(3).

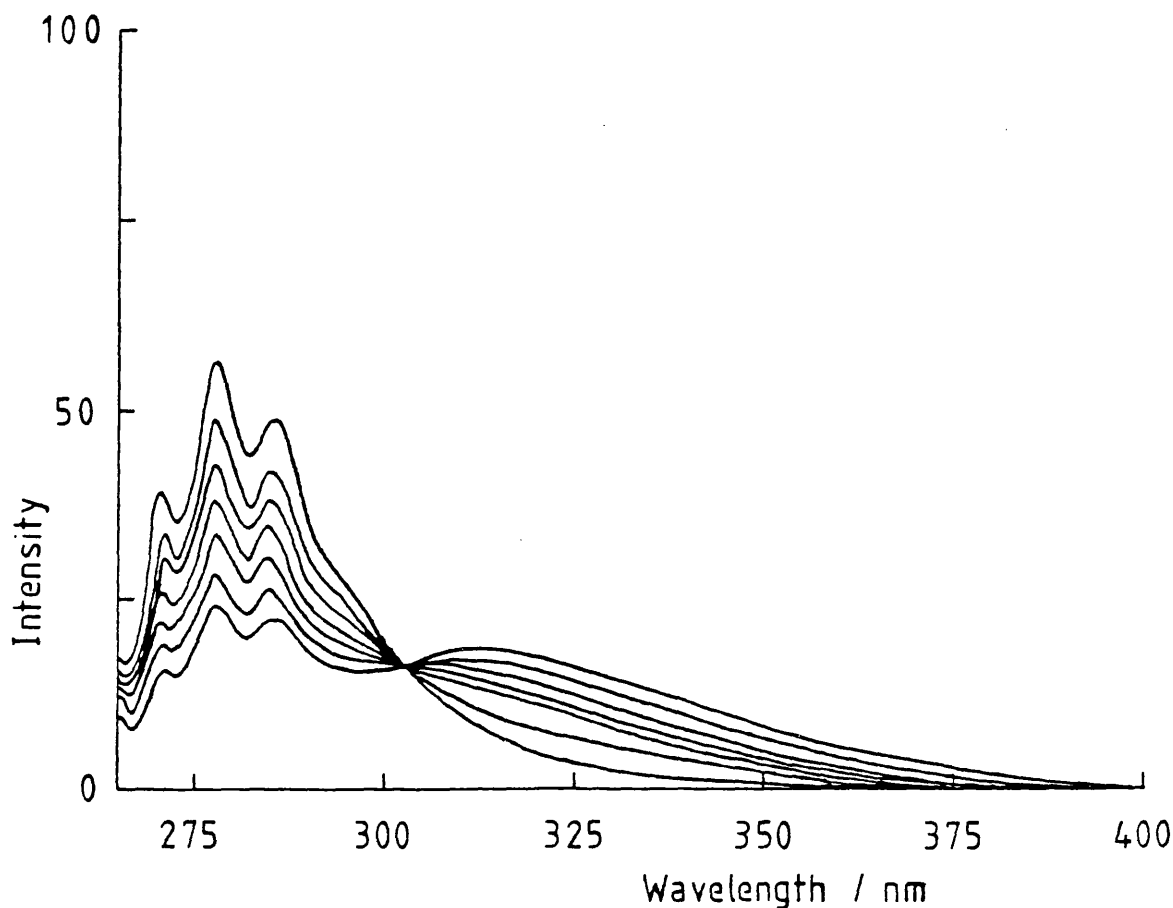


FIGURE 3.(3). Fluorescence Spectra of Aerated Cyclohexane Solutions of Benzene (OD 0.1 @ 265nm) Containing Varying Amounts of N,N'-dimethyl-1,4-diazacyclohexane Solution ($\lambda_{exc}=265nm$) at 20°C. (1) 0.0M, (2) $5.0 \times 10^{-3}M$, (3) $1.0 \times 10^{-2}M$, (4) $1.5 \times 10^{-2}M$, (5) $2.0 \times 10^{-2}M$, (6) $2.5 \times 10^{-2}M$, (7) $4.0 \times 10^{-2}M$.

After correcting the fluorescence data, to account for any absorption of the incident radiation by the amine, at the excitation wavelength of 265nm, the Stern-Volmer plot yielded the quenching rate constant (k_q). However, an additional problem also arose in this experiment, due to the characteristically broad and structureless nature of the amino emission. A considerable proportion of the apparent benzene fluorescence after quenching, was in fact due to the underlying amine emission, giving an elevated value for the intensity of the residual benzenoid emission and a correspondingly lower value for k_q . A second evaluation of the quenching rate constant was made therefore, involving an estimation of the contribution to the 'benzene' fluorescence from the amine in each solution, as shown in Figure 3.(4).

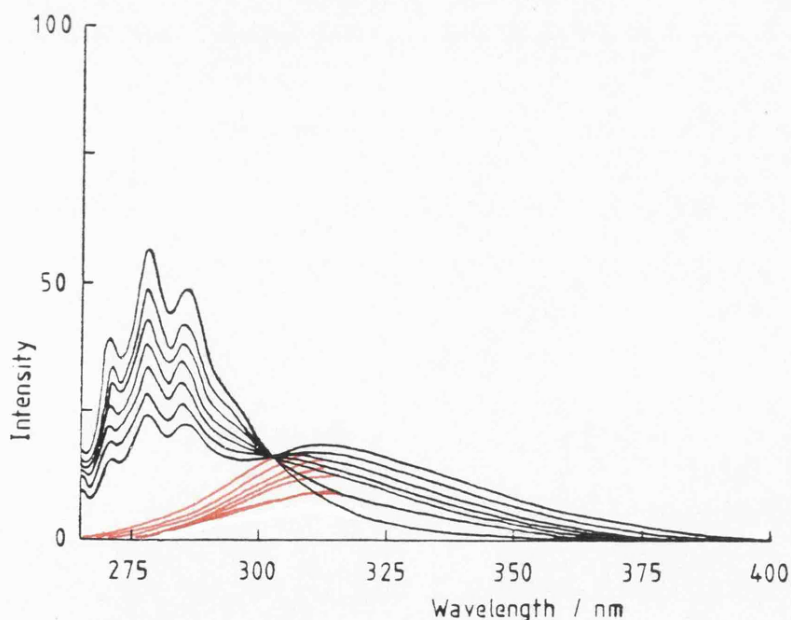


FIGURE 3.(4). Fluorescence Spectra of Aerated Cyclohexane
Solutions of Benzene (OD 0.1 @ 265nm)
Containing Varying Amounts of N,N'-dimethyl-
1,4-diazacyclohexane, Showing the Estimated
Contribution from the Amine to the 'Benzene'
Fluorescence.

(3) N-methylazacycloheptane - the addition of varying amounts of N-methylazacycloheptane solution to a cyclohexane solution of benzene (OD 0.1 at 265nm), resulted in the appearance of a new band in the fluorescence spectrum due to the amine. The amino emission increased in intensity with increase in the concentration of amine present, in the range $4 \times 10^{-4} \text{ mol dm}^{-3}$ to $2 \times 10^{-2} \text{ mol dm}^{-3}$. A quantitative assessment of the quenching of the benzenoid fluorescence was made difficult however, because the N-methylazacycloheptane emission maximised at 288nm and therefore overlapped the benzenoid fluorescence quite considerably. An approximation of the quenching rate constant was made by monitoring the change in the intensity of the benzene fluorescence at $\sim 267\text{nm}$, but the emission was only very weak in this region.

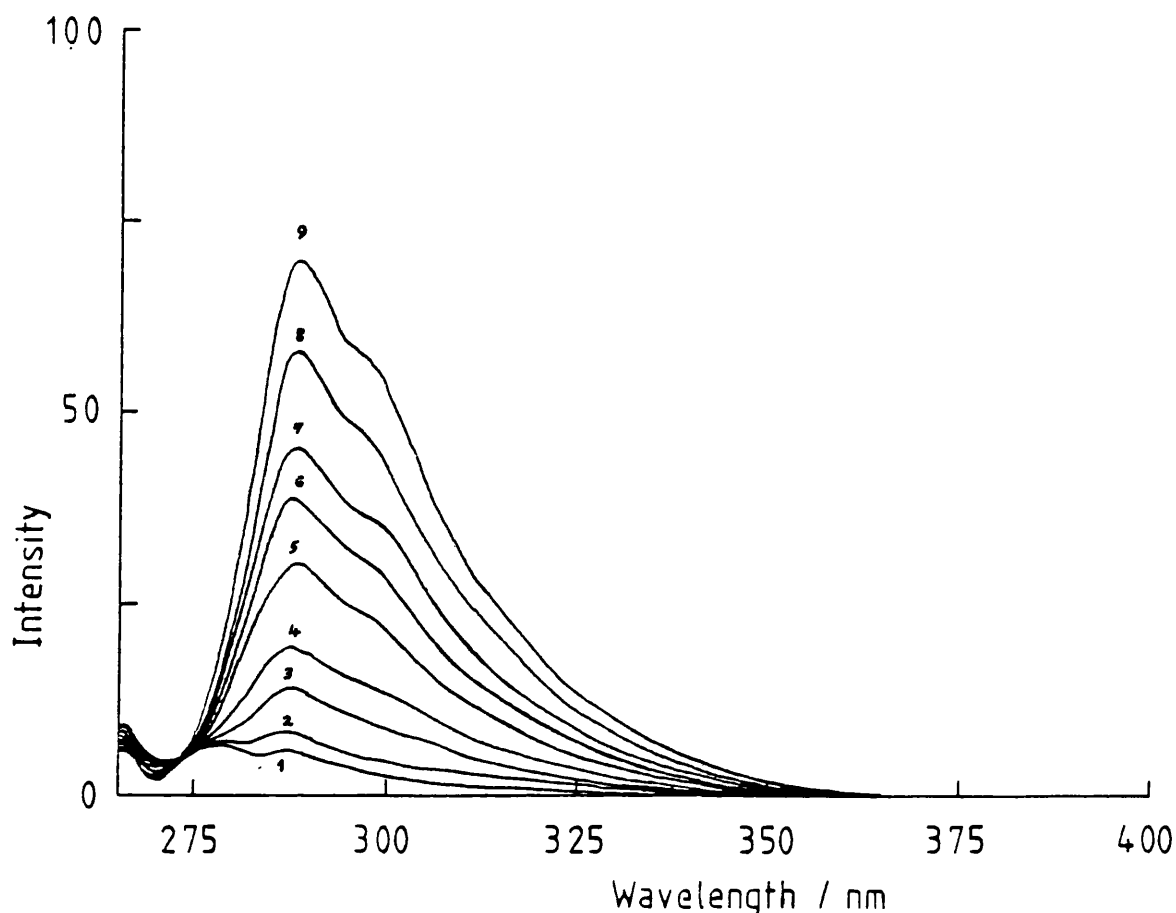


FIGURE 3.(5). Fluorescence Spectra of Aerated Cyclohexane
Solutions of Benzene (OD 0.1 at 265nm) with
Varying Amounts of N-methylazacycloheptane
at 20°C. (1) 0.0M, (2) $4.0 \times 10^{-4}\text{M}$,

FIGURE 3.(5). (3) $1.2 \times 10^{-3} \text{M}$, (4) $2.0 \times 10^{-3} \text{M}$, (5) $4.0 \times 10^{-3} \text{M}$, (6) $6.0 \times 10^{-3} \text{M}$, (7) $8.0 \times 10^{-3} \text{M}$,
(Contd.) (8) $1.2 \times 10^{-2} \text{M}$, (9) $2.0 \times 10^{-2} \text{M}$.

Since the N-methylazacycloheptane was found to absorb the incident radiation quite significantly at the excitation wavelength ($\epsilon=13$ at 265nm), the possibility arose that the observed amino emission might simply be due to direct excitation of the amine. To investigate this question further, a second fluorescence quenching experiment was undertaken, using concentrations of the amine in the range $1.0 \times 10^{-4} \text{mol dm}^{-3}$ to $1.4 \times 10^{-3} \text{mol dm}^{-3}$. Once again, the addition of the amine was accompanied by a characteristic amino emission, which increased in intensity with the concentration of the amine present. Although the optical densities of the solutions were found to increase with amine content, the majority of the incident radiation was still clearly absorbed by the aromatic chromophore, suggesting that excitation of the amine had arisen by an indirect pathway.

(4) N-methylazacyclooctane - since the N-methylazacyclooctane was known to absorb quite strongly at wavelengths appropriate for excitation, a $1.0 \times 10^{-2} \text{mol dm}^{-3}$ stock solution of the amine was prepared and the concentration of the amine used in the quenching experiment, restricted to the range 1.0×10^{-4} to $1.0 \times 10^{-3} \text{mol dm}^{-3}$, to reduce the degree of amine absorption at 265nm. The addition of the quencher, led to the appearance of a characteristic amino emission in the fluorescence spectra, maximising at 286nm (one of the emission maxima for benzene), which made a quantitative assessment of the benzenoid fluorescence quenching by the N-methylazacyclooctane virtually impossible. Since the u/v absorption spectra of the solutions did not vary appreciably

in the concentration range studied, direct excitation of the amine chromophore, was not believed to be significant.

(5) Triethylamine and N-methyldiethylamine - a quantitative evaluation of the fluorescence quenching ability of both triethylamine and N-methyldiethylamine was again not possible, due to the considerable overlap of the benzenoid and amino emissions, despite the fact that with N-methyldiethylamine, the fluorescence maximised to the red of that of benzene, at $\sim 295\text{nm}$. The concentration of amine was varied in the range 2×10^{-3} to $1.6 \times 10^{-2} \text{ mol dm}^{-3}$, but since both amines have low molar extinction coefficients at 265nm ($\epsilon \approx 2$), the change in optical density of the solutions was only small. The behaviour of N-methyldiethylamine is discussed in more detail later.

(6) N-methylazacyclohexane - N-methylazacyclohexane (N-methylpiperidine), was found to quench the benzenoid fluorescence, but there was no evidence from the fluorescence measurements, to suggest that the quenching process resulted in the excitation of the amino species. A value for the quenching rate constant (k_q) was obtained from a Stern-Volmer plot of the change in the benzenoid fluorescence intensity (F_0/F) versus the concentration of the quenching agent added.

(7) N-methyl-1-aza-4-oxacyclohexane - our studies indicated that N-methyl-1-aza-4-oxacyclohexane (N-methylmorpholine), caused virtually no quenching of the benzenoid fluorescence, even at an upper concentration of $9.0 \times 10^{-2} \text{ mol dm}^{-3}$, in cyclohexane solution.

The rate constants (k_q) for the quenching of benzene fluorescence by the tertiary aliphatic amines in aerated cyclohexane solution at 20°C , are summarised in Table 3.(3).

<u>AMINE</u>	$k_q \times 10^9$ ($M^{-1}s^{-1}$)
$MeN(CH_2)_6$	4.51
$MeN(CH_2)_5$	2.59
$MeN(CH_2)_4$	8.99
$MeN \text{ (cyclohexane ring) } NMe$	5.32 7.64 ^(a)

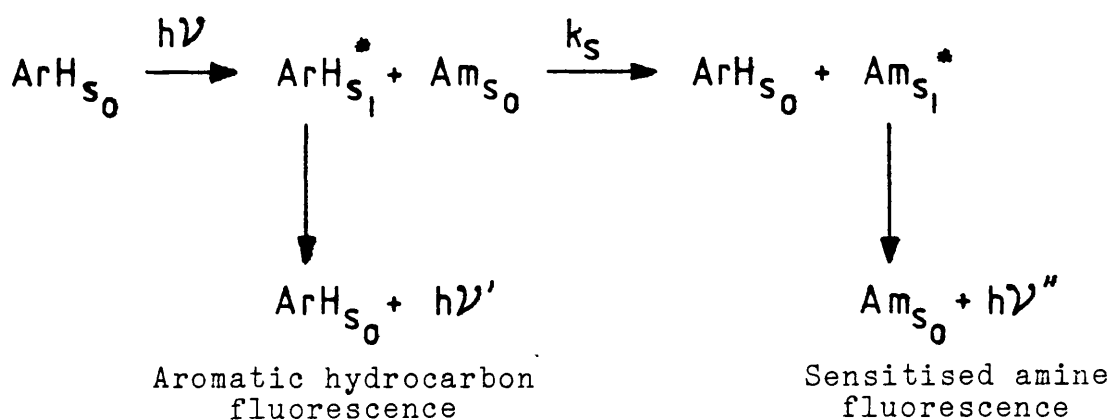
(a) After adjustment of the fluorescence data to account for the estimated underlying amino emission.

TABLE 3.(3). Rate Constants (k_q) for the Quenching of Benzene Fluorescence by a Series of N-methylated Alicyclic Amines, in Aerated Cyclohexane Solution at 20°C.

From the limited data available, it appeared that in cyclohexane solution, the quenching of the benzenoid fluorescence by the tertiary alicyclic amines occurred at rates approaching the diffusion controlled limits. (In cyclohexane solution; $k_{diff} = 1.0 \times 10^{10} \text{ mol}^{-1}\text{dm}^{-3}\text{s}^{-1}$ at 20°C⁽¹⁵⁷⁾).

In the case of N,N'-dimethyl-1,4-diazacyclohexane, the quenching rate constant was found to increase in magnitude, as predicted, when an allowance was made in the fluorescence measurements, for the underlying amino emission. In view of the necessary approximations made in evaluating the quenching rate constants however, a detailed analysis of the data will not be undertaken.

We attribute the appearance of a characteristic amino emission in our quenching experiments, particularly with N-methylazacyclo-pentane, -heptane and -octane and N,N'-dimethyl-1,4-diazacyclohexane as being due to energy transfer from the singlet excited state benzene to the amine species, as shown in Scheme 3.(3).., where k_s represents the rate



SCHEME 3.(3). Schematic Representation of Energy Transfer from Singlet Excited State Benzene to a Ground State Tertiary Amine Resulting in Sensitisation of Amine Fluorescence.

constant for the sensitisation process.

The earliest examples of singlet-singlet collisional energy transfer were provided by the work of Dubois and co-workers⁽¹⁵⁸⁻¹⁶⁰⁾ using biacetyl as the quencher molecule. Due to the feeble absorption of light by biacetyl in the near ultraviolet and visible regions, the rate constant for the commonly occurring long-range dipole-dipole energy transfer process was found to be small. Dubois and his colleagues demonstrated that the addition of biacetyl to aerated solutions of several ketones and aromatic hydrocarbons (benzene, alkylbenzenes and naphthalenes)^(161,162), led to a quenching of the fluorescence of the hydrocarbon, accompanied by sensitisation of the fluorescence of biacetyl. The energy transfer process appeared to be diffusionally controlled, the rate constant k_{ET} , obtained from Stern-Volmer analysis being close to the diffusion controlled rate constant k_{diff} , calculated from the modified Debye equation^(163,164) shown below in Equation 3.(13).

$$\frac{k_{\text{diff}}}{2000\eta} = \frac{8RT}{2000\eta} \quad - \text{Eqn. 3.(13).}$$

where R is the gas constant, T the temperature and η the viscosity of the solvent (poises).

We believe that the results of our experiments provided the first example of the sensitisation of tertiary aliphatic amine fluorescence by energy transfer from the singlet excited state of an aromatic hydrocarbon, in this case benzene.

3.3. SENSITISATION EXPERIMENTS.

A series of experiments were carried out in cyclohexane solution at 20°C, designed to assess quantitatively, the sensitisation of the amine emission resulting from energy transfer from benzene in its singlet excited state.

3.3.(1). Experimental.

The same stock solutions of benzene (OD 1.0 at 265nm) and the amine ($1.0 \times 10^{-1} \text{ mol dm}^{-3}$) in cyclohexane were used, as in the quenching experiments detailed in Section 3.2. However, in these sensitisation experiments, the concentration of amine present in the solution was kept at a constant value of $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ and the concentration of benzene varied, as detailed in Table 3.(4).

The concentration of benzene present in each solution was determined by the application of the Beer-Lambert Law. The optical density of a solution containing a known amount of benzene stock solution (0.5 cm^3 in 5.0 cm^3) was accurately measured at 265nm. Then using the molar extinction coefficient of benzene at this wavelength ($\epsilon_{265} = 24$), the concentration of benzene present in solution could be calculated. As can

Volume Amine Solution (cm ³)	Volume Benzene Solution (cm ³)	[Benzene] x 10 ⁻³ (moldm ⁻³)
0.5	0.0	0.0
0.5	0.1	0.8
0.5	0.2	1.6
0.5	0.3	2.4
0.5	0.4	3.2
0.5	0.5	4.0
0.5	0.6	4.8
0.5	0.7	5.6
0.5	0.8	6.4

TABLE 3.(4). A Representative Sample of the Compositions
of the Solutions Used in the Sensitisation
Experiments in Aerated Cyclohexane Solution
at 20°C.

be seen from Table 3.(4)., the amount of benzene used, was varied in the concentration range 8.0×10^{-4} to 6.4×10^{-3} moldm⁻³. The u/v absorption spectra of the solutions were recorded so that the effect of added benzene upon the optical density of the solutions at the excitation wavelength, could be monitored.

The sensitisation of the amine fluorescence in aerated solution was evaluated according to the method of Dubois et al.(159,160) by plotting the change in fluorescence intensity of the amine (F_A/F_{A_0}), versus the concentration of the benzene sensitiser added, where

F_{A_0} = intensity of the amine (acceptor) fluorescence in the absence of benzene (sensitiser)

F_A = intensity of the amine fluorescence in the presence of varying concentrations of benzene.

Having plotted the graph, the gradient $d(F_A/F_{A_0})/d[\text{Benzene}]$ is given by the expression shown in Equation 3.(14).

$$\frac{d(F_A/F_{A_0})}{d[\text{Benzene}]} = \frac{\epsilon_D}{\epsilon_A} \frac{k_s \tau_{D_S}}{1 + k_s \tau_{D_S} [\text{Amine}]} \quad - \text{Eqn. 3.(14)}.$$

where ϵ_D = molar extinction coefficient of the donor species (benzene) at 265nm

ϵ_A = molar extinction coefficient of the acceptor species (amine) at 265nm

τ_{D_S} = lifetime of singlet excited state benzene in aerated n-hexane solution at 20°C

k_s = rate constant for the sensitisation process



The values obtained for the rate constant (k_s) for the sensitisation process will be discussed below.

3.3.(2). Results and Discussion.

On the basis of the results obtained from the quenching experiments in cyclohexane solution, the tertiary aliphatic amines clearly underwent energy transfer interactions with the singlet excited state benzene to different extents. Whereas for N-methylazacyclopentane the sensitisation of the amine emission was very strong, there was no evidence to suggest that energy transfer to N-methyl-1-aza-4-oxacyclohexane had taken place, to yield the amine in its singlet excited state.

(1) N-methylazacyclopentane - the addition of 0.1cm^3 portions of the benzene stock solution to a $1.0 \times 10^{-2} \text{mol dm}^{-3}$ solution of N-methylazacyclopentane in cyclohexane, resulted in an increase in the intensity of the amine fluorescence, which was dependent upon the concentration of benzene present. The sensitisation of the amino emission was accompanied by

only minor fluorescence from the benzene chromophore, as shown in Figure 3.(6).

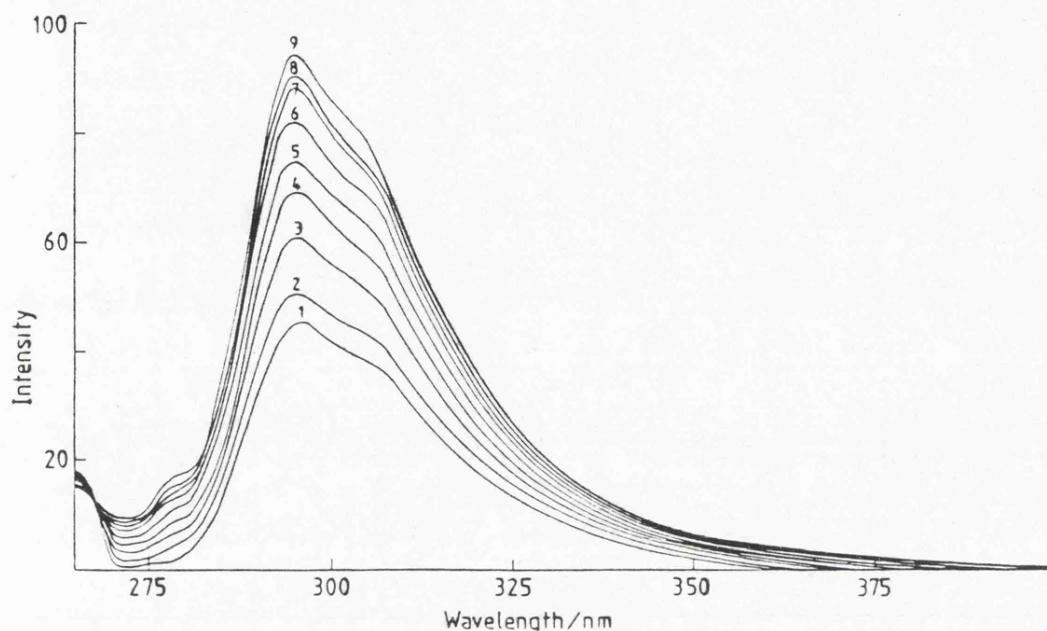


FIGURE 3.(6). Fluorescence Spectra of Aerated Cyclohexane Solutions of N-methylazacyclopentane ($1.0 \times 10^{-2} \text{ moldm}^{-3}$) Containing Varying Amounts of Benzene Stock Solution (OD 1.0 @ 265nm).
 (1) 0.0M, (2) $8.0 \times 10^{-4} \text{M}$, (3) $1.6 \times 10^{-3} \text{M}$,
 (4) $2.4 \times 10^{-3} \text{M}$, (5) $3.2 \times 10^{-3} \text{M}$, (6) $4.0 \times 10^{-3} \text{M}$,
 (7) $4.8 \times 10^{-3} \text{M}$, (8) $5.6 \times 10^{-3} \text{M}$,
 (9) $6.4 \times 10^{-3} \text{M}$.

Although the u/v absorption spectra of the solutions indicated that a large proportion of the excitation energy was being absorbed by the benzene chromophore, the lack of any substantial benzenoid fluorescence, clearly demonstrated that efficient energy transfer was taking place from the excited aromatic hydrocarbon to the amine species, with the resultant enhancement of the amine fluorescence.

(2) N,N'-dimethyl-1,4-diazacyclohexane - the emission from this amine was found to increase as the concentration of

benzene present in the solution was increased, but the enhancement of the fluorescence in aerated cyclohexane solution, was partially masked, by the concomitant emission from the benzene chromophore. The sensitisation effect was however far more apparent in degassed solutions (purged with dry nitrogen), where the fluorescence from the N,N'-dimethyl-1,4-diazacyclohexane was enhanced very considerably.

(3) N-methylazacyclooctane and N-methyldiethylamine - since the molar extinction coefficient of N-methylazacyclooctane was quite large at 265 ($\epsilon=50$), the sensitisation experiment was carried out using the amine at a concentration of only $2 \times 10^{-4} \text{ moldm}^{-3}$. The addition of benzene caused some sensitisation of the amine emission, but as the benzene concentration was increased above $\sim 3 \times 10^{-3} \text{ moldm}^{-3}$, the enhancement of the amine emission was obscured by the fluorescence of the benzene. An accurate assessment of the rate constant for the sensitisation process was therefore not possible. Although the sensitisation of N-methyldiethylamine fluorescence was also accompanied by emission from the benzene chromophore, the amine emission maximised to the red of that of benzene, at 295nm, and therefore a quantitative estimation of the rate of sensitisation could be made. The amine emission appeared to reach a limiting value at a benzene concentration of $\sim 7 \times 10^{-3} \text{ moldm}^{-3}$.

(4) N-methylazacycloheptane and triethylamine - an unexpected result was obtained when the sensitisation experiment was carried out using N-methylazacycloheptane as the acceptor species. The addition of benzene to the amine solution did not result in any sensitisation of the fluorescence from the N-methylazacycloheptane. Instead, the opposite effect was observed, and the amine emission was slightly quenched,

accompanied by the appearance of a new broad fluorescence band, well to the red of the amine, maximising at around 350nm. On the basis of our intramolecular studies, we attributed the new emission to an intermolecular fluorescent exciplex formed between the benzene and N-methylazacycloheptane.

When triethylamine was used as the amine species, the addition of the benzene stock solution produced two effects. At low concentrations of benzene (up to $\sim 4 \times 10^{-3} \text{ mol dm}^{-3}$) the benzene appeared to weakly sensitise the amine emission which broadened at longer wavelengths. As the benzene concentration was increased further, (up to a final level of $1.6 \times 10^{-2} \text{ mol dm}^{-3}$), the fluorescence from the benzene gradually became more significant and a broad structureless emission maximising at around 345nm could clearly be seen. As in the previous example, we interpreted this as being due to an intermolecular fluorescent exciplex between the benzene and the amine. A representative selection of the fluorescence spectra showing the emergence of the exciplex emission is given in Figure 3.(7).

(5) N-methylazacyclohexane - fluorescence from this amine in cyclohexane solution was not found to be sensitised by the addition of the benzene stock solution. Increasing the concentration of benzene present in the solution simply increased the intensity of the characteristic benzenoid fluorescence, leaving the amine emission unchanged. No sensitisation experiment was carried out using N-methyl-1-aza-4-oxacyclohexane, as the acceptor species.

The rate constants evaluated for the sensitisation process (k_s) are summarised below in Table 3.(5). A value of $5.7 \times 10^{-9} \text{ s}$ was used for the lifetime of singlet excited

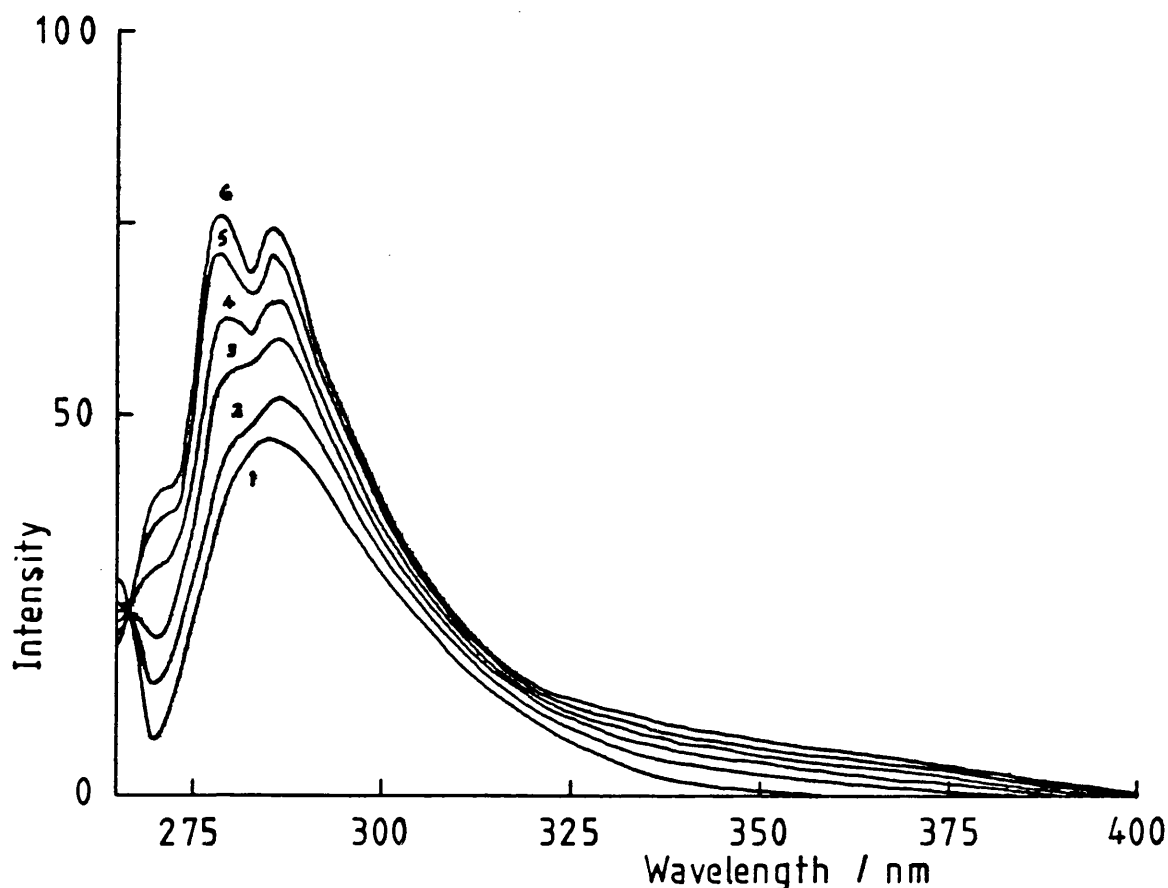


FIGURE 3.(7). Spectra of Aerated Cyclohexane Solutions of
Triethylamine ($1.0 \times 10^{-2} \text{ mol dm}^{-3}$) Containing
Varying Amounts of the Benzene Stock Solution
(OD 1.0 @ 265nm). (1) 0.0M, (2) $2.0 \times 10^{-3} \text{M}$,
(3) $4.0 \times 10^{-3} \text{M}$, (4) $8.0 \times 10^{-3} \text{M}$, (5) $1.2 \times$
 10^{-2}M , (6) $1.6 \times 10^{-2} \text{M}$.

state benzene in aerated n-hexane solution⁽¹⁵³⁾.

Although there was considerable variation in the magnitudes of the rate constants for the sensitisation process, from the limited data available, it appeared that the rate of energy transfer from the first singlet excited state of benzene to the singlet state of the tertiary amines was close to diffusion controlled, in aerated cyclohexane solution.

Furthermore, the results of our sensitisation experiments also gave us some indication of the relative energies of the first singlet excited states of benzene and the series of tertiary aliphatic amines studied. The observation of

<u>AMINE</u>	$k_s \times 10^{10}$ ($M^{-1}s^{-1}$)
MeN(CH ₂) ₇	4.60
MeN(CH ₂) ₄	1.86
MeNEt ₂	0.40
MeN  NMe	1.16

TABLE 3.(5). Rate Constants (k_s) for the Sensitisation of Amine Fluorescence by Energy Transfer from Singlet Excited State Benzene in Aerated Cyclohexane Solution at 20°C.

efficient energy transfer to both N-methylazacyclopentane and N,N'-dimethyl-1,4-diazacyclohexane for example, suggested that the singlet excited states of both of the amines lay energetically below that of benzene, making the sensitisation process a favourable decay route for channelling the excitation energy.

Whilst both N-methylazacyclooctane and N-methyldiethylamine underwent sensitisation, clearly there was a partitioning of the energy between the amine and the benzene, as shown by the fluorescence from both of the chromophores, suggesting that the excited amines were not appreciably lower in energy than singlet excited benzene. In the cases of both N-methylazacycloheptane and triethylamine however, an additional deactivation pathway appeared to be accessible to the excited aromatic chromophore. Although the triethylamine underwent a small amount of sensitisation at low benzene concentrations, both amines were observed to form a fluorescent intermolecular exciplex with the benzene, suggesting that the energy of the exciplex lay below that of the singlet excited state amine, in each case. The lack of any sensi-

tisation of amine emission with N-methylazacyclohexane and N-methyl-1-aza-4-oxacyclohexane, indicated that the excited singlet states of the amines were at energetically higher levels than the excited benzene, making energy transfer unfavourable.

3.3.(3). Concentration Effects Upon Sensitised Amine Fluorescence.

Although in the majority of our sensitisation experiments, the concentration of benzene was limited to the range 0.8×10^{-3} to $6.4 \times 10^{-3} \text{ moldm}^{-3}$, the use of higher levels of benzene in the sensitisation of triethylamine emission in cyclohexane solution, clearly led to an enhancement of the formation of a fluorescent intermolecular exciplex. The effect of using higher concentrations of the aromatic hydrocarbon was therefore investigated in greater detail.

Using stock solutions of benzene (OD 1.0 at 265nm) and the tertiary amines ($1.0 \times 10^{-1} \text{ moldm}^{-3}$) in cyclohexane, the following solutions (5cm^3) were prepared, as detailed in Table 3.(6). The fluorescence spectra of both the aerated and degassed solutions were recorded in each case.

Volume Amine Solution (cm^3)	Volume Benzene Solution (cm^3)	[Benzene] $\times 10^{-2}$ (moldm^{-3})
0.5	0.0	0.0
0.0	2.0	1.6
0.5	2.0	1.6

TABLE 3.(6). Solutions Used to Investigate the Effect of Higher Benzene Concentration ($1.6 \times 10^{-2} \text{ moldm}^{-3}$) Upon the Sensitisation of Amine Fluorescence.

With N-methylazacyclopentane, the addition of the benzene solution resulted in substantial sensitisation of the amine emission, (which increased in intensity by a factor of 2.5) accompanied by weak fluorescence from the benzene. A similar result was obtained using N,N'-dimethyl-1,4-diazacyclohexane, but we found no evidence from our fluorescence measurements to suggest that intermolecular exciplex formation occurred in either of these systems. The situation was different however for N-methylazacycloheptane and N-methylazacyclooctane. The addition of the benzene solution caused a decrease in the intensity of the amino emission at $\sim 290\text{nm}$, and led to the appearance of a broad new structureless emission band, maximising at around 350nm , as shown in Figure 3.(8). We attribute this new long wavelength band, to

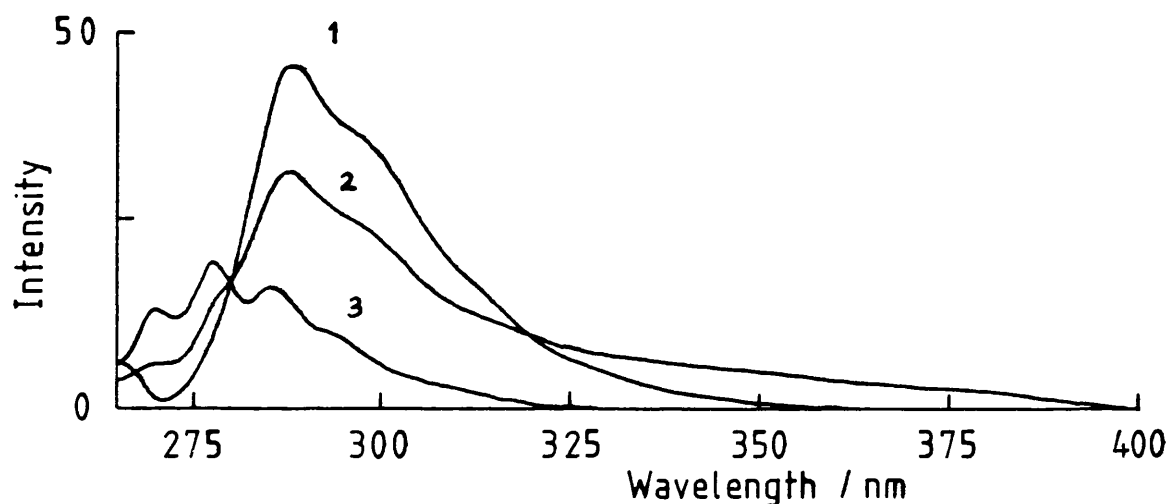


FIGURE 3.(8). Fluorescence Spectra of Aerated Cyclohexane Solutions of N-methylazacycloheptane ($1.0 \times 10^{-2} \text{ mol dm}^{-3}$) Containing Varying Amounts of Benzene. (1) 0.0M , (2) $1.6 \times 10^{-2}\text{M}$, (3) Benzene Blank Solution; $1.6 \times 10^{-2}\text{M}$.

emission from a fluorescent intermolecular exciplex formed between the benzene and the tertiary amine

When experiments were carried out with N-methylazacyclo-

hexane and N-methyl-1-aza-4-oxacyclohexane, the addition of benzene at a concentration of $1.6 \times 10^{-2} \text{ mol dm}^{-3}$ appeared to cause neither sensitisation of the amine emission nor fluorescent exciplex formation. The observed fluorescence spectrum simply resembling an additive combination of the spectra of the amine and benzene blank solutions. On the basis of our sensitisation results, it was apparent that in cyclohexane solution, the ability of an amine to form an intermolecular fluorescent exciplex with benzene in its excited singlet state, was dependent upon both the energy of the amine singlet excited state relative to that of the aromatic chromophore and the concentration of the benzene present in solution.

3.4. VARIABLE TEMPERATURE STUDIES.

3.4.(1). Introduction.

From our work on the quenching of benzene fluorescence by a series of tertiary aliphatic amines and our subsequent sensitisation experiments, we had established that at low benzene concentrations, energy transfer from singlet excited state benzene to the amine species was possible in non-polar solvents like cyclohexane. However, although in some of our experiments a fluorescent intermolecular exciplex had been observed, we had no direct evidence to support the possible intermediacy of an exciplex in the energy transfer process. That exciplexes play an important role in many photochemical reactions, has been widely established in the literature, notably in the work of Caldwell and Creed⁽⁷¹⁾ and Bryce-Smith and his co-workers⁽⁶⁸⁾ studying the mechanisms of photocycloaddition reactions. We therefore decided to carry out a variable temperature study on the interaction of

N-methylazacyclo-pentane and benzene, to determine whether or not our observed energy transfer from the aromatic hydrocarbon to the amine was accompanied by the formation of an intermediate fluorescent exciplex.

3.4.(2). Experimental.

Stock solutions of benzene (OD 0.7 at 265nm) and N-methylazacyclopentane ($1.0 \times 10^{-1} \text{ moldm}^{-3}$) were prepared using methylcyclohexane as the solvent. (Cyclohexane will not form a clear transmitting glass at low temperatures, unlike methylcyclohexane and is therefore unsuitable). A number of solutions were then prepared (5cm^3) containing 2.5cm^3 of the benzene stock solution and variable amounts of N-methylazacyclopentane, to find a solution which gave a moderately intense amino emission at room temperature, when excited at 265nm.

The variable temperature study was carried out on a solution containing 2.5cm^3 benzene solution and 0.25cm^3 N-methylazacyclopentane solution, giving an effective amine concentration of $5.0 \times 10^{-3} \text{ moldm}^{-3}$. The solution was then carefully transferred to a quartz cell of 1mm path length and thoroughly purged with a stream of dry nitrogen. The cell, which had been mounted in a dewar fitted with a quartz finger was cooled by the passage of a stream of dry nitrogen around the sample compartment, which had previously been circulated through a 5 metre copper coil immersed in a dewar of liquid nitrogen. The temperature was adjusted by variation of the nitrogen flow rate through the copper cooling coil and accurately monitored using a thermocouple linked to a digital thermometer.

Using an excitation wavelength of 265nm the fluorescence spectrum of the solution was recorded over the temperature

range $+16^{\circ}\text{C}$ to -178°C (289 - 95K) at approximately 10° intervals, noting the average temperature of the system during the time taken to record each spectrum.

3.4.(3). Results and Discussion.

The results of the variable temperature study on the excited state interaction of benzene with N-methylazacyclopentane in methylcyclohexane are summarised diagrammatically in Figures 3.(9). and 3.(10).

As can clearly be seen from the data given in Figure 3.(9). the emission observed at room temperature was clearly characteristic of N-methylazacyclopentane, maximising at around 295nm. Lowering the temperature however, resulted in a diminution of the signal from the amine until at -80°C the fluorescence now resembled that of a weak benzenoid emission. Further reductions in the temperature below -80°C , resulted in an increase in the intensity of the characteristic benzenoid fluorescence. Limitations in the cooling procedure employed, prevented us from investigating the excited state interaction between the two species below about -170°C . Based upon the results of our studies on the intramolecular systems, we anticipated that an intermolecular exciplex, if formed, would give an emission maximising at around 350-360nm. From the complete lack of any new emission bands to the red of the benzenoid and amino fluorescence, even though exciplex formation is favoured at lower temperatures, we concluded that the sensitisation of the amine fluorescence by energy transfer from singlet excited state benzene, did not involve the intermediacy of a fluorescent intermolecular exciplex.

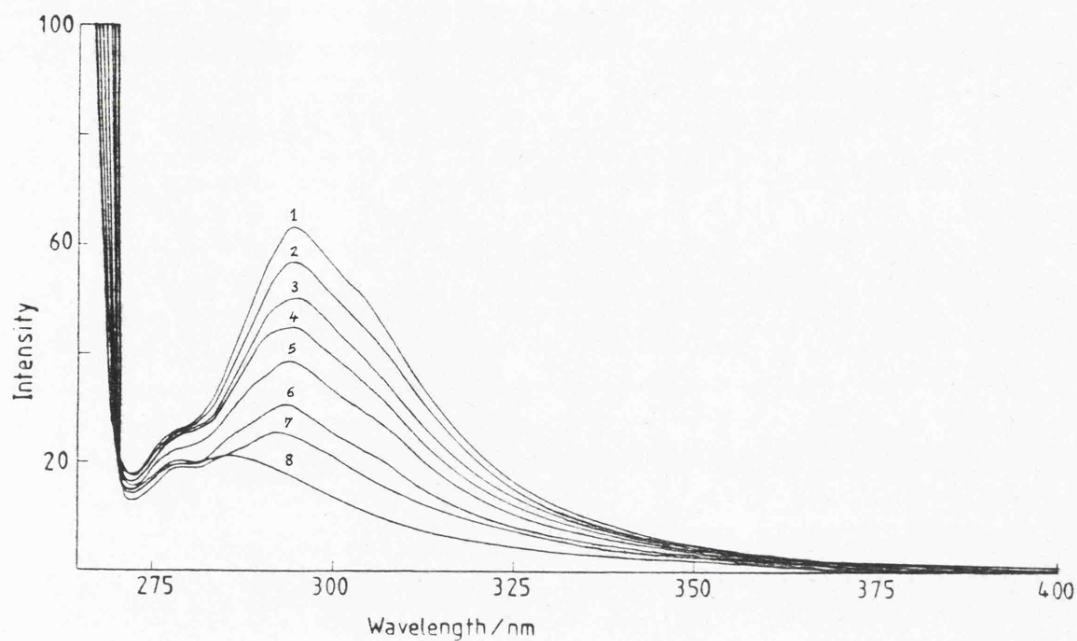


FIGURE 3.(9). Variable Temperature Fluorescence Spectra
of the Solution of Benzene and N-methyl-
azacyclopentane in Methylcyclohexane, Over
the Temperature Range $+16^{\circ}\text{C}$ to -79°C ,
(1) $+16^{\circ}\text{C}$, (2) $+6^{\circ}\text{C}$, (3) -17°C , (4) -27°C ,
(5) -34°C , (6) -42°C , (7) -50°C , (8) -79°C .

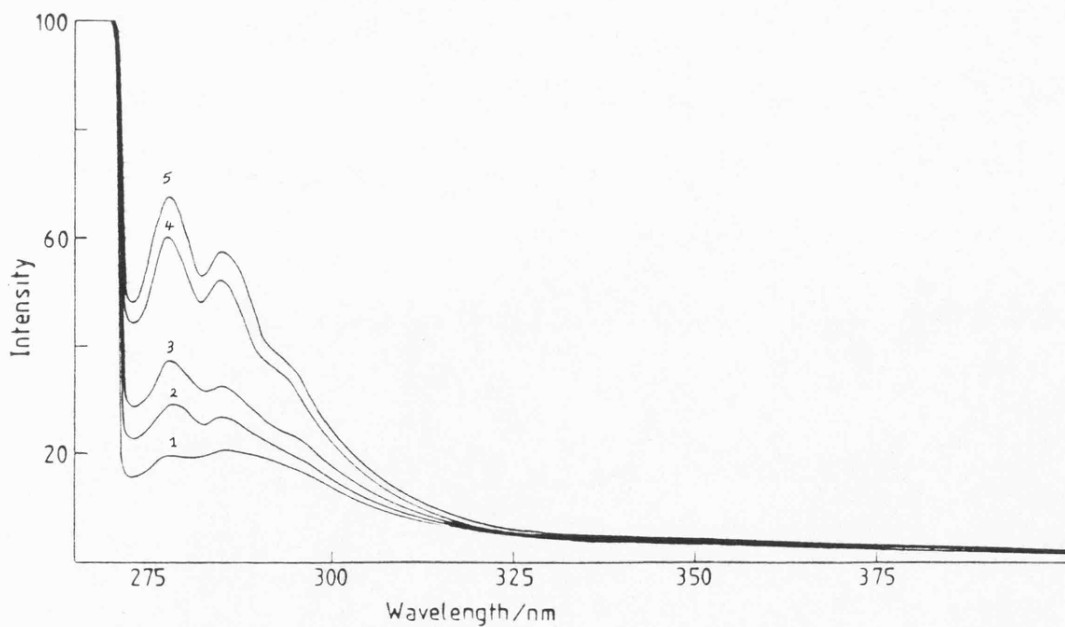


FIGURE 3.(10). Variable Temperature Fluorescence Spectra
of a Methylcyclohexane Solution of Benzene
and N-methylazacyclopentane, Recorded Over
the Temperature Range -79°C to -169°C ,
(1) -79°C , (2) -100°C , (3) -118°C ,
(4) -148°C , (5) -169°C .

3.5. THE ADDITION OF HIGH CONCENTRATIONS OF NEAT
BENZENE TO SOLUTIONS OF TERTIARY AMINES IN
CYCLOHEXANE.

3.5.(1). Introduction.

Our sensitisation experiments using benzene at a concentration of $1.6 \times 10^{-2} \text{ mol dm}^{-3}$, had indicated that with the three amines, triethylamine, N-methylazacycloheptane and N-methylazacyclooctane, intermolecular fluorescent exciplex formation could occur. Further evidence in support of these findings, has been provided in a recent piece of work by Leismann and Mattay⁽¹⁶⁵⁾ also studying the interaction of triethylamine with benzene in cyclohexane solution. They too observed the formation of an intermolecular fluorescent exciplex between the two species, but their experiments involved the utilisation of far higher concentrations of benzene. Keeping the concentration of the aromatic hydrocarbon constant, at $5.6 \times 10^{-1} \text{ mol dm}^{-3}$, they varied the concentration of triethylamine within the range 7.0×10^{-3} to $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ and studied the effect upon exciplex formation, finding that the intensity of the exciplex fluorescence increased with amine concentration. Their results are summarised pictorially in Figure 3.(11)., and as can be seen, the appearance of the exciplex emission which maximised at around 345nm, was accompanied by the quenching of the benzenoid fluorescence. Clearly intermolecular exciplex formation occurred in the presence of high concentrations of benzene, therefore we extended our investigations on the photochemical behaviour of the benzene-tertiary amine systems to cover the use of very high benzene concentrations⁽⁵⁶⁾.

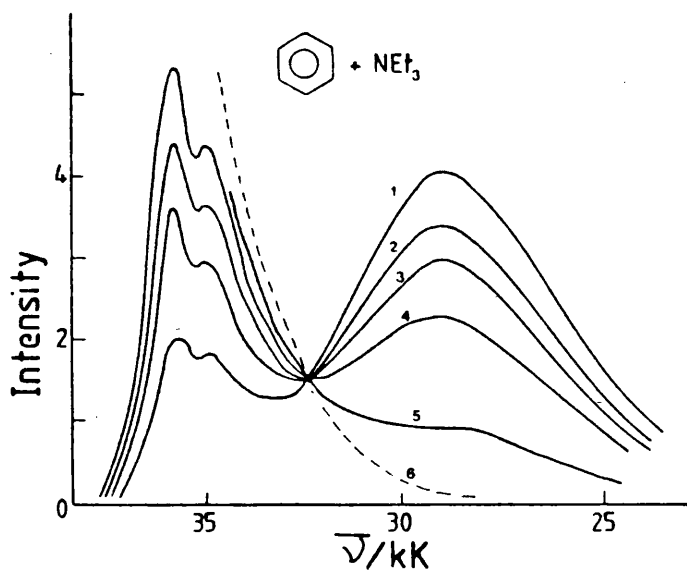


FIGURE 3.(11). Fluorescence Spectra of Cyclohexane
Solutions of Benzene ($5.6 \times 10^{-1} \text{ moldm}^{-3}$)
Containing Varying Amounts of Triethyl-
amine⁽¹⁶⁵⁾. (1) $1.0 \times 10^{-1} \text{M}$, (2) $5.0 \times$
 10^{-2}M , (3) $4.0 \times 10^{-2} \text{M}$, (4) $3.0 \times 10^{-2} \text{M}$,
(5) $7.0 \times 10^{-3} \text{M}$, (6) 0.0M .

3.5.(2). Experimental.

A cyclohexane solution of the tertiary amine (OD 0.1 at 275nm) was prepared in a quartz cuvette (1cm^2) and varying amounts of neat benzene added using either a 10 μl or a 100 μl syringe. After thorough agitation of the cell contents, the cuvette was stoppered, the fluorescence spectrum of the solution recorded, at an excitation wavelength of 275nm and then the next portion of benzene syringed into the cell. All the fluorescence measurements were made on aerated solutions. The results obtained from three of the systems studied will be discussed in detail in Section 3.5.(3).

A representative selection of the solutions prepared, showing the concentration of benzene present in each case are summarised in Table 3.(7). In calculating the concentration of benzene present in the cuvette for each solution,

it was assumed that the capacity of the cell was 3cm^3 and the density of benzene was taken as $\rho=0.879\text{ gcm}^{-3}$.

Amount  (ul)	$[\text{benzene}] \times 10^{-3}$ (mol dm ⁻³)	Amount  (ul)	$[\text{benzene}] \times 10^{-1}$ (mol dm ⁻³)
0.1	0.38	40.0	1.50
0.5	1.88	50.0	1.88
1.0	3.75	60.0	2.25
2.0	7.50	70.0	2.63
3.0	11.25	80.0	3.00
4.0	15.00	90.0	3.38
5.0	18.75	100.0	3.75
6.0	22.50	150.0	5.63
8.0	30.00	200.0	7.50
10.0	37.50	250.0	9.38
20.0	75.00	500.0	18.75
30.0	112.50	750.0	28.13

TABLE 3.(7). Conversion Table Showing the Amount Added (ul) and Concentration of Benzene Present in Cyclohexane Solutions of Tertiary Amines.

3.5.(3). Results and Discussion.

3.5.(3).1. Triethylamine in Cyclohexane Solution with Varying Amounts of Benzene Added (ul).

In the first part of our investigation, we tried to simulate our sensitisation experimental conditions. Working with a cyclohexane solution of triethylamine (OD 0.1 at 265nm), we varied the amount of benzene present in solution over the concentration range 3.75×10^{-4} to 3.75×10^{-2} mol-dm⁻³ (0.1-10ul benzene) and monitored the change in the fluorescence spectra. The results are summarised diagram-

matically in Figure 3.(12). The fluorescence spectra show

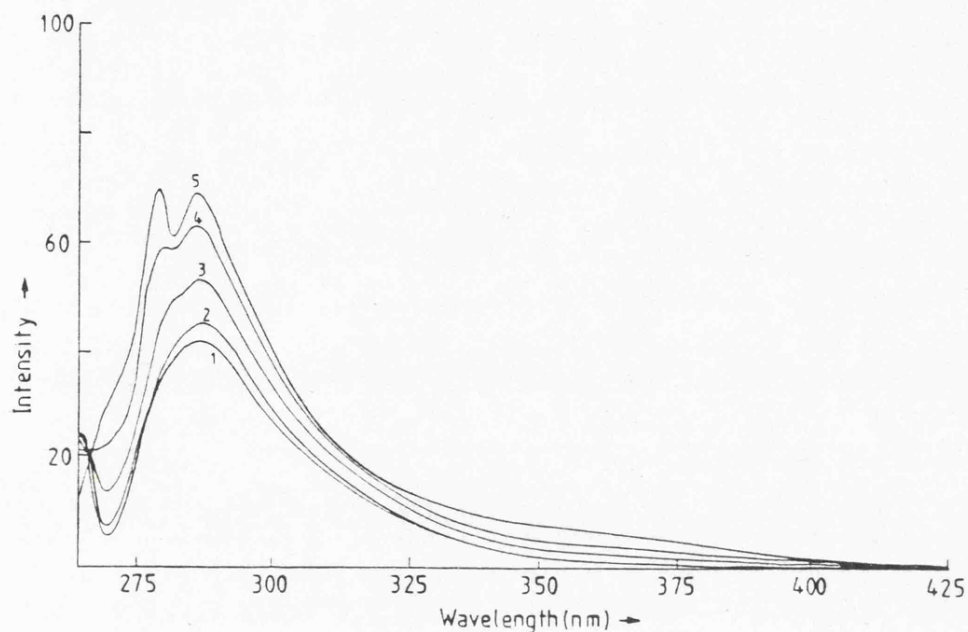


FIGURE 3.(12). Fluorescence Spectra of Aerated Cyclohexane Solutions of Triethylamine (OD 0.1 at 265nm) Containing Varying Amounts of Benzene (μl).
(1) 0.0M, (2) 0.1μl; 3.75×10^{-4} M, (3) 0.7μl; 2.63×10^{-3} M, (4) 2.0μl; 7.50×10^{-3} M, (5) 6.0μl; 2.25×10^{-2} M.

that at these concentration levels, the addition of benzene initially caused a small amount of sensitisation of the triethylamine fluorescence, followed by the appearance of a broad, weak emission maximising at around 345-350nm, which we believe was due to an intermolecular exciplex. The shorter wavelength emission now resembled that of benzene, showing discrete wavelength maxima at 279 and 286nm.

The next stage of the experiment was carried out using a different cyclohexane solution of triethylamine (OD 0.1 at 275nm) and an excitation wavelength of 275nm. Far greater quantities of benzene were added to the amine solution, ultimately reaching a benzene concentration of 2.81 moldm^{-3} . A selection of the fluorescence spectra obtained are summarised in Figure 3.(13).

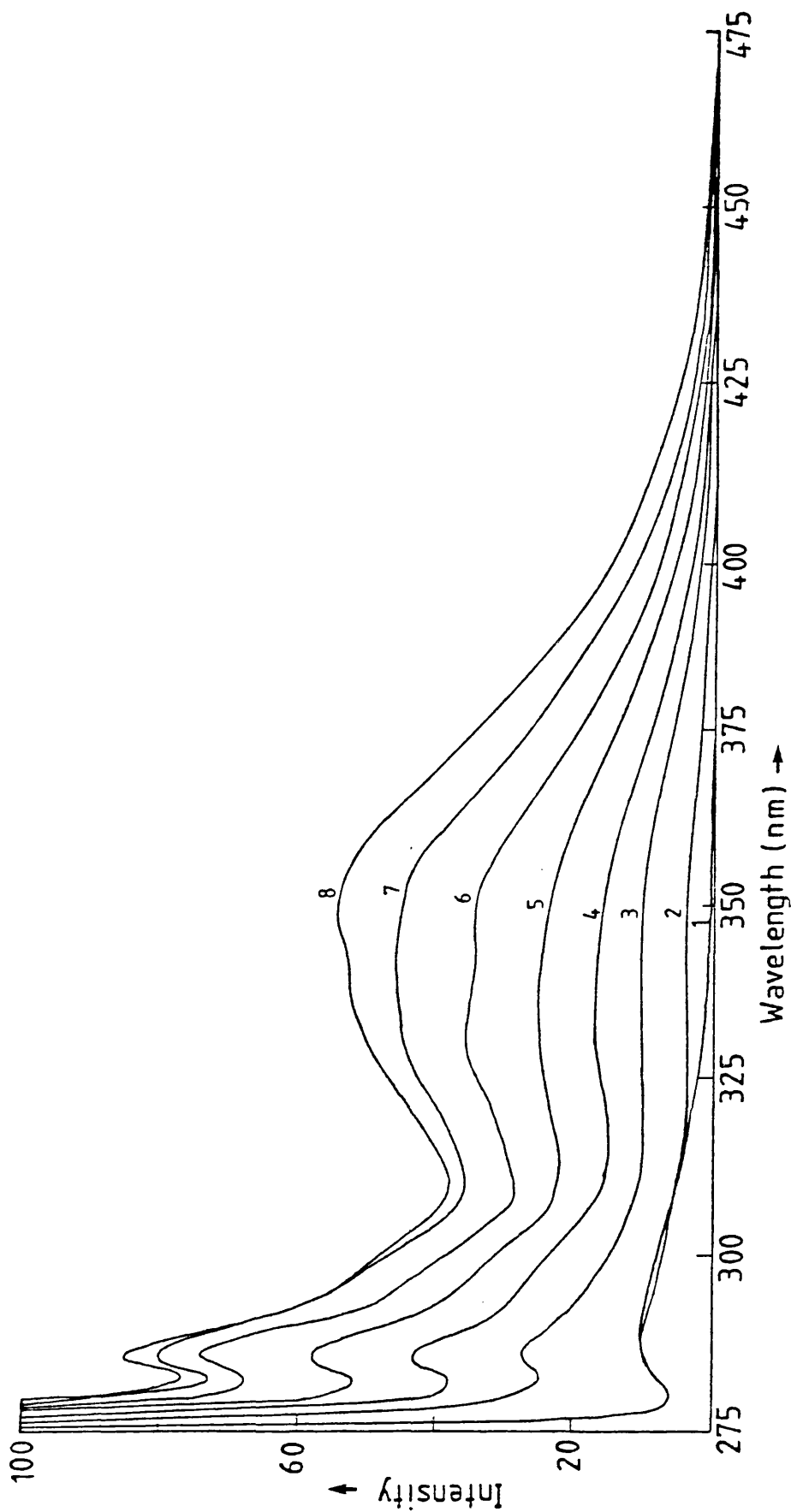


FIGURE 3.(13).

Fluorescence Spectra of Aerated Cyclohexane Solutions of Triethylamine

(OD 0.1 at 275nm) Containing Varying Amounts of Benzene (ul).	(1) 0.0M,
(2) 10ul; $3.75 \times 10^{-2}M$, (3) 50ul; $1.88 \times 10^{-1}M$, (4) 90ul; $3.38 \times 10^{-1}M$,	
(5) 150ul; $5.63 \times 10^{-1}M$, (6) 250ul; $9.38 \times 10^{-1}M$, (7) 400ul; 1.50M,	
(8) 750ul; 2.81M.	

Increasing the concentration of benzene in solution over the range $3.75 \times 10^{-2} \text{ moldm}^{-3}$ to $5.63 \times 10^{-1} \text{ moldm}^{-3}$, resulted in an increase in the intensity of the characteristic benzene fluorescence, accompanied by a strengthening of the exciplex emission, which appeared to be maximising at around 335-340nm. An accurate assessment of the wavelength maximum of the exciplex was difficult, due to the broad nature of the emission band.

Whilst the addition of further portions of benzene to the solution simply caused the benzenoid fluorescence at 280nm to increase in intensity up to a limiting value, the wavelength maximum of the exciplex emission underwent a red shift as the concentration of benzene was increased from $9.38 \times 10^{-1} \text{ to } 2.81 \text{ moldm}^{-3}$. At a concentration of $9.38 \times 10^{-1} \text{ moldm}^{-3}$ (250 μ l benzene added) the exciplex emission appeared to be comprised of two bands maximising at 330nm and 350nm, with the shorter wavelength band slightly more intense. Then as the benzene concentration was raised, the intensity of the longer wavelength band increased at a faster rate than the band at 330nm, such that at a final concentration of 2.81 moldm^{-3} , the wavelength maximum of the exciplex emission had clearly undergone a red shift to 350nm. An appraisal of these results, along with those obtained from our experiments with N-methylazacyclopentane and N-methylazacycloheptane, will be made in Section 3.5.(3).3.

3.5.(3).2. N-methylazacyclopentane in Cyclohexane Solution with Varying Amounts of Benzene Added (μ l).

The fluorescence spectra of aerated cyclohexane solutions of N-methylazacyclopentane (OD 0.1 at 275nm) containing varying amounts of benzene, in the concentration range $1.88 \times 10^{-2} \text{ moldm}^{-3}$ to 2.81 moldm^{-3} are shown diagrammatically

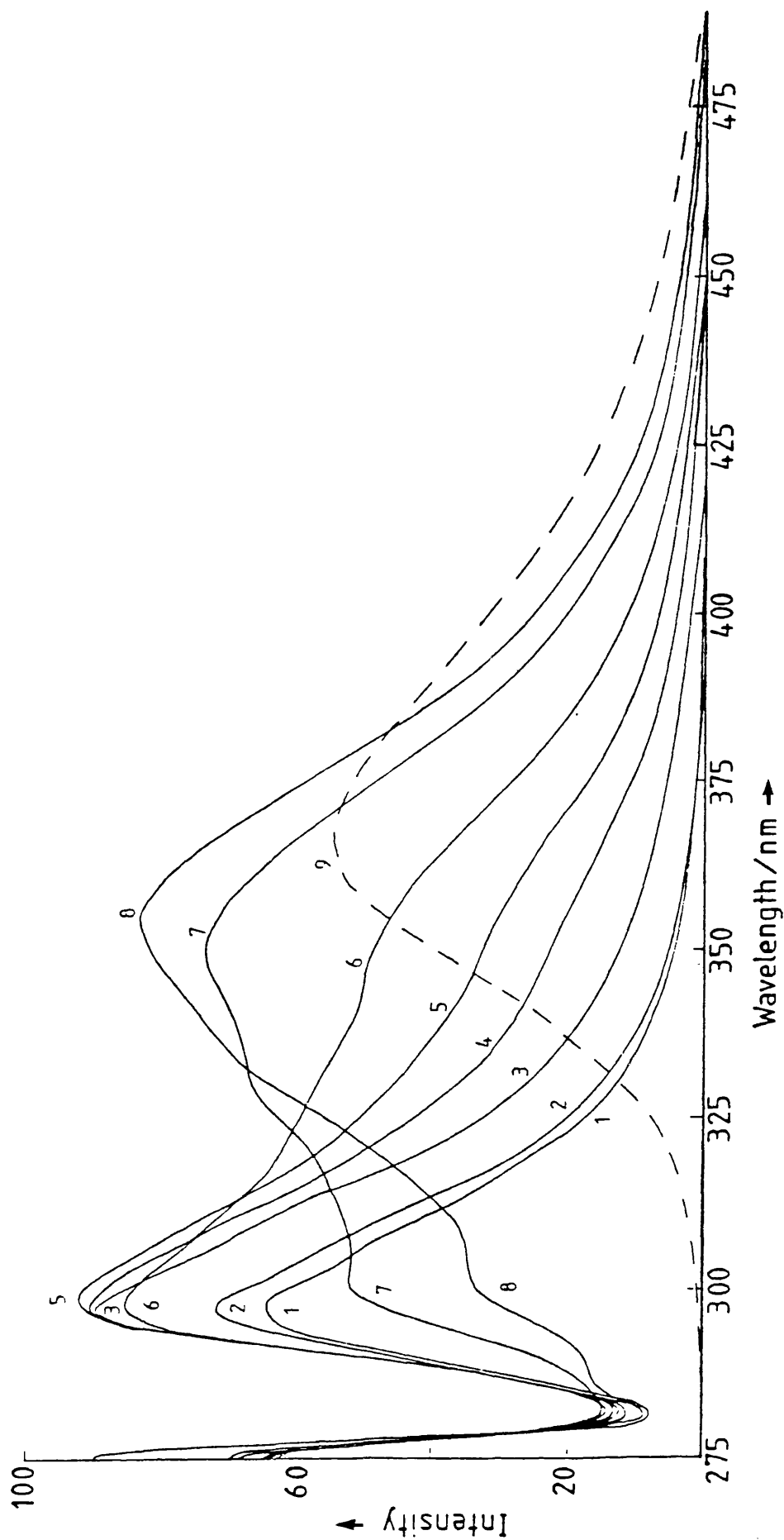


FIGURE 3.(14). Fluorescence Spectra of Aerated Cyclohexane Solutions of $\text{MeN}(\text{CH}_2)_4$ (OD 0.1 at 275nm) + Benzene (μl). (1) 0.0M, (2) 5 μl ; $1.88 \times 10^{-2}\text{M}$, (3) 50 μl ; $1.88 \times 10^{-1}\text{M}$, (4) 100 μl ; $3.75 \times 10^{-1}\text{M}$, (5) 150 μl ; $5.63 \times 10^{-1}\text{M}$, (6) 250 μl ; $9.38 \times 10^{-1}\text{M}$, (7) 500 μl ; 1.88M, (8) 750 μl ; 2.81M, (9) $\text{MeN}(\text{CH}_2)_4$ in Benzene OD 0.52 at 280nm.

in Figure 3.(14).

As can be seen from the data displayed in Figure 3.(14) ., the addition of benzene at a concentration of $1.88 \times 10^{-2} \text{ moldm}^{-3}$, caused sensitisation of the amino emission at 295nm, as anticipated on the basis of our earlier experimental results. Subsequent additions of benzene however, up to a total of 150 μ l ($5.63 \times 10^{-1} \text{ moldm}^{-3}$) not only enhanced the amino fluorescence, but also led to a marked broadening of the tail of the emission at longer wavelengths. We believe that this effect was being produced by an underlying emission from an intermolecular exciplex, but at this stage could not deduce an accurate value for the wavelength maximum of the emission. As the concentration of benzene was increased further to a maximum value of 2.81 moldm^{-3} , the characteristic amino emission at 295nm became much weaker in intensity, whilst in contrast, that of the emission at longer wavelengths, which we attribute to the fluorescent exciplex, was substantially increased. Furthermore, the wavelength maximum of the emission underwent a red-shift as the concentration of benzene was raised, an effect which could be clearly seen by comparing the spectra obtained at benzene concentrations of 1.88 and 2.81 moldm^{-3} . In the former case, the fluorescence spectrum appeared to show two maxima at 330nm and 350nm, whereas at the higher concentration, the exciplex emission clearly maximised at 355nm. A similar concentration dependence of the exciplex emission was noted in the benzene-triethylamine system.

For comparative purposes, Figure 3.(14). also shows the fluorescence spectrum of a solution of N-methylazacyclopentane in benzene (OD 0.52 at 280nm) with excitation at 280nm. As can be seen, the solution gave a broad, fairly

symmetrical, structureless emission maximising at around 365nm.

3.5.(3).3. N-methylazacycloheptane in Cyclohexane Solution Containing Varying Amounts of Benzene (ul).

The effect of adding benzene to an aerated cyclohexane solution of N-methylazacycloheptane (OD 0.1 at 275nm) was also studied, using concentrations of benzene in the range 3.75×10^{-2} up to 1.88 mol dm^{-3} . The fluorescence spectra of a selection of the solutions are shown in Figure 3.(15).

In agreement with the results obtained in our earlier sensitisation experiments, the addition of benzene to the amine blank solution, at a concentration of $3.75 \times 10^{-2} \text{ mol dm}^{-3}$, was sufficient to cause a diminution of the characteristic amino fluorescence at around 288nm, with the appearance of a broad poorly resolved band to the red of the amine emission. As the benzene concentration was gradually raised, the short wavelength emission increased in intensity again, but had been blue-shifted slightly to 284nm, characteristic more of benzenoid fluorescence. The intensity of the exciplex emission was also considerably enhanced by the incremental addition of benzene, but it was found that the wavelength of maximal fluorescence showed a dependence upon the concentration of benzene present in solution. When the molarity of the benzene was around $1.5 \times 10^{-1} \text{ mol dm}^{-3}$, the exciplex fluorescence maximised at 335nm, then as the level of benzene was increased to $3.0 \times 10^{-1} \text{ mol dm}^{-3}$, the spectrum appeared to show maxima at both 335nm and 345nm, of roughly equal intensity and finally at very high benzene concentrations ($>1.5 \text{ mol dm}^{-3}$), the wavelength maximum had been red-shifted out to 355nm, although the emission band retained a shoulder at 335nm.

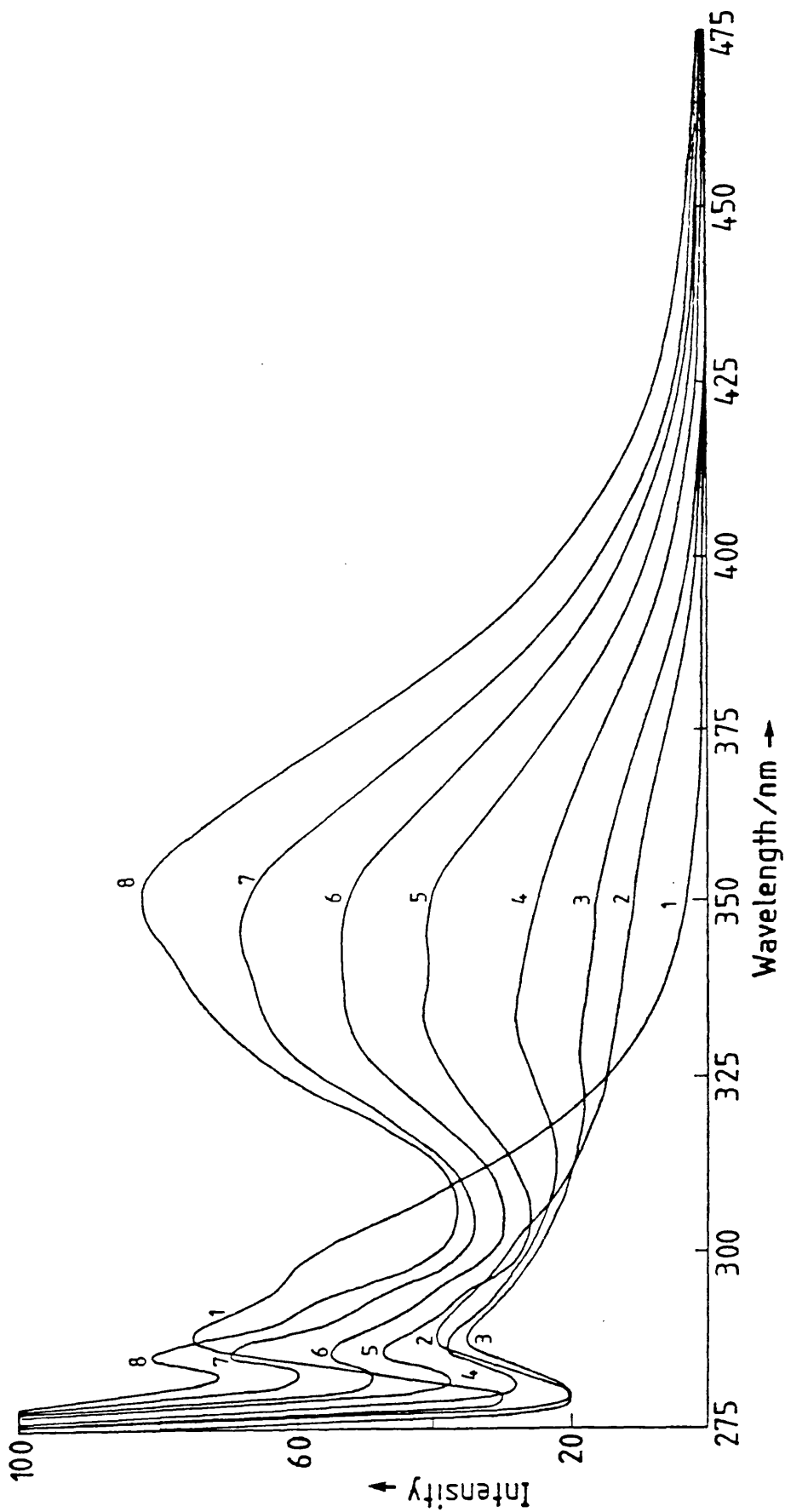


FIGURE 3.(15). Fluorescence Spectra of Aerated Cyclohexane Solutions of $\text{MeN}(\text{CH}_2)_6$ (OD 0.1 at 275nm) + Benzene (μl). (1) 0.0M, (2) $10\mu\text{l}$; $3.75 \times 10^{-2}\text{M}$, (3) $20\mu\text{l}$; $7.50 \times 10^{-2}\text{M}$, (4) $40\mu\text{l}$; $1.5 \times 10^{-1}\text{M}$, (5) $80\mu\text{l}$; $3.0 \times 10^{-1}\text{M}$, (6) $125\mu\text{l}$; $4.69 \times 10^{-1}\text{M}$, (7) $200\mu\text{l}$; $7.5 \times 10^{-1}\text{M}$, (8) $500\mu\text{l}$; 1.88M .

Clearly the concentration of benzene present in the solution plays an important part in determining first, whether an intermolecular fluorescent exciplex can be formed and then at what wavelength the emission from the exciplex maximises. Our interpretation of the observed dependency of fluorescent exciplex formation upon the benzene concentration, was that it was necessary for the initially created non-fluorescent collision-complex to be solvated, or at least partially solvated by the benzene. When this solvation could not occur, the unstable encounter complex formed between the amine and the benzene was thought to collapse, with the energy being channelled into the excited singlet state of the amine. At sufficiently high concentrations however, ($> \sim 1 \times 10^{-1} \text{ mol dm}^{-3}$), the benzene molecules were able to diffuse to the collision complex before it had time to fall apart and the energy of the complex was reduced by the increased solvating power of the benzene. Further increases in the benzene concentration led to more efficient solvation of the excited complex, as the cyclohexane molecules in the solvation shell were increasingly replaced by the more polar benzene molecules, causing the observed red-shift in the exciplex fluorescence band from $\sim 335\text{nm}$ out to around 355nm . A phenomenon which has previously been described^(104,120,166).

Evidence to support the proposal that the stability of the excited species was related to the degree of polarity in the solvation shell, was provided by consideration of the fluorescence properties of triethylamine, N-methylazacyclopentane and N-methylazacycloheptane in aerated benzene solutions, (OD 0.1 at 290nm). Excitation at 280nm , resulted in a broad structureless emission, maximising at around

365nm in the case of N-methylazacyclopentane (as shown in Figure 3.(14).), which we attributed to fluorescence from the intermolecular benzene-amine exciplex solvated by benzene. On the basis of this result therefore, it appeared that even at benzene concentrations of around 1.5 moldm^{-3} , the intermolecular exciplex formed between the aromatic hydrocarbon and the amine, was not completely solvated by benzene molecules.

3.5.(3).4. Cyclohexane Solutions of N-methylazacyclooctane and N-methylazacyclohexane Containing Varying Amounts of Benzene (μl).

In the case of N-methylazacyclooctane, the addition of benzene, even at relatively low concentrations ($7.5 \times 10^{-2} \text{ moldm}^{-3}$), was sufficient to cause very substantial quenching of the characteristic amino emission at 287nm, with the appearance of a weak exciplex emission at around 345nm. Increasing the concentration of benzene up to a maximum level of 2.81 moldm^{-3} (750 μl added), resulted in enhanced emission from the intermolecular benzene-amine exciplex, with a weak emission at shorter wavelengths due either to residual amine emission or fluorescence from the benzene. Once again the wavelength maximum of the emission underwent a red-shift to around 355nm at very high concentrations of the aromatic hydrocarbon.

The addition of benzene (up to a maximum concentration of $5.63 \times 10^{-1} \text{ moldm}^{-3}$) to a cyclohexane solution of N-methylazacyclohexane (OD 0.1 at 275nm), did not appear to result either in sensitisation of the amine emission at 325nm or lead to the formation of an intermolecular fluorescent exciplex. The spectrum simply took on the appearance of a characteristic benzenoid emission. This result indicated

that energy transfer from singlet excited state benzene to N-methylazacyclohexane was not an energetically favourable process.

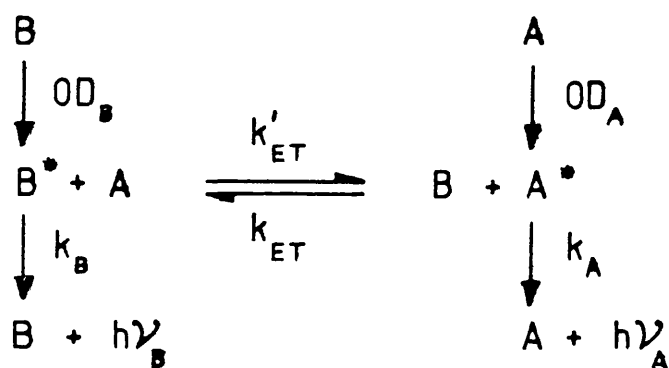
3.6. REVERSIBLE ENERGY TRANSFER.

In a recent piece of closely related work by Halpern and Wryzykowska⁽¹⁶⁷⁾, the authors carried out a detailed kinetic investigation into the energy transfer processes which occurred between the benzene and saturated tertiary aliphatic amines in the excited state. Using n-hexane solutions of benzene and N-methyldiethylamine, they studied the effect of varying the excitation wavelength upon the interactions between the two species. It was found that the nature of the absorption spectra of these two compounds, enabled almost exclusive photoexcitation of the amine chromophore at 222nm, in the presence of benzene, whilst excitation at 261nm led predominantly to excitation of the aromatic chromophore.

With excitation at 222nm, (keeping the amine concentration fixed at $3.0 \times 10^{-4} \text{ mol dm}^{-3}$ and varying the concentration of benzene in the range 1.0×10^{-3} to $1.0 \times 10^{-2} \text{ mol dm}^{-3}$), the authors observed quenching of the amine fluorescence by benzene, accompanied by an emission from the aromatic hydrocarbon. Analysis of the non-exponential decay curves, indicated that the benzene quenched the N-methyldiethylamine excited state at the diffusion controlled rate in n-hexane solution. The appearance of the benzene emission was attributed to energy transfer from the photoexcited amine to benzene ($k_{ET} \approx 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

At 261nm excitation however, (keeping the concentration of benzene fixed at $6.35 \times 10^{-3} \text{ mol dm}^{-3}$ and varying the N-methyldiethylamine concentration in the range 0 to $3.0 \times$

$10^{-2} \text{ moldm}^{-3}$), fluorescence was observed from both benzene and the N-methyldiethylamine, indicating that sensitisation of the amine emission had occurred, as a result of energy transfer from the singlet excited state benzene ($k'_{\text{ET}} = 2.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). The authors interpreted these results by proposing the existence of a reversible energy transfer process between the N-methyldiethylamine and the benzene as shown in Scheme 3.(4)., the direction of energy transfer



SCHEME 3.(4). Schematic Representation of the Reversible Energy Transfer Between the Tertiary Amine (A) and Benzene (B) in n-hexane Solution⁽¹⁶⁷⁾.

being determined by the excitation wavelength used. Rate constants for the energy transfer processes suggested that transfer from the amine to benzene was about four times more efficient than the reverse process.

We subsequently decided to study the benzene-N-methyldiethylamine system under our experimental conditions, using cyclohexane as the solvent, and 265nm excitation. A representative selection of the fluorescence spectra obtained from aerated cyclohexane solutions of benzene (OD 0.1 at 265nm) containing concentrations of amine in the range 0 to $1.6 \times 10^{-2} \text{ moldm}^{-3}$, are shown in Figure 3.(16).

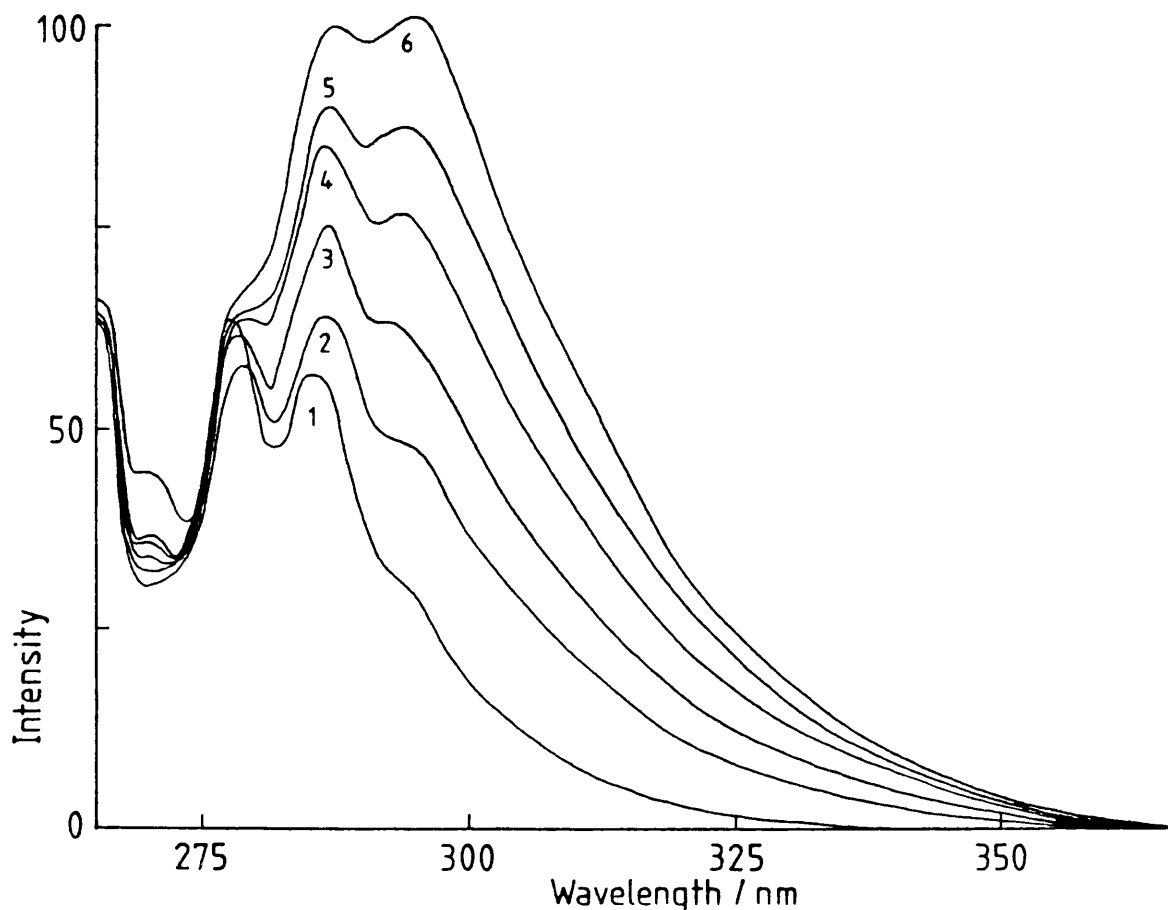


FIGURE 3.(16). Fluorescence Spectra of Aerated Cyclo-
hexane Solutions of Benzene (OD 0.1 at
265nm) Containing Varying Concentrations
of N-methyldiethylamine at 20°C (λ_{exc} 265nm).
(1) 0.0M, (2) 4.0×10^{-3} M, (3) 6.0×10^{-3} M,
(4) 1.0×10^{-2} M, (5) 1.2×10^{-2} M,
(6) 1.6×10^{-2} M.

As can clearly be seen, the addition of increasing amounts of N-methyldiethylamine solution resulted in a red-shift in the λ_{max} of the fluorescence band from 285nm out to 295nm and a steady increase in the intensity of the emission. We attributed the majority of the emission to fluorescence from the N-methyldiethylamine, indicating that energy transfer had taken place from the singlet excited state benzene to the ground state amine. The second apparent maximum at 285nm, was we believe, due to the residual benzenoid fluorescence. Under the conditions of our experiment, there was no

appreciable change in the optical density of the solutions upon adding the amine, suggesting that in agreement with the findings of Halpern, the excitation energy predominantly entered the aromatic hydrocarbon. A further increase in the concentration of the amine to $4.0 \times 10^{-2} \text{ mol dm}^{-3}$, resulted in a broadening of the emission at longer wavelengths, which we ascribed to fluorescence from an intermolecular exciplex, maximising at around 345-350nm. The enhancement of the amine emission was not as clearly defined in our sensitisation experiment however, due to the substantial fluorescence from the benzene chromophore as the concentration of the aromatic hydrocarbon was increased. Never-the-less, both sets of experimental data demonstrated that in cyclohexane solution, energy transfer could take place from benzene in its singlet excited state to N-methyldiethylamine, a typical tertiary monoamine, at an excitation wavelength of 265nm.

We also very briefly investigated the interaction of the two systems, at an excitation wavelength of 230nm, again in cyclohexane solution at 20°C. In the first experiment, we considered the effect of adding varying amounts of benzene, in the concentration range 1.0×10^{-2} to $3.0 \times 10^{-2} \text{ mol dm}^{-3}$, to a solution of N-methyldiethylamine in cyclohexane (OD 0.1 at 230nm). The addition of the aromatic hydrocarbon was found to cause a reduction in the intensity of the amine fluorescence at 295nm, accompanied by the emergence of a characteristic benzenoid emission with wavelength maxima at 272, 278 and 286nm. However, on the basis of these results, we were reluctant to attribute the appearance of benzene fluorescence to an energy transfer process from the excited state N-methyldiethylamine to ground state benzene, because of the substantial increases in the optical densities of the

solutions at the excitation wavelength of 230nm. It appeared far more likely that under these conditions, the benzene was competing very effectively with the amine for absorption of the incident energy, and was therefore undergoing direct excitation into the singlet excited state.

The next stage in the investigation, involved the addition of portions of N-methyldiethylamine in cyclohexane solution (OD 1.0 at 230nm), to a solution of benzene in cyclohexane ($1.0 \times 10^{-2} \text{ mol dm}^{-3}$). As the concentration of the tertiary amine was steadily increased, the emission was red-shifted to 295nm (characteristic of fluorescence from the amine) and increased in intensity. Once again the optical densities of the solutions of benzene and N-methyldiethylamine showed considerable variation with the amount of amine added, which made it difficult to rationalise the results in terms of sensitisation of the amine emission by energy transfer from singlet excited state benzene. We considered therefore that although the amine fluorescence could have been enhanced by a sensitisation process, direct excitation of the chromophore was also responsible for the observed intensity increase when using 230nm excitation in cyclohexane solution.

3.7. SENSITISATION EXPERIMENTS IN TETRAHYDROFURAN SOLUTION.

3.7.(1). Introduction.

The results of both our quenching and sensitisation experiments with N-methyl-1-aza-4-oxacyclohexane (N-methylmorpholine), indicated that there was little if any tendency for the amine to undergo energy transfer processes with singlet excited state benzene, in cyclohexane solution at

20°C. This we attributed to the relative energy of the N-methyl-1-aza-4-oxacyclohexane singlet excited state being higher than that of the benzene, making energy transfer from the aromatic hydrocarbon energetically unfavourable under these experimental conditions.

We therefore decided, to carry out a limited investigation into the use of tetrahydrofuran as a solvent for our sensitisation experiments, anticipating that solvation of the amine by the more polar tetrahydrofuran, would reduce the energy of its singlet excited state, relative to that of benzene and thereby possibly facilitate energy transfer to the amine. Experiments were carried out according to the procedure detailed in Section 3.3., using tetrahydrofuran solutions of benzene (OD 1.0 at 265nm) and the tertiary amine ($1.0 \times 10^{-1} \text{ moldm}^{-3}$). The following amine systems were studied, (1) N-methyl-1-aza-4-oxacyclohexane (2) N-methylazacyclohexane (3) triethylamine.

3.7.(2). Results and Discussion.

(1) N-methyl-1-aza-4-oxacyclohexane - with this amine, we initially carried out a quenching experiment in which the concentration of amine was varied in the range 2.0×10^{-3} to $3.0 \times 10^{-2} \text{ moldm}^{-3}$, to determine whether or not any interaction occurred between the amine and benzene in its excited singlet state, in tetrahydrofuran solution. In contrast to the results obtained in cyclohexane solution, the addition of the amine was found to cause a gradual diminution in the intensity of the benzenoid fluorescence, as the concentration of the amine was increased. Furthermore, the quenching of the fluorescence from the aromatic hydrocarbon, was accompanied by the appearance of a broad, poorly resolved emission at longer wavelengths (to the red of $\sim 320\text{nm}$).

The diffuse nature of the emission however, made it difficult to determine the wavelength maximum of this new band accurately. It appeared therefore that in tetrahydrofuran solution, energy transfer occurred between the singlet excited state benzene molecule and the ground state amine molecule, during the quenching of the aromatic hydrocarbon fluorescence, leading to sensitisation of the emission from the amine. The possibility also arose that the long wavelength emission might be due to the formation of a fluorescent intermolecular exciplex between the two chromophores. From a Stern-Volmer plot of (I_0/I) versus [amine], the rate constant (k_q) for the quenching of benzene fluorescence by N-methyl-1-aza-4-oxacyclohexane, in tetrahydrofuran solution was evaluated. (The lifetime of singlet excited state benzene was taken as; $\tau = 5.7 \times 10^{-9}$ s). The magnitude of k_q in aerated solution was found to be $k_q = 8.12 \times 10^9 \text{ mol}^{-1}\text{dm}^3\text{s}^{-1}$, indicating that the quenching occurred at a rate approaching the diffusion controlled limit.

In the sensitisation experiment, benzene was added to a solution of N-methyl-1-aza-4-oxacyclohexane in tetrahydrofuran ($1.0 \times 10^{-2} \text{ mol dm}^{-3}$) over the concentration range 8.0×10^{-4} to $8.0 \times 10^{-3} \text{ mol dm}^{-3}$. A characteristic benzenoid emission was observed in the fluorescence spectra, which increased in intensity with the concentration of the aromatic hydrocarbon present, but this was accompanied by the appearance of a broad structureless band which maximised at around 350-360nm. Based on the results of our work, using very high concentrations of benzene in cyclohexane solution and a knowledge of the emissive characteristics of the tertiary aliphatic amines in tetrahydrofuran solution (which will be dealt with in Chapter (4)), we attributed this long

wavelength emission, to fluorescence from a benzene-amine intermolecular exciplex, which was solvated by tetrahydrofuran.

(2) N-methylazacyclohexane - a representative selection of the fluorescence spectra obtained from tetrahydrofuran solutions of N-methylazacyclohexane (OD 0.1 at 265nm), containing varying amounts of benzene (8.0×10^{-4} to 1.6×10^{-2} moldm $^{-3}$) are shown in Figure 3.(17). The addition of benzene had clearly given rise to a characteristic benzenoid emission at shorter wavelengths, (maxima at 278 and 286nm) but more importantly had resulted in the appearance of a broad relatively structureless emission maximising to the red of the amine. Increasing the concentration of benzene present, not only increased the intensity of the fluorescence from both the excited state species, but also caused the appearance of some asymmetry in the broad emission. At a benzene concentration of $\sim 1.5 \times 10^{-2}$ moldm $^{-3}$, the emission clearly maximised at 355nm, however, this was accompanied by a shoulder on the emission band at around 335nm. We interpreted this dual emission as arising from both the excited state N-methylazacyclohexane ($\lambda_{\text{max}} \sim 345\text{nm}$) and an intermolecular exciplex between benzene and the amine ($\lambda_{\text{max}} \sim 355\text{nm}$). As in the previous example, changing the solvent system from cyclohexane to the more polar tetrahydrofuran, appeared to have brought about a sufficient lowering in the energy of the excited singlet state of the amine, relative to that of benzene, that energy transfer from the aromatic hydrocarbon to the ground state amine molecule was now energetically favourable. The intermediacy of an intermolecular fluorescent exciplex in this energy transfer process was not established however.

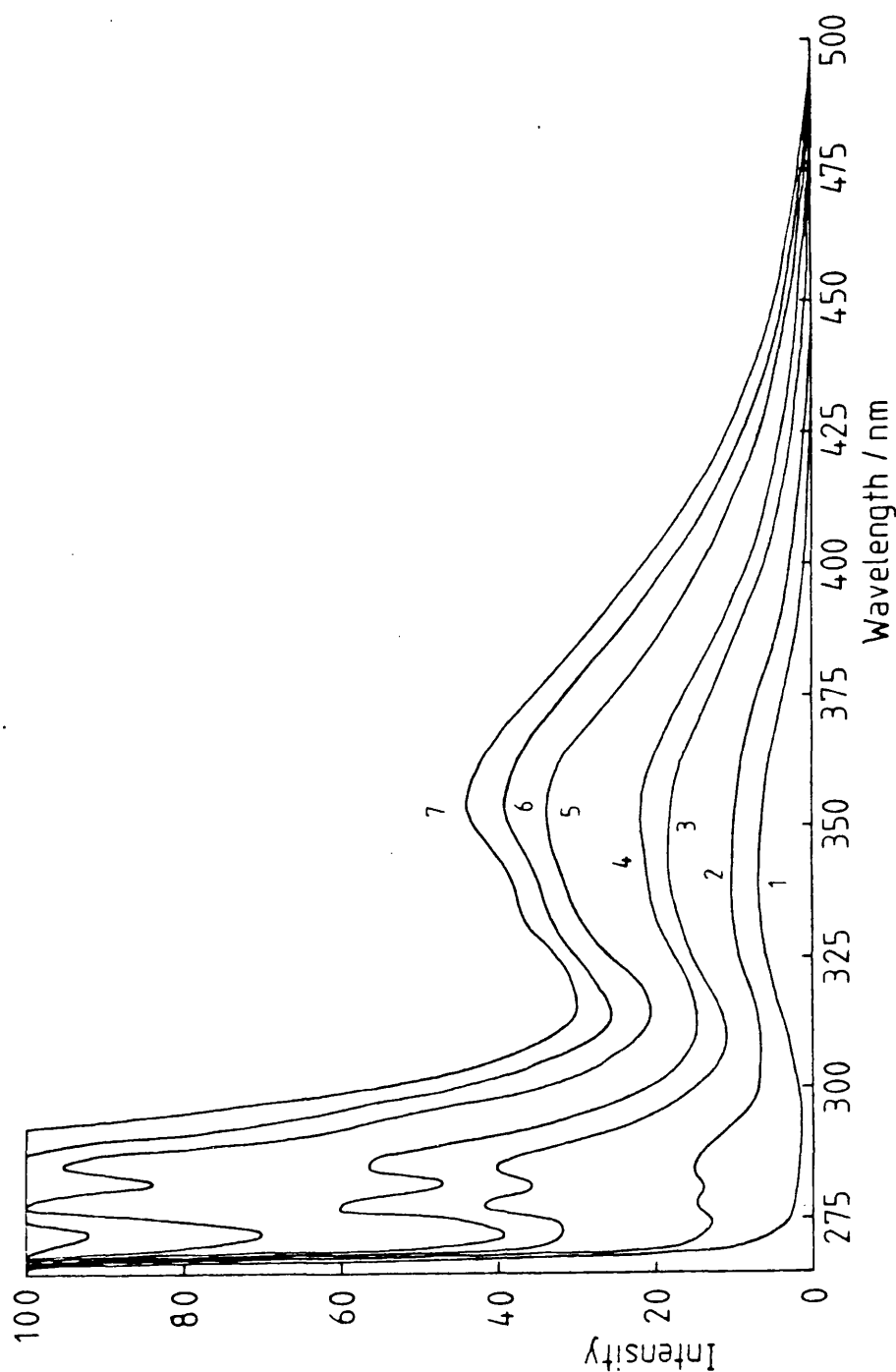


FIGURE 3.(17). Fluorescence Spectra Obtained from THF Solutions of $\text{MeN}(\text{CH}_2)_5$ ($1.0 \times 10^{-2}\text{M}$) + Varying Amounts of Benzene Solution (OD 1.0 at 265nm). (1) 0.0M, (2) $8.0 \times 10^{-4}\text{M}$, (3) $2.4 \times 10^{-3}\text{M}$, (4) $4.0 \times 10^{-3}\text{M}$, (5) $8.0 \times 10^{-3}\text{M}$, (6) $1.2 \times 10^{-2}\text{M}$, (7) $1.6 \times 10^{-2}\text{M}$.

(3) Triethylamine - due to the considerable absorption of triethylamine at the excitation wavelength of 265nm, the amine concentration was reduced to $2.5 \times 10^{-3} \text{ moldm}^{-3}$ in this sensitisation experiment. The addition of benzene (2.0×10^{-3} to $1.2 \times 10^{-2} \text{ moldm}^{-3}$) brought about a slight enhancement of the emission from the amine at 335nm and led to a substantial amount of fluorescence from the aromatic hydrocarbon.

In the earlier work of Leismann and Mattay⁽¹⁶⁵⁾ studying the excited state interaction of benzene with triethylamine in cyclohexane solution, the authors had observed the formation of an intermolecular exciplex at high concentrations of benzene (0.56 moldm^{-3}), a finding which we confirmed in our own experiments using benzene at concentrations up to 2.8 moldm^{-3} ⁽⁵⁶⁾. We attributed a red-shift in the exciplex emission on increasing the concentration of benzene present, to the gradual solvation of the benzene-triethylamine exciplex by the small polar benzene molecule. We therefore decided to re-examine the interaction of triethylamine ($1.0 \times 10^{-2} \text{ moldm}^{-3}$) with benzene (2.0×10^{-3} to $1.6 \times 10^{-2} \text{ moldm}^{-3}$) in cyclohexane solution, but this time in the presence of tetrahydrofuran (137 μ l; 0.56 moldm^{-3}), another small polar solvating molecule. Although a detailed analysis of the results was difficult, there had clearly been a change in the fluorescence spectrum upon the addition of the tetrahydrofuran, as shown in Figure 3.(18)., with a slight increase in the intensity of the fluorescence at longer wavelengths.

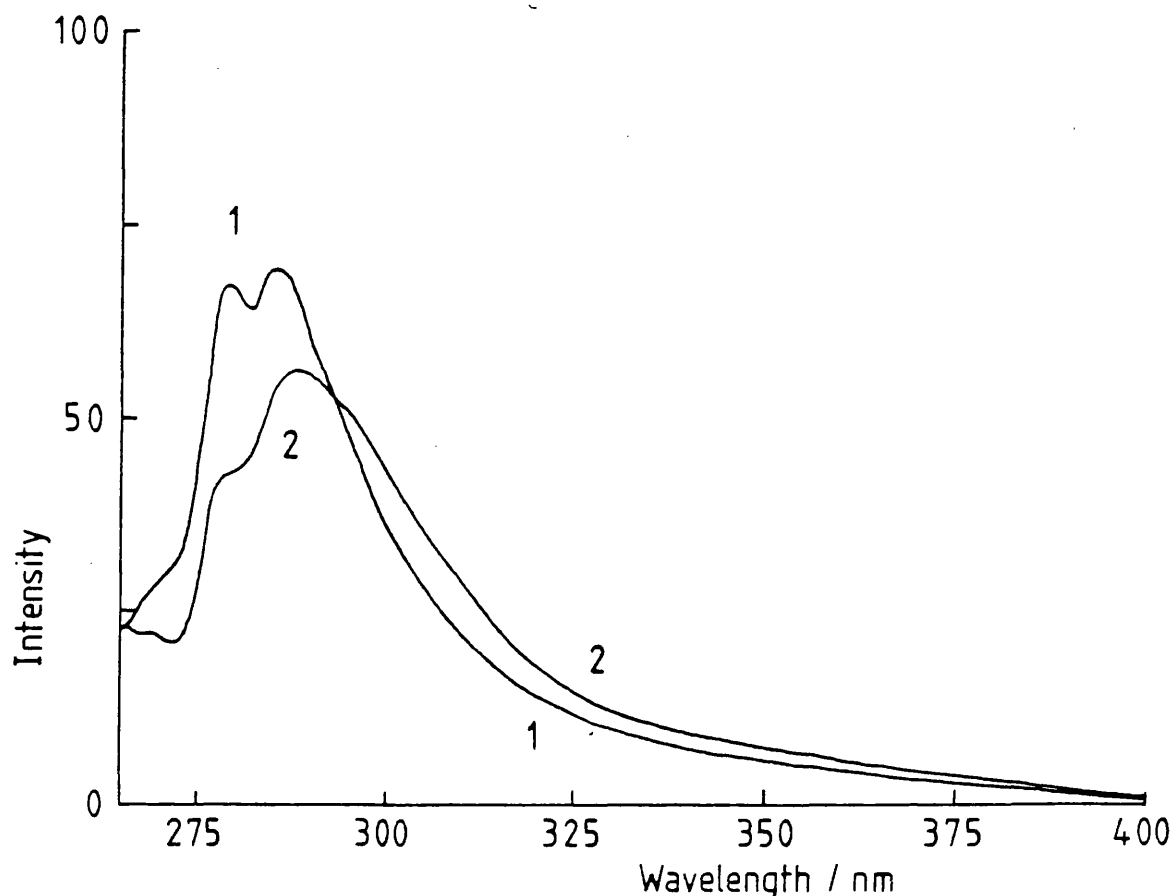


FIGURE 3.(18). Fluorescence Spectrum of an Aerated Cyclohexane Solution of Triethylamine ($1.0 \times 10^{-2} \text{ moldm}^{-3}$) and Benzene ($8.0 \times 10^{-3} \text{ moldm}^{-3}$) Before and After the Addition of Tetrahydrofuran. (1) 0.0M, (2) 137 μ l; 0.56M.

3.8. THE MECHANISM OF ENERGY TRANSFER.

In the phenomenon of electronic energy transfer, an excited state donor molecule (D^*), collapses to its ground state with the simultaneous transfer of its electronic excitation energy to an acceptor molecule (A). Whilst in general, the energy transfer (in this sensitisation process) occurs to a ground state species it is also possible for the acceptor species itself to be in an excited state, as for example in triplet-triplet annihilation which was dealt with in Chapter (1) Section 1.1.(3).2. The energy transfer process is characterised by the quenching of the emission associated with D^* and its replacement by an emission due to A^* , but in

the special case where the donor and acceptor species are identical, the term energy migration is used. The principle mechanisms of electronic energy transfer will be discussed in more detail in the following sections.

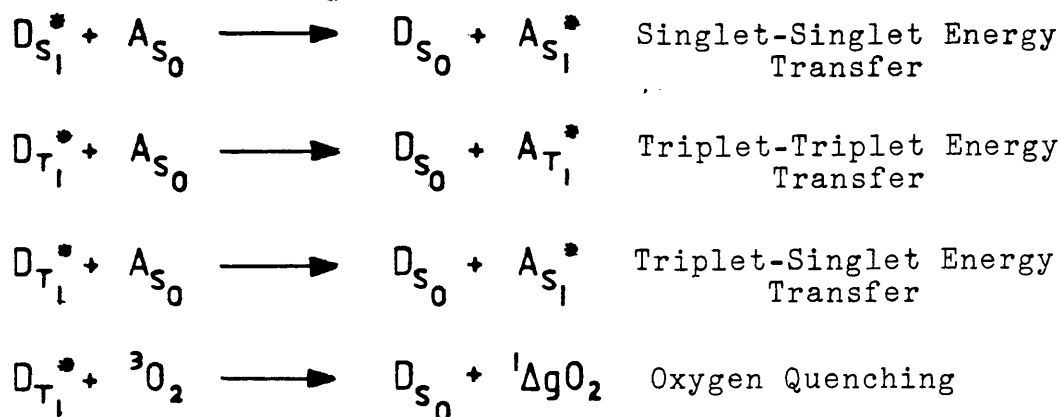
3.8.(1). Radiative Energy Transfer.

This process depends upon the acceptor molecule absorbing photons emitted by the donor molecule and consequently the rate of energy transfer will be affected by a number of factors, (i) the quantum efficiency of the donor emission, (ii) the number of acceptor molecules in the path of the emitted photon, (iii) the absorbing power of the acceptor and (iv) the extent of overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor. Due to the poor overlap of the benzene emission spectrum and the absorption of the tertiary alicyclic amines, it seems reasonable to discount this mechanism of energy transfer in our experiments.

3.8.(2). Non-Radiative Energy Transfer.

As a result of restrictions imposed upon the relative multiplicities of the initial and final excited species involved in the electronic energy transfer process, the only common transitions studied in organic photochemistry, are those shown in Scheme 3.(5). (In our sensitisation experiments, we were only concerned with the singlet-singlet mode of energy transfer between benzene and the tertiary alicyclic amines, in cyclohexane solution).

If we now consider an interaction between D^* and A, then the time-dependent perturbation theory, reveals that the effect of the interaction will be to cause the system ($D^* + A$) to change into the iso-energetic system ($D + A^*$) and vice versa.



SCHEME 3.(5). Common Electronic Energy Transfer Transitions.

In other words, the perturbation induces coupled radiationless transitions in both D and A, so that the excitation energy is shuttled backwards and forwards between D and A. The rate of energy transfer k_{ET} is related to the strength of the interaction between the two species, and provided $k_{ET} < k_{VR}$, the rate constant for vibrational relaxation, then the energy transfer process becomes unidirectional. The reason for this, is that under these conditions D^* will undergo energy transfer from its bottom vibrational level to produce A^* , and once formed, A^* will rapidly collapse to its lowest vibrational level, destroying the degeneracy of $(D^* + A)$ and $(D + A^*)$ and favouring the forward transfer of excitation energy. The situation is shown pictorially in Figure 3.(19). The condition for irreversible energy transfer is also detailed in Figure 3.(19)., namely that the $0 \rightarrow 0$ excitation energy of the donor D (E_D) is significantly greater than that of the acceptor A (E_A). In the case of organic molecules, the degeneracy of the two systems $(D^* + A)$ and $(D + A^*)$ is easily achieved due to the availability of a multitude of both vibrational and rotational sub-levels. A measure of the number of coupled iso-energetic donor and acceptor transitions can be estimated from the overlap of the emission spectrum of the donor and the absorption spectrum

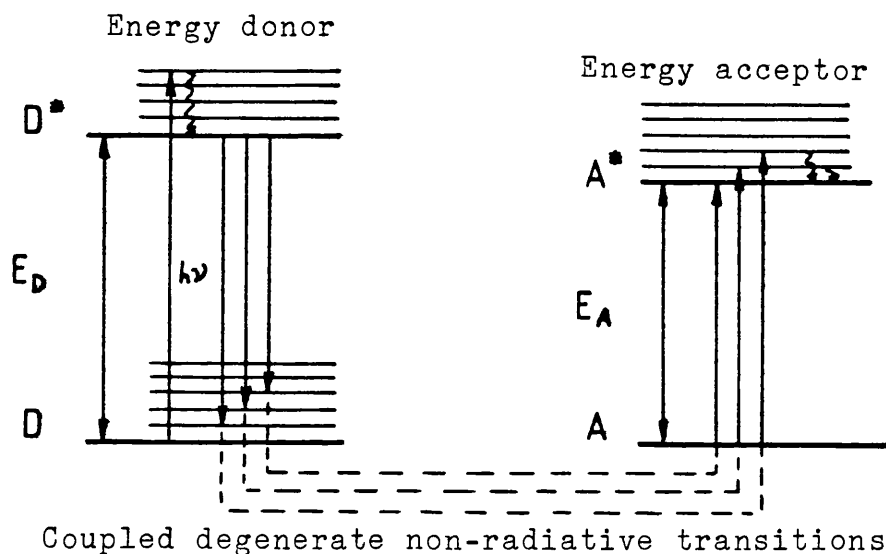


FIGURE 3.(19). Energy Level Scheme, Showing the Coupling of Iso-energetic Donor and Acceptor Transitions Necessary for Non-radiative Energy Transfer.

of the acceptor. It should be pointed out at this stage, that although the rates of both radiative and non-radiative energy transfer mechanisms depend upon this degree of overlap, in the latter process, it is necessary for a physical interaction to take place between D^* and A , prior to the emission. The two most important types of interaction which occur are either (a) electrostatic (or Coulombic) or (b) electron exchange interactions, both of which can independently induce energy transfer.

In the case of Coulombic interaction, the contribution of the normally dominant dipole-dipole term, has been treated by Förster, who proposed the existence of a critical transfer distance (R_0) between D^* and A at which energy transfer to A and internal deactivation of D^* were equally possible. Energy transfer by dipole-dipole interactions can be significant even at distances of $100\text{\AA}$ and the rate constants (k_{ET}) have been shown to be independent of solvent viscosity and can be much larger than k_{diff} . The only transfer processes

allowed by the Coulombic interaction are those in which there is no change in the spin of either of the components. Thus singlet-singlet energy transfer is fully allowed.

The electron exchange interaction has been analysed in detail by Dexter⁽¹⁶⁸⁾. Since the process involves the interchange of electrons between D* and A, energy transfer by this mechanism is a short-range phenomenon, necessitating orbital overlap of the two components. The energy transfer process can be given by the expression,



and involves the intervention of a bimolecular intermediate which could be either an exciplex or a collision complex.

By analogy to the behaviour of the closely related intramolecular systems, which readily formed fluorescent exciplexes (as discussed in Chapter (2)), we believe that the interaction of the excited state aromatic hydrocarbon with the amine, involved the initial formation of a non-fluorescent collision or encounter complex. In non-polar solvents like cyclohexane, subsequent breakdown of this complex enabled the excitation energy to be channelled into the amine, when the relative energy levels were appropriate, as for example with N-methylazacyclopentane, giving sensitised amino fluorescence. It appeared however, that the use of more polar media such as THF, or high concentrations of benzene such that the benzene also behaved as a small polar solvating molecule, favoured the conversion of the encounter complex into the fluorescent exciplex.

CHAPTER FOUR

The Photophysical Properties of Saturated Tertiary Alicyclic Amines.

4.1. INTRODUCTION.

A survey of the scientific literature over the last ten years or so, revealed that surprisingly little attention had been paid to the systematic investigation of the photo-physical properties of tertiary saturated aliphatic amines, particularly the alicyclic systems. It appeared that comparatively few amines had been studied and a large proportion of the work carried out in this area, had been directed at the behaviour of the excited state amines in the vapour phase.

Halpern and his co-workers have, over a number of years, quite extensively studied the behaviour of the cage-like and highly symmetrical amines, 1-azabicyclo-[2,2,2]-octane (ABCO) and 1,4-diazabicyclo-[2,2,2]-octane (DABCO). They found that the gas phase electronic absorption spectra of the compounds showed two strong bands in the region 165-250nm, each with well resolved vibrational structure⁽¹⁶⁹⁾. A detailed vibrational analysis of these bands indicated a substantial change in the equilibrium positions of the nuclei in the excited states, relative to those in the ground state, and for ABCO, the most prominent vibrational mode in the excited state corresponded to an approach to planarity of the nitrogen bearing end of the molecule. The authors assigned the first and second strong electronic absorption bands in the spectra of ABCO and DABCO to $n \rightarrow 3p_z$ and $n \rightarrow 4p_z$ Rydberg transitions respectively.

Further to their initial studies on the gas phase emission of DABCO⁽¹⁷⁰⁾, which gave a broad band in the region 285-370nm with a lifetime of 1040ns and high quantum yield of ~ 0.9 attributed to fluorescence, Halpern and Danziger⁽¹⁷¹⁾ investigated the photophysical properties of DABCO and its

closely related analogue 1,4-diaza-2-methylbicyclo-[2,2,2]-octane (2-methyl-DABCO), in the vapour phase and in n-hexane solution at 23°C. Data obtained from the vapour phase absorption and emission spectra of both diamines indicated that the addition of the methyl group had only a minimal effect upon the coupling of the lone pair electrons on the two nitrogen atoms, a conclusion confirmed by photoelectron spectroscopy studies. However there did appear to be a significant configurational change in 2-methyl-DABCO, such that the S_1 and S_0 geometries were more alike and methylation was found to appreciably enhance both the radiative and non-radiative relaxation, particularly the latter, with higher rate constants in n-hexane solution than in the vapour phase.

The ground states of the saturated tertiary amines are expected, in the absence of any over-riding steric interference, to involve tetrahedral bonding about the nitrogen atom, as seen for example in ABCO. However, by analogy to the behaviour of ammonia which has been spectroscopically demonstrated to be planar in the upper excited states^(172,173), it is presumed that in the absence of steric and structural constraints by the three alkyl groups, the configurationally relaxed excited singlet states of simple saturated tertiary amines are planar. Bearing this in mind therefore, Halpern⁽¹⁷⁴⁾ investigated the photophysical behaviour of the cage-amine 1-azabicyclo-[3,3,3]-undecane (ABCU), in which the three trimethylene bridges appear to constrain the nitrogen to a more planar configuration with respect to the α -carbon atoms. (X-ray diffraction studies on ABCU.HCl have shown that the C-N-C bond angles range from 115.0 to 115.9°⁽¹⁷⁵⁾). Above 200nm, four distinct electronic transitions were observed in the absorption spectrum, which were assigned to $n \rightarrow \text{Rydberg}$.

transitions. The shape of these transitions suggested that the upper state geometry of the ABCU was similar to that of the ground state, unlike the situation with ABCO, which was consistent with what was known about the ground state geometries of the two amines. The lowering of the transition energies of the ABCU relative to ABCO was explained in terms of the more planar bonding configuration of the nitrogen atom in ABCU, resulting in a larger contribution of atomic p character to the non-bonding orbital, with its resultant destabilisation. The fluorescence spectra of both amines resembled their respective absorption spectra, showing vibrational structure in the emissions.

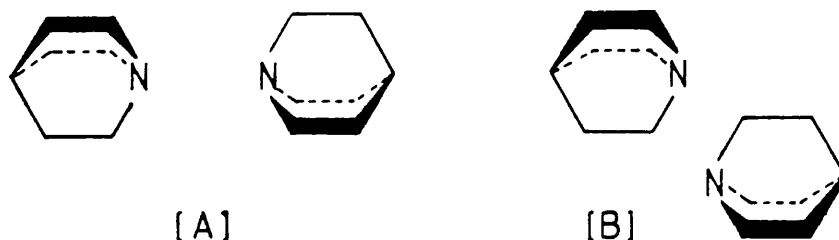
During the course of their investigations with ABCO in n-hexane solution at 24°C, Halpern and Maratos⁽¹⁷⁶⁾ noted a concentration dependence exhibited by the fluorescence spectra of the amine. They found that as the concentration of ABCO was increased from $5.5 \times 10^{-5} \text{ mol dm}^{-3}$, which gave ABCO monomer emission with λ_{max} at 273nm, to $5.5 \times 10^{-2} \text{ mol dm}^{-3}$, the monomer emission virtually disappeared accompanied by the emergence of a broad structureless band with λ_{max} at 376nm. It was proposed that the new emission, whose net quantum efficiency increased with increasing concentration of amine, was due to fluorescence from the ABCO excimer. Previously, virtually all studies on excimers had involved the use of aromatic hydrocarbons and their derivatives. Further evidence for the formation of an excimer was provided by the time dependence of the 376nm emission band, which showed a gradual build up after the excitation flash, indicative of a dynamic mechanism for the production of the species. Both the spectral and temporal properties mentioned were also observed for ABCO in the vapour phase, but the addition of

a small amount of an inert gas (n-hexane or cyclohexane) was required to observe the broad structureless excimer fluorescence. The formation of fluorescent excimers by saturated amines in the vapour phase has subsequently been analysed in kinetic terms⁽¹⁷⁷⁾, using the normal monomer/excimer kinetic scheme, but with the inclusion of an additional term to account for the quenching of the excimer by a ground state amine molecule. Analysis of the decay data, indicated that quenching of the excited monomer by the ground state amine was inefficient. The authors found that the addition of n-hexane vapour up to an overpressure of 90 Torr, caused a significant enhancement of the excimer emission which was interpreted in terms of vibrational relaxation (and stabilisation) within the monomer and excimer manifolds. The decrease in the excimer emission intensity at pressures greater than 90 Torr, was attributed to pressure effects on the excited state ABCO monomer. Variations in the emission intensities and decay data, implied that collisions between excited state ABCO and n-hexane molecules were effective in inducing both the radiative and non-radiative transitions.

The formation of intermolecular saturated amine excimers in n-hexane solution, has also been the subject of both a kinetic and thermodynamic treatment⁽¹⁷⁸⁾. Using ABCO and 1-azaadamantane (1-AA), the rate constants for excimer formation were found to be diffusion controlled, and the excimers once formed were quite tightly bound. The photophysical properties of non-excimer forming amines were compared with ABCO and 1-AA, and indicated that the radiative rate constants k_{f_M} , for the non-rigid amines like triethylamine and N-methylazacyclohexane were higher ($2.0 \times 10^7 \text{ s}^{-1}$) than

for ABCO and 1-AA ($5.9 \times 10^6 \text{ s}^{-1}$ and $1.1 \times 10^6 \text{ s}^{-1}$, respectively). It was suggested that this result may be a consequence of the inability of the structurally restricted cage amines to achieve a planar configuration at the nitrogen atom in their relaxed excited states.

Attempts have been made to rationalise the stability of these excimers using the exciton resonance (excitation dipole-dipole) and charge resonance (electrostatic) models, but neither approach appeared to be adequate either in explaining the binding energies or the structural specificity in excimer formation with the saturated amines. Halpern proposed two configurations for the excimers, one in which the amines were arranged 'head to head' (A), with the bridge systems staggered and the other arranged so that one of the N-C bonds of an amine was antiparallel to an N-C bond in its partner (B), as being most plausible. Based upon the structure shown in (A), several INDO calculations have been



carried out on a series of amine pairs, to try and elucidate which structural parameters were important in affecting the excimer stabilisation. Using the amine radical cation ($\text{N}^{\cdot+}$) for the excited amine, which represents the limit of excitation for Rydberg states, calculations indicated that a neutral ABCO molecule derived substantial stabilisation in association with the ABCO radical cation. A series of analogous calculations were carried out on the interaction of triethylamine with its radical cation, varying the con-

figuration of the two species. It was found that the greatest stabilisation was afforded when the two species remained pyramidal, and suggested that it was the ability of the amine to avoid going planar in the excited state which determined the excimer stability. The other suggestion made by Halpern concerning the excimers was that it was necessary for each of the three α, β C-C bonds to be directed parallel to the nitrogen lone pair orbital. This sort of orbital arrangement has been proposed for the 'through bond' ground state coupling in DABCO.

Fluorescence measurements in n-hexane solution, on several saturated flexible amines, such as triethylamine (TEA), tri-n-octylamine (TOA) and N-methylazacyclohexane have shown that the fluorescence intensity (I_f) increases with increase in temperature⁽¹⁷⁹⁾. Dimethylethylamine for example, undergoing an ~ 75 fold increase in I_f between -100 and 100°C . The authors rationalised these results in terms of an activated configurational change from the initially formed (non-fluorescent) state to a relaxed (fluorescent) state in these compounds. The involvement of a non-fluorescent excimer was ruled out because the thermal enhancement of the fluorescence was still observed at low concentrations. The invariance of I_f with temperature for the bicycloalkane amines, has been attributed to the rigidity of the nitrogen chromophore, hindering the attainment of the planar configuration in the relaxed excited state.

The fluorescence properties of trimethylamine (TMA) have been studied in the vapour phase by Matsumi et al.^(180,181) and more recently those of a series of simple tertiary saturated aliphatic amines, have been investigated again in the vapour phase, with respect to the effect of varying the

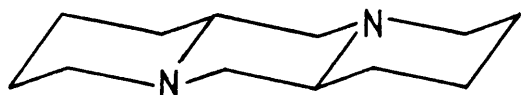
excitation wavelength⁽¹⁸²⁾. Phillips and his co-workers found that at low pressures, in the isolated molecule limit, the fluorescence spectra of the amines did not vary significantly with excitation wavelength. In all cases however, the fluorescence quantum yields (ϕ_f) and lifetimes (τ_f) were found to decline in magnitude as the excitation energy was increased (moving to shorter wavelengths). The addition of cyclohexane vapour (66 Torr) was found to offset the decline in the absolute quantum yields of fluorescence quite considerably. Further aspects of this work are detailed in Section 4.4.

One of the most relevant pieces of work to our own spectroscopic studies was undertaken by Halpern and Gartman (183) when they investigated the gas phase photophysical properties of the diamine, N,N'-dimethyl-1,4-diazacyclohexane (N,N'-dimethylpiperazine) in comparison with those of selected monoamines. N,N'-dimethyl-1,4-diazacyclohexane, has a lower degree of constraint than DABCO and their study was primarily aimed at determining the importance of structural rigidity on the degree of lone pair interaction in such a system. On the basis of the u/v absorption spectrum, which closely resembled that of the monoamines, N-methylazacyclohexane, triethylamine and N-methyl-1-aza-4-oxacyclohexane (N-methylmorpholine), maximising at around 205nm and photoelectron spectral data, the diamine in the ground state was considered to be a non-interacting dimer of trimethylamine.

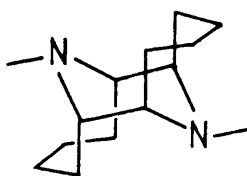
The fluorescence spectrum of N,N'-dimethyl-1,4-diazacyclohexane (DMDACH) however, was considerably red-shifted relative to the monoamines with a wavelength maximum at 313nm. Furthermore, the very long lifetime of DMDACH (770ns) relative to say triethylamine (45ns) and the lower fluores-

cence quantum yield 0.23 and 0.97 respectively, implied that there was a difference in the relaxed lowest electronically excited state of DMDACH relative to the monoamines. It appeared that in DMDACH, there was a low lying fluorescent excited state, which was not populated directly by a radiative transition from the ground state. The lower radiative rate constant for the diamine was therefore interpreted in terms of a need for the diamine to undergo both an electronic and a structural reorganisation in attaining the lowest excited state. Analysis of the decay data indicated the presence of two emitting states for DMDACH, with different radiative rate constants, the fast component was attributed to emission from the Franck-Condon (initially formed) state and the long component to emission from the conformationally (and electronically) relaxed excited state. The authors also proposed that at low total pressures, the two states were able to undergo interconversion.

More recently, Halpern and his co-workers⁽¹⁸⁴⁾, have extended their studies on DMDACH, by considering the photophysical properties of two structurally constrained N,N'-bis(alkylated)-1,4-diazacyclohexane derivatives shown below (34) and (35), and assessing the degree of delocalisation



[34]



[35]

of the excitation energy between the two nitrogen atom centres. On the basis of the photoelectron spectrum of

DMDACH, which was consistent with a diequatorial conformation of the N-methyl groups, and the u/v absorption spectra of the N,N'-bis-(alkylated)-1,4-diazacyclohexane derivatives, it was concluded that in n-hexane solution, an interaction between the nitrogen non-bonding orbitals was virtually absent in the ground state, the spectra all resembling those of tertiary mono-functional amines. The fluorescence spectrum of 12,14-diazacyclodecahydroanthracene (34) was found to closely resemble that of DMDACH, indicating that when the diamino ring was able to retain its cyclohexane structure, the excited state was excimeric in nature, with the excitation energy delocalised between the two nitrogen atoms. The fluorescence spectrum of (35) however, closely resembled that of an N-methylated monoamine, which suggested a considerable reduction in the degree of N-N coupling in the excited state, relative to DMDACH. The authors explained this result in terms of the twisted nature of the cyclohexane ring in this compound, distorting the orbital orientations necessary for the through-bond derived excited state coupling of the nitrogen atoms.

Another area which has received some attention in recent years, has been the effect of solvent upon both the spectroscopic and photophysical properties of the saturated tertiary aliphatic amines. Apart from the non-polar saturated hydrocarbon solvents like n-hexane, in which the saturated amines are highly fluorescent, it has been established that the only other class of common solvents in which the amines retain a reasonably high fluorescence quantum efficiency is the saturated ethers, like diethylether and tetrahydrofuran. As first noted by Muto et al.⁽¹⁸⁵⁾ using DABCO and more recently Van der Auweraer et al.⁽¹⁸⁶⁾ using triethylamine,

the fluorescence spectra of the amines are considerably red-shifted when ethers are used as solvents relative to the hydrocarbon solvents and the emission was substantially broadened. This and subsequent work by Halpern⁽¹⁸⁷⁾ using the simple monoamine diethylmethylaniline (DEMA) has established that the red-shift was accompanied by a diminution of the quantum yields and an increase in the fluorescence lifetimes. Working with model amino-ethers, Halpern established on the basis of their fluorescence properties, that a 1:1 amine-ether exciplex could not be invoked to explain the behaviour of the tertiary amines in the saturated ether solvent media. It was concluded that the observed wavelength shift was probably due to the ability of the ether solvents, with their high dielectric constants (relative to the hydrocarbons) to stabilise the Rydberg (or Rydberg-like) lowest excited state of the amine as proposed by Muto and his co-workers⁽¹⁸⁵⁾.

4.2. ULTRA-VIOLET ABSORPTION SPECTRA.

During our investigations into the excited state interactions of benzene with a series of N-methylated azacycloalkanes and selected acyclic tertiary amines, it was evident that there was a very appreciable variation in the ultraviolet absorption of the amines. Cyclohexane solutions of the tertiary amines ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $1.0 \times 10^{-2} \text{ mol dm}^{-3}$) were therefore prepared, to study this change in greater detail. The u/v absorption spectra of the tertiary alicyclic amines used and also those of triethylamine and N-methyldiethylamine are shown in Figure 4.(1). The molar extinction coefficients (ϵ) of the amines at 240, 250 and 265nm are given in Table 4.(1). The spectra were calibrated using

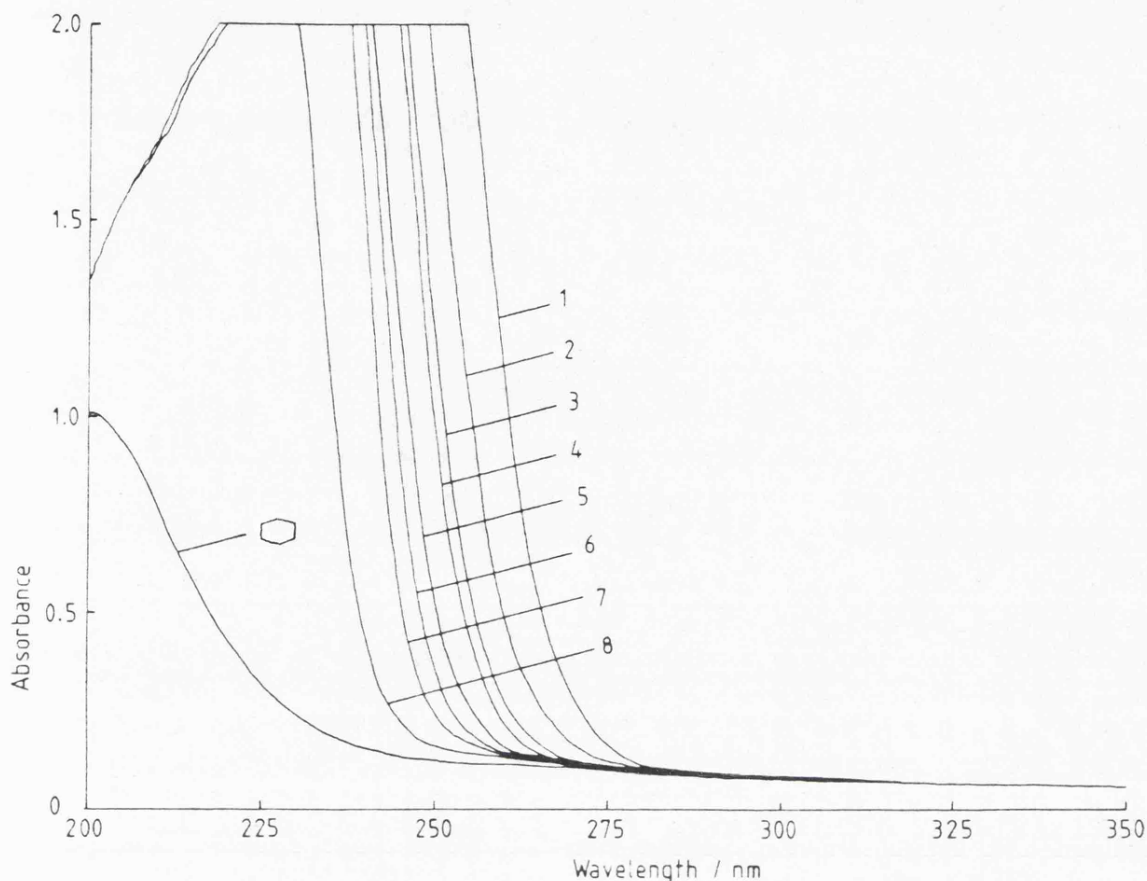


FIGURE 4.(1). U/V Absorption Spectra of Aerated Cyclohexane Solutions of Tertiary Alicyclic and Acyclic Saturated Amines ($1.0 \times 10^{-2} \text{ moldm}^{-3}$)
Recorded at 20°C. (1) MeN(CH₂)₇, (2) MeN(CH₂)₆, (3) MeN(CH₂)₄, (4) NEt₃, (5) MeNEt₂, (6) MeN(CH₂)₅, (7) MeN(CH₂)₃NMe, (8) MeN(CH₂)₅O.

Holmium Oxide glass standard, giving characteristic absorption peaks at wavelengths of 279.39, 287.5 and 360.9nm.

Overall, the intensity of absorption of the tertiary alicyclic amines in the wavelength range 200-280nm was found to decrease with reduction in the ring size of the N-methylazacycloalkane, the exception to this trend being N-methylazacyclohexane, whose absorption was considerably weaker than that of the five membered ring derivative. As can clearly be seen from the magnitude of the molar extinction coefficients at 240nm for example, the absorption of N-methyl-

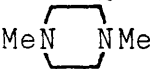
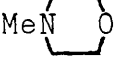
AMINE	ϵ (mol ⁻¹ dm ³ cm ⁻¹)		
	240nm	250nm	265nm
MeN(CH ₂) ₇	1025	360	42
MeN(CH ₂) ₆	520	165	13
MeN(CH ₂) ₅	160	24	4
MeN(CH ₂) ₄	350	88	5.5
NEt ₃	400	84	3
MeNEt ₂	171	32	2
	120	13	2
	28	4	1.5

TABLE 4.(1). Molar Extinction Coefficients (ϵ) of a Series of Tertiary Alicyclic Amines and Selected Acyclic Amines in Aerated Cyclohexane Solution, at Wavelengths of 240, 250 and 265nm.

azacyclooctane was substantially stronger than that of the other amines investigated. The variations in the u/v absorption of the tertiary amines with structure, also supported the trends shown both in our studies into intramolecular fluorescent exciplex formation and our intermolecular quenching and sensitisation experiments using aromatic hydrocarbon-amine systems. With particular reference to the fluorescence properties of the 1-naphthylethyl- derivatives in cyclohexane solution, (detailed in Chapter (2) Section 2.2.), we observed a marked increase in the quantum yield of intramolecular fluorescent exciplex formation (ϕ_{fE}), as the amine unit was changed from the azacyclopentyl- ($\phi_{fE} = 0.25$) to the azacyclotridecyl group ($\phi_{fE} = 0.42$), the exception to this trend being provided by the azacyclohexyl- system ($\phi_{fE} = 0.23$). Likewise, when we examined the intermolecular excited state interactions between benzene and the tertiary

aliphatic amines (see Chapter (3) Section 3.3.) we found that the sensitisation of amine fluorescence and the formation of an intermolecular exciplex was most pronounced for the azacyclo-pentyl, -heptyl and -octyl derivatives, along with the related molecule triethylamine. With both N-methylazacyclohexane and N-methyl-1-aza-4-oxacyclohexane, we found no evidence at all for the sensitisation of the amino emission, nor was an exciplex formed between either of the amines and the excited aromatic hydrocarbon.

In agreement with the findings of Halpern and his co-workers, studying the photophysics of N,N'-dimethyl-1,4-diazacyclohexane^(183,184) and DABCO⁽¹⁷¹⁾ in both the vapour phase and in n-hexane solution at 20°C, we had no evidence from the u/v absorption spectra of N,N'-dimethyl-1,4-diazacyclohexane, to suggest that an electronic interaction occurred between the two nitrogen atoms in the ground state species. Instead, the absorption spectrum closely resembled that of the other monoamines studied, appearing to maximise at around 200nm.

4.3. FLUORESCENCE MEASUREMENTS.

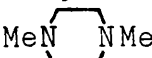
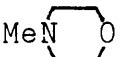
4.3.(1). Experimental.

The thorough investigations of Halpern et al.^(170,176,178,183) into the photophysical properties of saturated tertiary aliphatic amines, had demonstrated that these compounds exhibited fluorescence both in the gaseous phase and in non-polar solvents like n-hexane. The emission in n-hexane solution usually being broad and structureless in appearance. By analogy therefore, we primarily carried out our investigations into the fluorescence properties of the N-methylated azacycloalkanes in cyclohexane solutions (OD 0.1 at exci-

tation wavelengths of 240, 250 and 265nm). However, since the tertiary acyclic amines had also been shown to fluoresce in tetrahydrofuran solution⁽¹⁸⁵⁾, with the emission being substantially red-shifted from that observed in cyclohexane solution, we also looked at the behaviour of the tertiary alicyclic amines in both tetrahydrofuran solution (OD 0.1 at 250nm) and in benzene solution (OD 0.1 at 290nm). Quantum yields of fluorescence were evaluated relative to that of toluene in degassed cyclohexane solution ($\phi_{f_S} = 0.14^{(151)}$).

4.3.(2). Results.

The fluorescence wavelength maxima of the tertiary alicyclic amines in degassed solutions of cyclohexane, benzene and tetrahydrofuran, are detailed in Table 4.(2). For comparative purposes, the fluorescence data of triethylamine, a typical saturated tertiary acyclic amine, are also included. We noted the appearance of a degree of asymmetry in the fluorescence spectra of some of the amines in tetrahydrofuran solution, as a result of degassing the samples, accompanied by a small red-shift in the fluorescence maximum relative to the emission of the aerated solution. The quantum yields of fluorescence (ϕ_{f_M}), of the N-methylated azacycloalkanes and triethylamine, in degassed solutions of cyclohexane ($\lambda_{exc} = 240, 250 \text{ and } 265\text{nm}$) and tetrahydrofuran ($\lambda_{exc} = 250\text{nm}$) are given in Table 4.(3). It was not possible to evaluate the quantum yields of fluorescence of the amines in benzene solution. All of the amines studied in this present investigation, were found to be non-emissive in acetonitrile solution, presumably non-radiative decay pathways being energetically more favourable in this highly polar solvent.

AMINE	$\lambda_{\max}$ Values (nm)		
			THF
$\text{MeN}(\text{CH}_2)_7$	287	365	340 ^(a)
$\text{MeN}(\text{CH}_2)_6$	289	363	345
$\text{MeN}(\text{CH}_2)_5$	295	384	355
$\text{MeN}(\text{CH}_2)_4$	295	367	345 ^(a)
NEt_3	285	360	335
	316	-	380
	280	-	340 ^(a)

(a) Spectra red-shifted by $\sim 5\text{nm}$ after degassing solutions.

TABLE 4.(2). Fluorescence Wavelength Maxima (nm) of the Tertiary Alicyclic Amines and Triethylamine in Degassed Solutions of Cyclohexane, Benzene and Tetrahydrofuran, at 20°C .

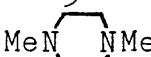
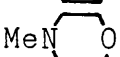
AMINE	(ϕ_f)			
	λ_E 240nm	λ_E 250nm		λ_E 265nm
			THF	
$\text{MeN}(\text{CH}_2)_7$	0.52	0.63	0.34	0.44
$\text{MeN}(\text{CH}_2)_6$	0.50	0.55	0.31	0.19
$\text{MeN}(\text{CH}_2)_5$	0.49	0.28	0.15	(0.01)
$\text{MeN}(\text{CH}_2)_4$	0.50	0.48	0.29	0.13
NEt_3	0.44	0.44	0.30	0.27
	0.48	0.23	0.09	-
	0.32	0.04	0.07	0.01

TABLE 4.(3). Quantum Yields of Fluorescence of a Series of Alicyclic Tertiary Amines in Degassed Cyclohexane and Tetrahydrofuran Solutions at the Excitation Wavelengths Shown, Relative to Toluene ($\phi_{fS} = 0.14^{(151)}$).

4.3.(3). Discussion.

At excitation wavelengths of 240 and 250nm, the fluorescence from the N-methylazacycloalkanes in cyclohexane solution, was found to be blue-shifted by about 8nm, as the ring size of the amine was increased, as shown in Table 4.(2). However, when we carried out the experiments at an excitation wavelength of 265nm, the emission of N-methylazacyclohexane was found to be greatly reduced in intensity and its wavelength red-shifted from 295nm out to around 320nm. Our earlier investigations into the u/v absorption of the alicyclic amines in cyclohexane solution had demonstrated that a $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ solution of N-methylazacyclohexane absorbed only weakly at 265nm. The concentration of the amine clearly had to be raised to around $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ therefore, before attaining an optical density of 0.1 at this excitation wavelength. We believe that under these conditions, the possibility arose of the amine molecules interacting with each other in the excited state, with the resultant formation of an intermolecular excimeric species and suggest that the long wavelength emission at $\sim 320\text{nm}$ emanated from this excited state complex.

The quantum yield data summarised in Table 4.(3)., showed that the N-methylazacycloalkanes, with the exception of the azacyclohexyl derivative, fluoresced quite strongly in cyclohexane solution at 20°C and although the quantum yields of fluorescence decreased slightly with decrease in ring size of the amine, remained consistently high at around 0.5 for excitation at both 240 and 250nm. Far greater variation was noted in the fluorescence quantum yields of the amines at 265nm excitation however, whilst the fluorescence from the N-methylazacyclooctane was still quite

strong (with $\phi_f = 0.44$), that of the other azacycloalkanes was reduced by a factor of about two thirds, suggesting that these amines were exhibiting concentration quenching. Halpern has observed this effect with several saturated tertiary amines, accompanied in some cases, by intermolecular excimer formation⁽¹⁷⁶⁾. Of the other amines studied, the quantum yields of triethylamine varied in a similar way to the N-methylazacycloalkanes, though showing a less pronounced reduction at 265nm excitation. The quantum yields of both N,N'-dimethyl-1,4-diazacyclohexane and N-methyl-1-aza-4-oxacyclohexane showed a marked reduction as the excitation wavelength was moved to the red of 240nm. This trend was particularly pronounced in the case of the -4-oxacyclohexane derivative, the quantum yield of which decreased from 0.32 at 240nm excitation to 0.04 at 250nm.

Although the u/v absorption spectrum of N,N'-dimethyl-1,4-diazacyclohexane (DMDACH) in cyclohexane solution was characteristic of a typical saturated tertiary monoamine indicating the lack of any ground state interaction between the non-bonding orbitals on the nitrogen atoms, this was clearly not the case in the lowest excited state of the compound. The large red-shift in the fluorescence maximum of DMDACH relative to the monoamines, in both cyclohexane and tetrahydrofuran solutions ($\lambda_{\max}$ values 316nm and 380nm respectively), was indicative of the formation of an intramolecular excimeric species. The need to use relatively high concentrations of the diamine at 250 and 265nm appeared to cause severe self quenching, particularly at the latter wavelength.

With the more polar solvent tetrahydrofuran, the tertiary alicyclic amines gave broad structureless emissions to the

red of those in cyclohexane solution. At 250nm excitation, the quantum yields of fluorescence of the N-methylazacycloalkanes were substantially lower than in cyclohexane solution, but showed little variation with the amino ring size, averaging ~ 0.3 . Once again the azacyclohexyl derivative was the exception to this trend, with a quantum yield of 0.15. The surprising feature of the amino fluorescence spectra in tetrahydrofuran solution, was the asymmetry of the emission bands, particularly after purging the solutions with dry nitrogen. It appeared that the fluorescence of the amines was made up of two overlapping bands, the relative intensities of which determined the wavelength maximum of the emission. Degassing the solutions enhanced the fluorescence from the longer wavelength component, and in some instances actually brought about a red-shift in the fluorescence maximum of around 5nm, as noted in Table 4.(2). We suggest that this apparent dual emission from the tertiary amines in tetrahydrofuran solution, was due to variations in the packing of the solvent molecules around the amine in the excited state.

Finally, when the fluorescence spectra of the tertiary amines were recorded in benzene solution, the wavelength maxima for the emissions were found to be around 360-365nm, well to the red of those in tetrahydrofuran solution (~ 345 nm). This result was somewhat surprising on the basis of the polarities of the two solvents, since tetrahydrofuran is more polar than benzene and would therefore be expected to stabilise the excited amine to a greater extent. Our interpretation of this result was that in benzene solution, the aromatic hydrocarbon was behaving both as a reaction partner and a small polar solvent molecule for the tertiary amines.

Consequently, we attributed the emission maximising at $\sim 365\text{nm}$, to fluorescence from an intermolecular benzene-amine exciplex, solvated by benzene molecules. As already discussed in Chapter (3), when we investigated the interaction of benzene with the tertiary alicyclic amines in cyclohexane solution, the emission from the exciplex was observed to undergo a red-shift as the concentration of benzene was raised to high levels. We believe that this wavelength change was brought about, by the increasing replacement of cyclohexane molecules in the solvation shell of the exciplex, by the more polar benzene molecules. Once again the N-methylazacyclohexane proved to be the exception to the trend, with an emission maximising at around 385nm . By analogy to the behaviour of the amine in cyclohexane solution at high concentrations, we tentatively propose that the emission may be due to an exciplex involving the interaction of benzene with an amine excimer, again solvated by benzene molecules.

4.4. FLUORESCENCE LIFETIME MEASUREMENTS.

4.4.(1). Experimental.

An investigation into the fluorescence lifetimes of the tertiary alicyclic amines in both cyclohexane and tetrahydrofuran solutions, was carried out using the pulse-sampling method⁽¹⁸⁸⁾. All fluorescence measurements were made on solutions thoroughly degassed by repeated freeze-pump-thaw-shake cycles and prepared to an optical density 0.1 at the excitation wavelength (λ_{excn} 240, 250 or 265nm). Usually about 12 measurements were made on each degassed sample, in order to compensate for any fluctuations either in the flash-lamp output or the instrumental response. Between 20 and 25 data points were then taken in digitising the fluorescence

decay profiles, to derive the fluorescence lifetimes (τ) of the saturated tertiary amines.

4.4.(2). Results and Discussion.

The fluorescence lifetimes of the saturated tertiary alicyclic amines, in both degassed cyclohexane and tetrahydrofuran solutions, are summarised in Table 4.(4). along with the excitation wavelengths employed. For comparative purposes, the data for triethylamine, a typical saturated acyclic tertiary amine, are also included in Table 4.(4).

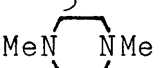
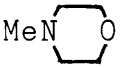
AMINE	τ (ns)			
	λE 240nm	λE 250nm	λE 265nm	
		 THF		
$MeN(CH_2)_7$	34	36	43	32
$MeN(CH_2)_6$	35	38	46	30
$MeN(CH_2)_5$	33	41	37	18
$MeN(CH_2)_4$	31	34	35	24
NEt_3	37	54	53	32
	116	110	39	105
	36	24	36	-

TABLE 4.(4). Fluorescence Lifetimes (ns) of the N-methylated Azacyclohexanes in Degassed Cyclohexane and Tetrahydrofuran Solutions at 20°C.

The relatively weak fluorescence from several of the amines, particularly when using tetrahydrofuran as the solvent, necessitated the utilisation of high sensitivity settings on our monitoring equipment, with the resultant problems associated with considerable fluctuations in the signal intensity. On some occasions, the distortion of the signal was found to be so severe, that it was necessary to

estimate the fluorescence decay profile. Further sources of experimental error arose in the need to digitise the decay data manually, prior to the evaluation of the fluorescence lifetimes. For the excitation wavelengths used in our experiments (240, 250 and 265nm), the fluorescence decays of the tertiary amines were analysed on the basis of a single exponential component. In view of the possible inaccuracies in our instrumentation and analytical procedures therefore, it is stressed that the lifetimes quoted in Table 4.(4). are the approximate values, rather than the absolute fluorescence lifetimes. We were however, able to make an assessment of the variations in the fluorescence lifetimes of the tertiary amines as a result of changing either the solvent polarity or the excitation wavelength, on the basis of the available data.

At excitation wavelengths of 240 and 250nm, the fluorescence lifetimes of the N-methylazacycloalkanes in degassed cyclohexane solution at 20°C, were not markedly different, ranging from about 30-40ns, as shown in Table 4.(4). We did however, observe a small, though consistent enhancement of the fluorescence lifetimes, upon moving from 240 to 250nm excitation. This trend was found to be more pronounced for the saturated acyclic amine triethylamine, the lifetime of which was increased from 37 to 54ns. A further increase in the excitation wavelength from 250 to 265nm, caused a reduction in the lifetimes of all of the amines, particularly triethylamine and N-methylazacyclo-pentane and -hexane. This was consistent with the use of higher concentrations of the amines leading to concentration quenching. In a recent piece of related work⁽¹⁸²⁾, investigating the photophysics of selected saturated tertiary aliphatic amines in the vapour

phase, Phillips et al. found that at high pressures, the fluorescence lifetimes of both trimethylamine (TMA) and triethylamine (TEA), decreased with increase in pressure of the amine, which was attributed to the presence of a self-quenching process, depopulating the excited states of both amines.

For ammonia, two absorptions have been assigned to the molecule in the near u/v region, these being the $n_N \rightarrow 3s$ Rydberg transition at 217nm (the S_1 absorption) and the $n_N \rightarrow 3p$ Rydberg transition at 169nm (the S_2 absorption), of which the S_1 absorption is the stronger of the two. By direct analogy to the behaviour of the ammonia molecule therefore, it has been proposed that the emitting state of the simple trialkylamines, both in the vapour phase and in non-polar solvents like cyclohexane, is a Rydberg state. Subsequent experiments with tertiary amines like trimethylamine have clearly demonstrated the presence of two regions of absorption in the u/v, corresponding to the expected Rydberg transitions, but alkylation of the nitrogen atom has been found to reverse the relative intensities of the S_1 and S_2 absorptions. This effect has been previously noted upon alkylation of a number of ketones, sulphides and azoalkanes as well⁽¹⁸⁹⁾. Phillips and co-workers found that in the vapour phase, excitation of simple tertiary amines like TEA and TPA (tri-n-propylamine) below 240nm, caused population of both the 3s and 3p Rydberg states of the amines. By restricting the excitation wavelengths in our experiments to the range 240-265nm, we believe this primarily caused the N-methylazacycloalkanes to undergo $n_N \rightarrow 3s$ Rydberg transitions.

Again by analogy to the behaviour of the ammonia molecule, it has been proposed that the simple tertiary aliphatic

amines adopt a planar conformation about the nitrogen atom upon excitation into the first singlet excited state. Based upon the ground state structures of the amines therefore, it should be more favourable for the azacyclopentyl derivative to achieve an sp^2 hybridised excited state than the azacyclohexyl derivative and the results of our fluorescence studies on the alicyclic amines do appear to support this. The differing abilities of the amines to become planar is also thought to affect the formation of fluorescent exciplexes with aromatic hydrocarbons. De Schryver et al.⁽¹⁴³⁾ for example, have recently shown that triethylamine is a better quencher of 2-methylnaphthalene fluorescence than N-methylazacyclohexane and attributed this mainly to the structural differences between the amines.

In many ways, the description of a Rydberg state is similar to that of an excited charge-transfer complex and will therefore be affected by factors such as temperature and solvent polarity. Since the Rydberg orbital will be larger and more diffuse in tetrahydrofuran solution than in cyclohexane solution, the probability of non-radiative decay from the excited state should be enhanced. Our results confirm this trend and the amine systems studied showed a diminution of fluorescence quantum yield as the solvent polarity was increased, suggesting that a greater proportion of the decay was occurring from the initially formed non-fluorescent Franck-Condon excited state species. The somewhat surprising result however, was the small increase in the fluorescent lifetimes of the amines upon changing the solvent polarity from cyclohexane to tetrahydrofuran. Halpern⁽¹⁸⁷⁾ has similarly observed an increase in the fluorescence lifetimes of simple monoamines like diethyl-

methylaniline (DMA) on changing from non-polar to ether solvents such as THF and diethylether.

4.5. NITROGEN-15 NMR SPECTROSCOPY.

4.5.(1). Introduction.

A study of the nitrogen-15 nmr spectroscopy of the N-methylazacycloalkanes and selected saturated tertiary amines was undertaken⁽¹⁹⁰⁾, to investigate the effects of molecular structure upon the electron density and hence electron donating ability of the nitrogen atom in these compounds. A number of authoritative texts on the principles and applications of ^{15}N nmr spectroscopy have been written including that of Levy and Lichter⁽¹⁹¹⁾, therefore a detailed treatment of the technique will not be made here. The pioneering work in nitrogen nmr was carried out using the ^{14}N isotope (natural abundance 99.64%), but although the chemical shifts extended over a range of several hundred parts per million, the chief stumbling block to the use of this nucleus, was its spin quantum number $I=1$. The associated quadrupole moment provided a very efficient relaxation mechanism for the nucleus, consequently the ^{14}N relaxation times were very short causing severe line broadening in the spectra (with linewidths of up to 1000Hz reported in the literature). For this reason, attention was switched to ^{15}N , with its very low natural abundance of only 0.36% and although the initial studies necessitated the use of enriched samples, narrow well resolved lines were obtained in the nmr spectra. The major breakthrough in the ^{15}N nmr spectroscopy field occurred in the early 1970's, when it was established that the detection of resonances at the natural abundance level was feasible, using either time-averaging frequency sweep techniques⁽¹⁹²⁾ or the

pulsed Fourier-transform method⁽¹⁹³⁾.

We utilised the latter technique in our experiments, details of which will be briefly discussed below. The sensitivity of F.T. nmr is derived from the fact that the entire spectrum is monitored simultaneously not sequentially, as in both frequency sweep and field sweep nmr. The short high power excitation pulse and acquisition of the free inductive decay signal (FID), normally takes ~ 1 second, therefore typical experiments involve data accumulation for about 10^3 to 10^4 scans prior to the Fourier transformation, to give the usual nmr spectrum as a function of frequency. Repetition rates of the scans are dependent upon the ^{15}N spin relaxation times, those for the spin-lattice relaxation (T_1) being highly variable. Since the signal strength is directly proportional to the number of scans N and the noise accumulation related to $\sqrt{N}$, the signal-to-noise ratio (S:N) of the ^{15}N spectra increases as a function of $\sqrt{N}$. The majority of the ^{15}N natural abundance nmr spectra, are recorded using wide-band proton decoupling leading to the observation of the ^{15}N signals as singlets. When coupled, the resulting loss in signal-to-noise ratio is often too severe to obtain worthwhile spectra.

The ^{15}N spin-lattice relaxation process in tertiary amines, oximes and other strongly basic nitrogen containing compounds, is greatly enhanced by the addition of paramagnetic relaxation reagents, which enable the use of faster pulse repetition rates in the F.T. nmr. The reagents must however satisfy certain additional requirements, namely that they cause no significant shifting of the resonances or excessive line broadening, the latter being essential to prevent loss of sensitivity and resolution. It is also desirable that all

nuclei are affected as uniformly as possible by the paramagnetic relaxation reagent (PARR). A compound which satisfies this requirement in organic solvent systems, is tris(acetylacetonato)chromium (III), $\text{Cr}(\text{acac})_3$, which was used extensively in our own studies.

The non-suitability of internal reference standards in ^{15}N nmr spectroscopy due to the solvent sensitivity of the resonance line positions, has necessitated the use of an external standard. Although the resonance position of nitromethane (CH_3NO_2) is influenced by the solvent and can in turn affect the resonance position of a substrate, it has the advantage of giving strong signals, both with and without added $\text{Cr}(\text{acac})_3$ and of lying at the low-field end of the nitrogen spectrum. Hence neat, partly enriched nitromethane is an inherently reproducible external standard. However, it does have one disadvantage, since by convention, the chemical shift of nuclei deshielded relative to the reference are algebraically positive, almost all nitrogen values referred to it are negative, since it resonates at low-field. To get round this problem, a standard corresponding to maximum shielding would be better and anhydrous liquid ammonia has proved to be suitable, giving a chemical shift at 25°C of 0.0ppm. Nitromethane was utilised as the reference sample in our spectra, with a chemical shift of 379.60ppm. The nitrogen resonance positions are affected by protonation of the nitrogen, which is thought to remove the diamagnetic shielding effect of the lone pair, and by changes in the solvent, hence chemical shift comparisons under different conditions are not valid in ^{15}N nmr. Furthermore it cannot be assumed that trends observed under one set of conditions, will be maintained under another set.

4.5.(2). Results and Discussion.

The wide-band decoupled nitrogen-15 nmr spectra of a series of saturated aliphatic tertiary amines were recorded in CDCl_3 solution, at 25°C . The observed chemical shifts of the amines, are detailed in Table 4.(5)., relative to both ^{15}N enriched nitromethane and anhydrous liquid ammonia at 25°C .

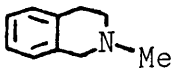
<u>AMINE</u>	<u>δ (ppm)</u> <u>$(\text{CH}_3^{15}\text{NO}_2)$</u>	<u>δ (ppm)</u> <u>(liq. NH_3)</u>
$\text{MeN}(\text{CH}_2)_{12}$	-354.21	25.39
$\text{MeN}(\text{CH}_2)_7$	-354.37	25.23
$\text{MeN}(\text{CH}_2)_6$	-344.91	34.69
$\text{MeN}(\text{CH}_2)_5$	-343.93	35.67
$\text{MeN}(\text{CH}_2)_4$	-340.66	38.94
$\text{MeN} \begin{array}{c} \diagup \quad \diagdown \\ \text{NMe} \end{array}$	-347.84	31.76
$\text{MeN} \begin{array}{c} \diagup \quad \diagdown \\ \text{O} \end{array}$	-348.66	30.94
NEt_3	-335.93	43.67
$\text{Et}_2\text{N}(\text{CH}_2)_{11}\text{OH}$	-337.56	42.04
$\text{Me}_2\text{NCH}_2\text{CH}_2\text{OH}$	-366.62	12.98
$\text{MeN}(\text{CH}_2\text{CH}_2\text{OH})_2$	-364.00	15.60
	-351.60	28.00

TABLE 4.(5). ^{15}N Chemical Shifts (ppm) for a Series of Saturated Tertiary Aliphatic Amines in CDCl_3 Solution at 25°C , in the Presence of the Paramagnetic Relaxation Reagent $\text{Cr}(\text{acac})_3$ ($\sim 100\text{mg}$).

By analogy to the behaviour of the saturated acyclic aliphatic amines, which have been studied quite extensively in the literature, the N-methylazacycloalkanes and related compounds were found to resonate at the high-field end of the nitrogen-15 nmr spectrum, with chemical shifts in the range 25-40ppm. It appeared that a reduction in the ring size of the amine from the eight to the five membered ring, resulted in an increasing deshielding of the nitrogen, characterised by a consistent down-field shift in the nmr resonance. Enlarging the ring from the eight to the thirteen membered ring, did not appear to cause any further change in the ^{15}N resonance position. In contrast to this, it has been previously shown that reducing the ring size of the azacycloalkane below the pentane derivative, actually increases the shielding around the nitrogen atom, so much so that in aziridine, the nitrogen resonates up-field of ammonia at $\sim$ -10ppm. This result in fact closely parallels the behaviour of cyclopropane and its derivatives in ^{13}C nmr, giving rise to a characteristic signal at around 0-5ppm. The other point to note about the data in Table 4.(5)., is the effect upon the chemical shift of adding an electronegative functional group or a heteroatom, γ to the nitrogen atom. In the cases of both N,N'-dimethyl-1,4-diazacyclohexane and N-methyl-1-aza-4-oxacyclohexane, this results in a shielding of the nitrogen and subsequent up-field shift in the resonance relative to the azacyclohexane derivative. The additional shielding induced by the γ -substituent finds close parallels in both the acyclic aliphatic amines and the ^{13}C resonance positions of the analogous hydrocarbons. Further examples of the enhanced shielding are provided by N,N-dimethyl-2-hydroxyethylamine and N-methyl-bis-(2-hydroxyethyl)amine, with

chemical shifts of ~ 13 and 15.5 ppm, respectively, compared with ~ 47 ppm for triethylamine.

4.6. MISCELLANEOUS AMINES.

4.6.(1). N-alkylated Azacycloalkanes.

We carried out a preliminary investigation into the effects of varying the alkyl substituent on the nitrogen atom of the azacycloalkanes, with respect to both the wavelength maxima and the fluorescence quantum yields (ϕ_f), at 250nm excitation. Measurements were made on degassed cyclohexane and tetrahydrofuran solutions of the amine (OD 0.1 at 250nm) and ϕ_f values determined relative to toluene. The data for the N-alkylated azacycloalkanes studied are summarised in Table 4.(6)., along with the corresponding results for the N-methylated derivatives.

<u>AMINE</u>			THF	
	$\lambda_{\max}(\text{nm})$	ϕ_f	$\lambda_{\max}(\text{nm})$	ϕ_f
$\text{MeN}(\text{CH}_2)_4$	295	0.48	345	0.29
$\text{Me}(\text{CH}_2)_7\text{N}(\text{CH}_2)_4$	298	0.51	345	0.06
$\text{Me}(\text{CH}_2)_9\text{N}(\text{CH}_2)_4$	298	0.46	342	0.05
$\text{MeN}(\text{CH}_2)_5$	295	0.28	355	0.15
$\text{Me}(\text{CH}_2)_2\text{N}(\text{CH}_2)_5$	290	0.22	340	0.05
$\text{Me}(\text{CH}_2)_7\text{N}(\text{CH}_2)_5$	291	0.34	340	0.03
$\text{Me}(\text{CH}_2)_9\text{N}(\text{CH}_2)_5$	291	0.33	337	0.03

TABLE 4.(6). Wavelength Maxima (nm) and Fluorescence
Quantum Yields of Selected N-alkylated Aza-
cyclopentane and -hexane Derivatives in
Degassed Cyclohexane and Tetrahydrofuran
Solutions at 20°C.

Our results in cyclohexane solution, indicated that varying the straight chain alkyl substituent on the azacycloalkanes from the methyl group to the decyl group, had little effect either on the wavelength maxima of the fluorescence, or the quantum yield of the fluorescence from the excited state amine. However, in the more polar solvent tetrahydrofuran, the replacement of the methyl group by a long chain hydrocarbon unit, caused a dramatic reduction in the fluorescence quantum yield by about 75-80%. Clearly non-radiative decay from the excited state of the amine has been favoured over radiative decay in this solvent medium, though the reasons for this trend are not altogether apparent. If the long alkyl chain had partially participated in the solvation of a neighbouring amine molecule for example, one would have expected the wavelength maximum of the emission to be less red-shifted in the pseudo-mixed solvent system than in pure tetrahydrofuran solution. We observed little variation in the maxima of the fluorescence bands upon varying the alkyl substituent.

4.6.(2). N-methyl-1,2,3,4-tetrahydroisoquinoline.

Further to our investigations into the fluorescence properties of the N-(1'-naphthyl)ethyl derivatives of both 1,2,3,4-tetrahydroquinoline (32) and its -isoquinoline analogue (33), which were detailed in Chapter (2) Section 2.5., the N-methylated derivative of 1,2,3,4-tetrahydroisoquinoline was synthesised. The fluorescence characteristics of the compound were then studied in both degassed cyclohexane and tetrahydrofuran solutions using 265nm excitation, to ensure that the excitation energy primarily entered the aromatic chromophore. In cyclohexane solution, we observed considerable quenching of the benzenoid fluorescence,

accompanied by a broadening of the tail of the emission at longer wavelengths, which we believe was due to the formation of an intramolecular exciplex with the amino group in the molecule. It was difficult to determine the wavelength maximum of this new band with any accuracy, although it appeared to be at around 320nm. The quantum yield was evaluated for the combined monomer and exciplex fluorescence ($\phi_{f_M} + \phi_{f_E} = 0.018$). In tetrahydrofuran solution, we observed a single broad and very weak emission maximising at $\sim 350\text{nm}$ ($\phi_{f_E} = 0.01$), due to the intramolecular exciplex.

4.6.(3). Amino-alcohols.

The fluorescence properties of several amino-alcohols were studied, to determine whether the presence of hydroxyl groups in close proximity to the amine, affected either the wavelength maxima or the fluorescence quantum yields. The possibility arose in these systems, that the hydroxyl groups could form intramolecular hydrogen bonds to the nitrogen atoms. The data obtained for the amino-alcohols, along with that for the related non-hydroxylated compound triethylamine, are summarised in Table 4.(7)., using 250nm excitation. The hydroxyl groups appeared to cause a significant reduction in the quantum yield of fluorescence from the amines, particularly for the hydroxyethyl derivatives. In fact, the emission was so weak in cyclohexane solution, that in some cases neither the wavelength maximum nor the quantum yield could be evaluated. The lack of emergence of any new emission at longer wavelengths was not surprising, since tertiary amines have been found to be non-fluorescent in polar solvents such as acetonitrile and methanol. The surprising feature of this work, involved the results of our experiments in tetrahydrofuran solution, using the hydroxyethyl derivatives. The

<u>AMINE</u>			THF	
	$\lambda_{\max}(\text{nm})$	ϕ_f	$\lambda_{\max}(\text{nm})$	ϕ_f
NEt ₃	285	0.44	335	0.30
Et ₂ N(CH ₂) ₁₁ OH	287	0.31	335	0.05
Me ₂ NCH ₂ CH ₂ OH	294	0.01	357	0.06
MeN(CH ₂ CH ₂ OH) ₂	290	-	360	0.05
N(CH ₂ CH ₂ OH) ₃	-	-	363	0.02

TABLE 4.(7). Fluorescence Data for Selected Amino-alcohols
in Degassed Cyclohexane and Tetrahydrofuran
Solutions at 20°C.

fluorescence underwent a larger red-shift (~ 290 - 360nm) than anticipated, upon moving to the more polar solvent and furthermore, the fluorescence quantum yields were higher than in cyclohexane solution. It appeared that the tetrahydrofuran afforded some additional stability to the amino-alcohols, possibly resulting from the ability of the solvent molecule to hydrogen bond with the hydroxyl group or groups in the amine. (Considerable difficulties were experienced in solubilising the amino-diol and triol derivatives in cyclohexane solution).

CHAPTER FIVE

Studies on the Photo-
Physical Properties of
 α,ω Diaminoalkanes.

5.1. INTRODUCTION.

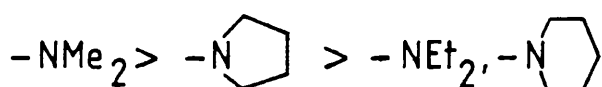
In a continuation of their earlier work on the photo-physical and spectroscopic properties of the symmetrical and conformationally constrained cage amines, 1-aza-bicyclo-[2,2,2]-octane (ABCO) and 1,4-diazabicyclo-[2,2,2]-octane (DABCO), in both the vapour phase and n-hexane solution, Halpern and Chan⁽¹⁹⁴⁾ investigated the behaviour of some structurally related but configurationally more flexible diamines. The photophysical properties of two open-chain diamines, N,N,N',N'-tetramethyl-1,2-diaminoethane (TMDE) and N,N,N',N'-tetramethyl-1,3-diaminopropane (TMDP) were considered, in comparison with those of N,N'-dimethyl-1,4-diazacyclohexane (DMDACH) and the simple monofunctional amine trimethylamine (TMA). The authors found that although the absorption spectra of the diamines resembled those of the monoamines, the fluorescence maxima were markedly red-shifted relative to that of TMA and furthermore, the radiative rate constants (k_R) for the diamines, were all considerably smaller than for the monoamine. It was concluded from this, that the α,ω -diaminoalkanes had lowest excited states which were excimeric in nature, but that these states were not directly reachable via a radiative transition from the ground state(s). The fluorescence spectrum of TMDP however contained two distinct bands, one at 290nm assigned to the monomer fluorescence and the other at 365nm attributed to excimer emission. In the vapour phase, the ratio of the excimer to monomer fluorescence (R) was found to decrease strongly as the excitation wavelength was decreased, but remained constant at a higher value, in the presence of a sufficient overpressure of a buffer gas and in solution, R was reduced as the viscosity of the solvent increased.

A more detailed investigation into the photophysical properties of the α,ω -diaminoalkanes, has been undertaken by Davidson and Whelan⁽¹³³⁾, studying the effects of varying (1) the length of the polymethylene chain linking the two nitrogen atoms and (2) the structure of the amine group, upon both the quenching of the amine fluorescence and intramolecular fluorescent excimer formation. Using a series of N,N,N',N'-tetraethyl- α,ω -diaminoalkanes (36) in cyclohexane solution, they observed efficient excimer formation with two and three methylene groups in the connecting chain accompanied by quenching of the amine fluorescence. By analogy to the formation of intramolecular excimers by aromatic hydrocarbons, the most efficient formation occurred with a propyl connecting chain. Further increases in the chain length of (36)

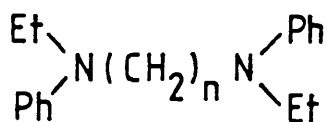


[36]

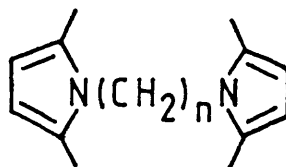
($n=4$ to 6), resulted in quenching of the amine fluorescence, but did not lead to excimer formation. No quenching was apparent for the larger chain derivatives. The structure of the amine group affected both the wavelength maxima and the quantum yields of fluorescence of the excimer emission. Comparing the efficiencies of excimer formation for the diaminopropane derivatives, they were found to decrease in the order;



No intramolecular excimer formation, nor any appreciable fluorescence self quenching was shown by the α,ω -dianilinoalkanes (37) and the α,ω -dipyrrolylalkanes (38).



[37]



[38]

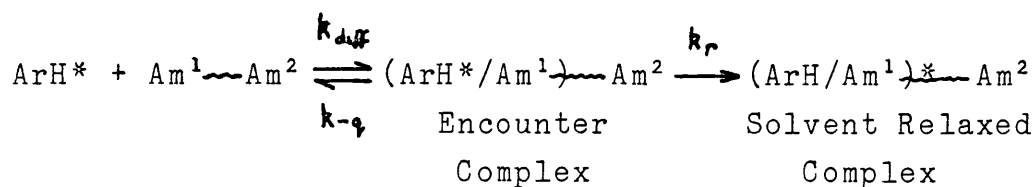
The observation of amine fluorescence quenching with up to six methylene groups in the linking chain suggested that the geometry of the complex involved in the quenching process, was less critical than that for fluorescent excimer formation. The possible involvement of a 'through-bond' interaction to explain the formation of an intramolecular excimer in the diaminoethanes has been suggested.

Having considered the self quenching of the α,ω -diaminoalkanes, Davidson and Whelan went on to investigate the abilities of the diamines to quench the fluorescence from a series of aromatic hydrocarbons in cyclohexane solution⁽³⁴⁾. In some earlier work by Knibbe⁽¹²⁹⁾, it was shown that during the quenching of aromatic hydrocarbon fluorescence by amines, the use of high concentrations of the amine, could in some cases, result in both a quenching and a red-shifting of the exciplex emission, attributable to the formation of an intermolecular ternary complex. The possibility therefore arose that in the quenching by the α,ω -diaminoalkanes, the second amino group would be in a position ready to interact with the exciplex, leading to enhanced quenching of the hydrocarbon fluorescence and perhaps the formation of a termolecular complex.

Using a series of N,N,N',N'-tetraethyl- α,ω -diaminoalkanes, it was found that in all cases the diamines were more efficient quenchers of naphthalene fluorescence than triethylamine, but the efficiency varied with the length of the

connecting chain between the nitrogen atoms. The short chain diamines, having 2 or 3 methylene groups, were found to be highly efficient at quenching the naphthalene fluorescence and yet gave relatively low quantum yields of exciplex emission. The weak fluorescence band, which was red-shifted in comparison with the naphthalene-triethylamine exciplex, was attributed at least in part, to an intermolecular ternary excited complex (exterplex) emission. The solvent dependency of the emission indicated the dipolar nature of the species and suggested that the exterplex was of the DDA type (where D represents a donor molecule and A an acceptor molecule). For chain lengths of $(\text{CH}_2)_n$, $n=4$ and 5, there was no significant exterplex emission, but the exciplex fluorescence was relatively quenched, suggesting that the geometric requirements for fluorescent exterplex formation were more severe than those for the termolecular complex involved in the quenching of the exciplex fluorescence.

Finally, although the long chain diamines with 6 or more methylene groups in the linkage were all found to form exciplexes with naphthalene, with efficiencies similar to that of triethylamine, they quenched the aromatic hydrocarbon fluorescence more efficiently than the monoamine. Davidson and Whelan interpreted these results, by considering the encounter complex formed between the aromatic hydrocarbon and the ground state diamine quencher molecule. The suggested scheme for the diffusion controlled quenching of aromatic hydrocarbon fluorescence by the α,ω -diaminoalkanes is given in Scheme 5.(1). It was proposed that for the diamines with $n \leq 5$, the exterplex formation occurred directly from the encounter complex, since the second amino group was ideally situated to interact with the encounter complex before the



SCHEME 5.(1). Schematic Representation of the Fluorescence Quenching Behaviour of the α,ω -diamino-alkanes.

the solvent reorganisation process generated the relaxed exciplex. With $n > 5$ however, the second amino group was thought to be insufficiently close to form the ternary complex, but was suitably placed to reform the encounter complex, if the first amino group diffused away from the excited aromatic hydrocarbon. This multi-collisional quenching process was therefore responsible for the more efficient quenching of the aromatic hydrocarbon fluorescence by the long chain α,ω -diaminoalkanes, relative to the monoamine.

Studies on the effects of varying both the structure of the amino groups and the nature of the aromatic hydrocarbon, established that the short-chain α,ω -diaminoalkanes with terminal azacyclopentyl units, were the most efficient of the diamines studied, at forming the exterplexes with naphthalene and pyrene. Furthermore the α,ω -diaminoalkanes were found to quench the first singlet excited states of both rose bengal and rhodamine B in methanol solution⁽¹³⁵⁾. The very efficient quenching by the short-chain derivatives, appeared to be due to the formation of a termolecular complex between the diamine and the fluorescent dye molecule, as observed with the simple aromatic hydrocarbons.

5.2. FLUORESCENCE MEASUREMENTS.

5.2.(1). Experimental.

In an extension of the earlier work of Davidson and Whelan, we examined the photophysical properties of a series of α,ω -bis-(1-aza-4-oxacyclohexyl)alkanes, to determine the effect of chain length upon intramolecular fluorescent excimer formation. Since it had been shown by ourselves and others^(185,187), that the saturated tertiary aliphatic amines fluoresced quite strongly in saturated ether solvents like diethylether and tetrahydrofuran, we studied the emission spectra of the diamines in both aerated and degassed cyclohexane and tetrahydrofuran solutions. The fluorescence spectra of a number of α,ω -diaminoalkanes with either azacyclopentyl or azacyclohexyl terminal amino groups, were also recorded in tetrahydrofuran solution. In several cases, we were unable to record the emission spectra of the diamines without using large slit widths on both the excitation and emission monochromators. Under these circumstances therefore, it was not possible to evaluate quantum yields of fluorescence either for the monomer (ϕ_{f_M}) or the excimer (ϕ_{f_E}).

5.2.(2). Results and Discussion.

The fluorescence wavelength maxima of the monomeric and or excimeric emissions are detailed in Tables 5.(1). and 5.(2). and the quantum yields of fluorescence given in Table 5.(3). All measurements were made using excitation at 250nm.

The data obtained from the series of α,ω -bis-(1-aza-4-oxacyclohexyl)alkanes, suggested that in both cyclohexane and tetrahydrofuran solution the diamines formed intramolecular fluorescent excimers. The intensity of the emission

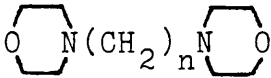
α,ω -Diamino- alkane 	$\lambda_{\max}$ (nm)			
			THF	
	<u>Monomer</u>	<u>Excimer</u>	<u>Monomer</u>	<u>Excimer</u>
n=2	-	380	-	398
n=3	-	380	-	399
n=8	278	380	325	395
n=10	(278)	380	-	395
n=12	278	(380)	330	395

TABLE 5.(1). Fluorescence Wavelength Maxima $\lambda_{\max}$ (nm) for
Selected α,ω -bis-(1-aza-4-oxacyclohexyl)
alkanes in Degassed Cyclohexane and Tetra-
hydrofuran Solutions.

Diamine Chain Length	 $\text{N}(\text{CH}_2)_n\text{N}$ 	 $\text{N}(\text{CH}_2)_n\text{N}$ 
	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (nm)
n=2	355	355
n=3	350	370
n=6	345	335
n=8	345	335
n=10	345	335

TABLE 5.(2). Fluorescence Wavelength Maxima $\lambda_{\max}$ (nm), for
a Series of Azacyclopentyl and -hexyl,
 α,ω -diaminoalkanes in Tetrahydrofuran Solution.

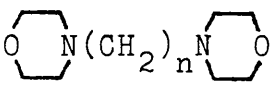
 $\text{O} \begin{array}{c} \diagup \quad \diagdown \\ \text{N}(\text{CH}_2)_n \text{N} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$	ϕ_f ($\bigcirc$)		ϕ_f (THF)	
	Monomer	Excimer	Monomer	Excimer
n=2	-	0.19	-	0.16
n=3	-	0.22	-	0.10
n=8	0.06	0.05	0.02	0.05
n=10	0.01	0.11	-	0.11
n=12	-	0.05		

TABLE 5.(3). Quantum Yields of Fluorescence from a Series of α,ω -bis-(1-aza-4-oxacyclohexyl)alkanes in both Cyclohexane and Tetrahydrofuran Solution (λ_E 250nm).

varied with chain length, the short-chain diamines giving exclusively excimeric emission, whereas for the longer chains (n=8 to 12), the weaker excimeric fluorescence was accompanied by a monomeric emission at 278nm in cyclohexane solution or $\sim$ 325nm in tetrahydrofuran solution. It was also noted that the longer wavelength emission attributed to fluorescence from the excimer, showed an apparent dependency upon the solvent polarity, being red-shifted in the more polar solvent. This suggests that in contrast to the excimers formed by α,ω -diarylalkanes, which are thought to derive the majority of their stability from exciton resonance, the α,ω -diaminoalkanes, particularly the 1-aza-4-oxacyclohexyl derivatives, are also stabilised by charge-transfer interactions and are therefore affected by changes in the solvent polarity. Furthermore, although the quantum yields of excimer fluorescence (ϕ_{f_E}) were greatest for the short chain diamines (with n=2 and 3), it appeared that the usual geometrical requirements for excimer formation were relaxed in the α,ω -bis-(1-aza-4-oxacyclohexyl)alkanes, enabling the

longer chain diamines (with $n \geq 8$) to also form fluorescent excimers. The stability of these species may well reflect the ability of the γ -oxygen atoms to interact with the amino-groups and increase the binding energy of the excimers. Zachariasse⁽⁸⁰⁾ has shown that by suitable enhancement of the binding energy excimer formation can be seen in the α,ω -dipyrenylalkanes for long chain derivatives,

Although the work of Whelan⁽¹³³⁾ had demonstrated the formation of an intramolecular excimer by 1,3-bis-(azacyclopentyl)propane in cyclohexane solution, the evidence for excimer formation in tetrahydrofuran solution was less convincing. The emission was asymmetrical and underwent a wavelength shift from ~ 335 to 350nm upon degassing the solution, suggesting that the fluorescence may be due to emission from two excited state species of different lifetimes. A similar effect was also noted in the fluorescence spectra of several of the N-methylated alicyclic amines in THF solution. We could not tell from our fluorescence measurements alone therefore, whether the emission was due at least in part, to an intramolecular excimer. The other bis-(azacyclopentyl) derivatives studied ($n=6, 8$ and 10) all gave broad structureless emissions maximising at around 340 to 345nm , but were considerably weaker in intensity than the fluorescence from the N-methylated monoamine, which suggested that the long chain diamines were exhibiting self-quenching. No quantum yield data were obtained for these compounds.

The α,ω -diaminoethane and -propane derivatives of azacyclohexane both gave an apparent excimeric emission, with λ_{max} values at 355 and 370nm , respectively. The bands were red-shifted relatively to the emission from the diamino alkanes with $n=6, 8$ and 10 at 335nm , which we suggest was due

to fluorescence from the amine monomer. Once again the weakness of the emissions, prevented the evaluation of fluorescence quantum yields, particularly for the excimeric species.

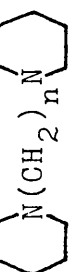
5.3. QUENCHING OF TRIPLET STATE AROMATIC HYDROCARBONS BY α,ω -DIAMINOALKANES.

5.3.(1). Experimental.

As will be shown in Chapter (6), the triplet yields of a series of compounds capable of forming intramolecular ternary complexes, decreased quite markedly as the solvent polarity was increased. In order to determine the cause of this change therefore, the ability of the α,ω -diaminoalkanes to quench the triplet states of naphthalene and anthracene in both cyclohexane and acetonitrile solutions was investigated, using the technique of nanosecond laser flash photolysis. Details of the instrumentation used for the measurements are given in Chapter (7) Section 7.8.(3). Solutions were prepared by the addition of the neat α,ω -diaminoalkanes to stock solutions of naphthalene or anthracene in either cyclohexane or acetonitrile (OD 1.0 at 249nm), giving a diamine concentration of $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ in each case. The solutions were thoroughly degassed by repeated freeze-pump-thaw-shake-cycles. Excitation was provided by single pulses from an excimer laser (Oxford Lasers Ltd.), using krypton fluoride as the lasing gas, operating at a wavelength of 249nm.

5.3.(2). Results and Discussion.

From an analysis of the decay profiles of the triplet-triplet absorption of naphthalene and anthracene, monitored at 415nm, we were able to estimate the quantum yields of triplet formation (ϕ_T) of both aromatic hydrocarbons, in the

Aromatic Hydrocarbon	Diamine Chain Length (n)	 ϕ_T^C	ϕ_T^A	 ϕ_T^C	ϕ_T^A	 ϕ_T^C	ϕ_T^A
Np	-	0.68(a)	0.68	0.68	0.68	0.68	0.68
Np	2	0.38	0.17	0.31	0.14	0.69	0.23
Np	3	0.55	0.22	0.61	0.20	0.70	0.27
Np	6	0.53	0.21	0.73	0.32	-	-
Np	8	0.57	0.18	0.66	0.37	0.71	0.47
Np	10	-	-	0.70	0.41	0.71	0.51
Np	12	-	-	-	-	0.65	0.42
An	-	0.72(a)	0.72	0.72	0.72	0.72	0.72
An	3	0.53	0.30	0.61	0.30	-	-

(a) It was assumed that the triplet yields of naphthalene and anthracene were invariant with solvent.

TABLE 5.(4). Quantum Yields of Naphthalene and Anthracene Triplet Formation in Degassed Cyclohexane Solutions (ϕ_T^C) and Acetonitrile Solutions (ϕ_T^A) in the Presence of α,ω -Diaminoalkanes (1×10^{-2} moldm $^{-3}$).

α, ω -Diamino- alkane	NAPHTHALENE IN 			
	k_1 ($\times 10^5 \text{ s}^{-1}$)	τ_1 (μs)	k_2 ($\times 10^5 \text{ s}^{-1}$)	τ_2 (μs)
-	1.14	8.8	1.70	5.9
 N(CH ₂) _n N 				
2	1.26	8.0	1.69	5.9
3	1.43	7.0	2.26	4.4
6	1.14	8.8	1.91	5.2
8	1.43	7.0	1.96	5.1
 N(CH ₂) _n N 				
2	0.92	10.9	1.16	8.6
3	1.19	8.4	2.04	4.9
6	1.46	6.8	2.09	4.8
8	1.45	6.9	2.00	5.0
10	1.48	6.8	2.34	4.3
 N(CH ₂) _n N 				
2	1.45	6.9	2.02	5.0
3	1.21	8.3	1.98	5.1
8	1.45	6.9	2.08	4.8
10	1.39	7.1	2.11	4.7
12	1.31	7.6	1.84	5.4
ANTHRACENE IN 				
-	0.36	27.4	-	-
 N(CH ₂) ₃ N 	0.36	27.7	-	-
 N(CH ₂) ₃ N 	0.61	16.5	-	-

TABLE 5.(5). Triplet Lifetimes (τ_T) and Rates of Decay
of the Naphthalene and Anthracene Triplets
in Degassed Cyclohexane Solutions
Containing α, ω -Diaminoalkanes (1.0×10^{-2}
 mol dm^{-3}).

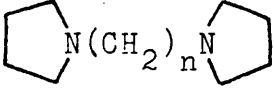
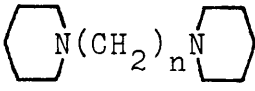
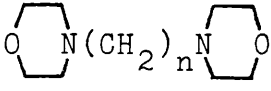
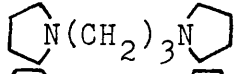
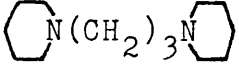
α,ω -Diamino- alkane	NAPHTHALENE IN MeCN	
	k ($\times 10^6 s^{-1}$)	τ (μs)
-	1.14 ^(a)	8.8
		
2	12.3	0.08
3	10.7	0.09
6	11.7	0.09
8	14.8	0.07
		
2	7.2	0.14
3	6.6	0.15
6	5.4	0.18
8	5.2	0.19
10	4.1	0.25
		
2	6.0	0.17
3	3.9	0.26
8	3.3	0.30
10	3.7	0.27
12	6.1	0.16
ANTHRACENE IN MeCN		
-	-	-
	0.31	3.25
	0.19	5.38

TABLE 5.(6). Triplet Lifetimes (τ_T) and Rates of Decay (k_T) of the Naphthalene and Anthracene Triplets in Degassed Acetonitrile Solutions, in the Presence of α,ω -Diamino-alkanes ($1.0 \times 10^{-2} \text{ moldm}^{-3}$).

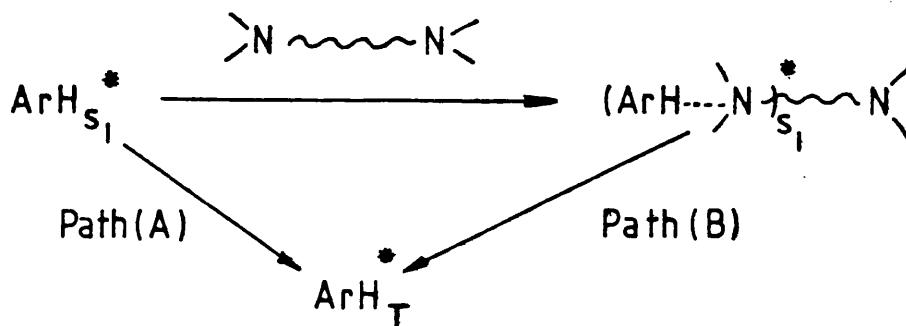
presence of the various α,ω -diaminoalkanes, as detailed in Table 5.(4). Furthermore, using the analytical procedure given in Appendix (I), the triplet lifetimes of the aromatic hydrocarbons and the rate constants for the triplet decays in cyclohexane and acetonitrile solutions were estimated and are shown in Tables 5.(5). and 5.(6)., respectively.

In previous work by Davidson and Whelan⁽³⁴⁾, it was shown that the rate constants (k_q) for the quenching of aromatic hydrocarbon fluorescence by the α,ω -bis-(azacyclopentyl and -hexyl) alkanes were typically of the order $5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in degassed cyclohexane solution. By suitable substitution into the Stern-Volmer equation shown below therefore, knowing the lifetime of the excited singlet

$$\frac{I_0}{I} = 1 + k_q \tau [\text{Quencher}] \quad \text{- Eqn. 5.(1).}$$

state species and the concentration of the quencher present, enabled the degree of fluorescence quenching by the diamines to be determined. For the systems studied, the proportion of unquenched singlet naphthalene remaining was found to be around 20%.

It appears therefore that two routes are available for the formation of the triplet state aromatic hydrocarbon, either via ISC from the unquenched naphthalene singlet (path A) or via the intermediacy of an excited complex (path B) as shown in Scheme 5.(2). The exact nature of the excited complex in non-polar solvents is not known, for example it could be either the initially formed encounter complex or the solvent relaxed exciplex, both of which can lead to triplet formation. From the data given in Table 5.(4). it can be seen that the yield of naphthalene triplet is noticeably lower in the presence of the 1,2-diaminoethanes



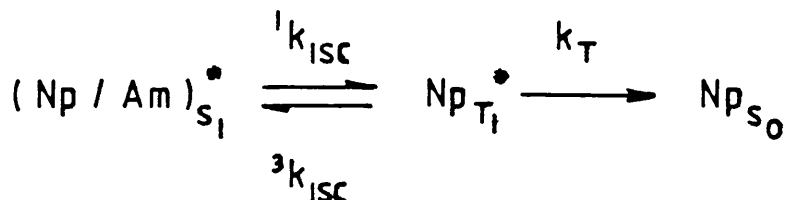
SCHEME 5.(2). Routes Available for Formation of Triplet State Aromatic Hydrocarbons in the Presence of α,ω -Diaminoalkanes in Degassed Cyclohexane Solution.

than the other diamines. It is possible that this may reflect the ability of the diaminoethanes to form ternary excited complexes with naphthalene in cyclohexane solution.

In acetonitrile solution, the triplet yields (ϕ_T^A) were found to be consistently lower than in cyclohexane solution and showed a less pronounced dependence upon the length of the polymethylene chain linking the two amino groups together. The lower yield of exciplex fluorescence in acetonitrile is consistent with the formation of radical ions either from the Franck-Condon excited complex or the solvent relaxed exciplex. Recombination of radical ions can yield the triplet state species, but in the cases studied, this route seems to be inefficient.

Our analysis of the decays of the triplet-triplet absorptions monitored at 415nm, (according to the procedure detailed in Appendix (I)), suggested that the decays were essentially first order in cyclohexane solution and either second order or a combination of two first order decays in acetonitrile solution. The usual bimolecular decay pathway is via triplet-triplet annihilation, but it appears to be

somewhat surprising that this process should be of the greatest importance for systems giving low triplet yields. Another possible explanation for the rapid triplet decay however, would be if the exciplex and the triplet species were in equilibrium with each other, as shown below in Scheme 5.(3). Under these conditions, the triplet hydro-



SCHEME 5.(3). Possible Scheme for the Decay of the Triplet State Aromatic Hydrocarbon Involving Two First Order Processes.

carbon would be decaying by two first order pathways, regenerating the exciplex by one route and decaying to the ground state by the other.

5.4. NITROGEN-15 NMR SPECTRA OF α,ω -DIAMINOALKANES.

Further to our studies on the ^{15}N Nmr spectroscopic properties of a series of tertiary saturated acyclic and alicyclic amines (detailed in Chapter (4) Section 4.5.), we investigated the ^{15}N Nmr behaviour of a number of α,ω -diaminoalkanes, to determine whether the length of the polymethylene chain between the nitrogen atoms affected the chemical shifts of the amino groups. Proton noise-decoupled spectra of the α,ω -diaminoalkanes were recorded in deuteriochloroform, in the presence of a paramagnetic relaxation reagent (PARR), $\text{Cr}(\text{acac})_3$, using nitrogen-15-enriched nitromethane as the external standard. The chemical shifts of the diamines are summarised in Table 5.(7)., relative to both $\text{CH}_3^{15}\text{NO}_2$ and NH_3 (liquid), along with the data for

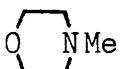
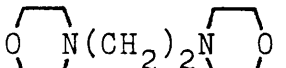
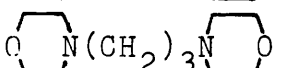
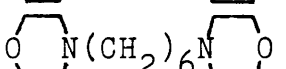
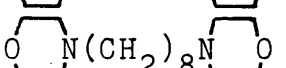
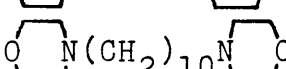
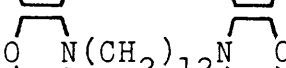
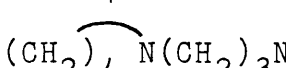
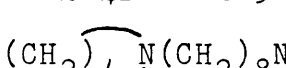
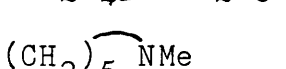
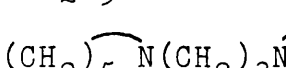
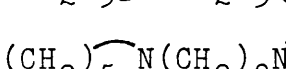
COMPOUND	δ (ppm) (CH ₃ ¹⁵ NO ₂)	δ (ppm) (liq. NH ₃)
	-348.66	30.94
	-340.66	38.94
	-338.87	40.73
	-337.89	41.71
	-337.72	41.88
	-337.72	41.88
	-337.72	41.88
	-340.66	38.94
	-329.07	50.53
	-328.09	51.51
	-343.93	35.67
	-333.32	46.28
	-332.50	47.10

TABLE 5.(7). Chemical Shifts (δ) in ppm from ¹⁵N
Proton-Noise Decoupled Nmr Spectra of
Selected α,ω -Diaminoalkanes in CDCl₃,
in the Presence of Cr(acac)₃.

the corresponding N-methylated saturated amines for comparison.

Discussion.

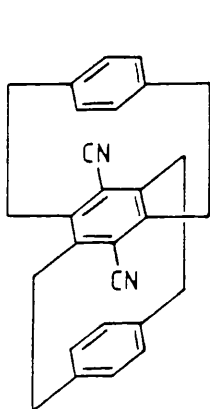
It appeared that linking two amino groups together with a polymethylene chain, deshielded the nitrogen atoms in the compound, causing them to resonate at lower field than in the N-methylated monoamine. The magnitude of the down-field shift increased with increasing chain length up to $n=8$, but remained constant thereafter. Although a detailed study was carried out only on the bis-(1-aza-4-oxacyclohexyl)alkanes, a similar trend was observed with the azacyclopentyl and -hexyl derivatives studied. Based upon our fluorescence measurements on the α,ω -diaminoalkanes, excimer formation was found to be most efficient for the short chain diamines ($n=2,3$), but we had no evidence from the u/v spectra of the compounds to suggest that a through space electronic interaction occurred between the two amino groups in the ground state. The ^{15}N Nmr chemical shifts of the diamines did however show some variation for the shorter chain derivatives relative to the others, which we believe was due to an electronic interaction occurring in these systems.

CHAPTER SIX

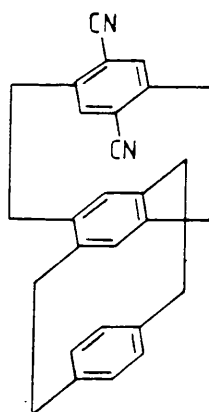
Intramolecular Poly- Chromophoric Systems.

6.1. INTRODUCTION.

In Chapter (1) Section 1.4., the formation of fluorescent excited ternary complexes or EXTERPLEXES was considered, involving as their name suggests, the simultaneous interaction of three chromophoric units in the excited state. In a large proportion of the examples quoted in that section, an intermolecular excited state interaction occurred between a mono- and a bi-chromophoric system, as for instance with naphthalene and selected α,ω -diaminoalkanes⁽³⁴⁾, leading to weak fluorescence from the ternary excited species. One exception to this trend however, was provided by the so-called 'triple decker' or trichromophoric cyclophanes (26) and (27), shown below⁽¹³⁶⁾. By the selective substitution of



[26]



[27]

the aromatic rings with electron withdrawing cyano groups, the formation of intramolecular fluorescent exterplexes of both the DAD (26) and DDA (27) configurations was studied and in agreement with the predicted zero dipole moment for the symmetrical cyclophane, the fluorescence λ_{max} properties of (26) showed little variation with solvent polarity.

In view of the general lack of attention paid to the formation of INTRA-molecular ternary exciplexes therefore, we decided to synthesise a number of polychromophoric systems

and investigate their photophysical properties. Our systems utilised an aromatic hydrocarbon as the excited acceptor group (either naphthyl or phenyl), linked to an array of two or more amino groups (the electron donor species) by a flexible dimethylene chain. The results of our photophysical measurements are detailed in the following sections, according to the aromatic chromophore present.

6.2. 1-NAPHTHYL DIAMINO DERIVATIVES.

6.2.(1). U/V Absorption Spectra.

The u/v absorption spectra of the 1-naphthyl diamino derivatives (OD 0.1 at 310nm) were recorded in aerated cyclohexane, benzene, tetrahydrofuran and acetonitrile solutions, in each case and compared with that of 1-methylnaphthalene. The absence of any new absorption bands in the spectra of the diamino derivatives, indicated the lack of either a charge-transfer interaction between the aromatic chromophore and the amino group, or an electronic interaction between the two amino groups in the ground state species. Although weaker in intensity, the u/v absorption spectra closely resembled that of 1-methylnaphthalene, giving absorption maxima at 264, 274, 284, 295 and 316nm. A similar result was also obtained with the u/v absorption spectra of the azacycloalkane derivatives, as shown in Figure 2.(1).

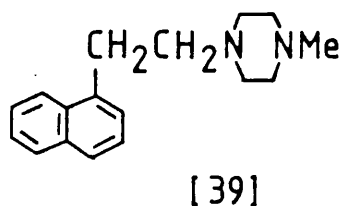
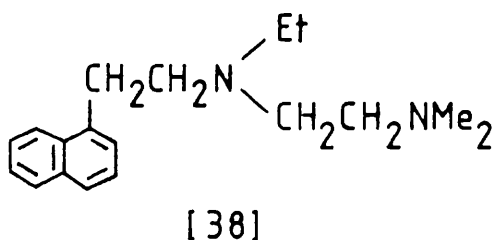
6.2.(2). Fluorescence Measurements.

The fluorescence spectra of the 1-naphthyl diamino derivatives were recorded in both aerated and degassed solutions, using 310nm excitation. Samples were degassed by purging the solutions with a stream of dry argon (research grade) as outlined in Chapter (7) Section 7.8.(1). All fluorescence quantum yields were determined using 1-methyl-

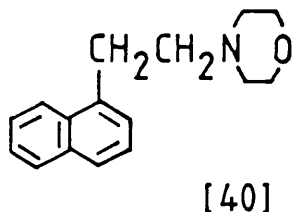
naphthalene in cyclohexane solution as the standard.

6.2.(2).1. Trichromophoric Systems.

A number of trichromophoric systems comprising an aromatic hydrocarbon as the excited acceptor group and two tertiary amino groups as electron donor species, were synthesised according to the procedures detailed in Chapter (7) Section 7.2. and their fluorescence properties investigated, in a range of solvents. The fluorescence wavelength maxima ($\lambda_{\max}$) of the 1-naphthylethyl diamino- derivatives (38) and (39) along with the quantum yields of residual naphthalene fluorescence (ϕ_{f_M}) and intramolecular fluorescent exciplex formation (ϕ_{f_E}) are given in Tables 6.(1). and 6.(2)., respectively. Also included in the Tables, are the spectro-



scopic data for a number of closely related compounds containing only one amino group. The fluorescence properties of compound (38) were compared with those of 1-NpCH₂CH₂NEt₂ and 1-Np(CH₂)₄NEt₂, whilst the data for compound (39) compared with that of N-(2-(1'-naphthyl)ethyl)azacyclohexane and N-(2-(1'-naphthyl)ethyl)-1-aza-4-oxacyclohexane (compound (40)).



Diagrammatic representations of the fluorescence spectra of compounds (38) and (39) in degassed cyclohexane, benzene,

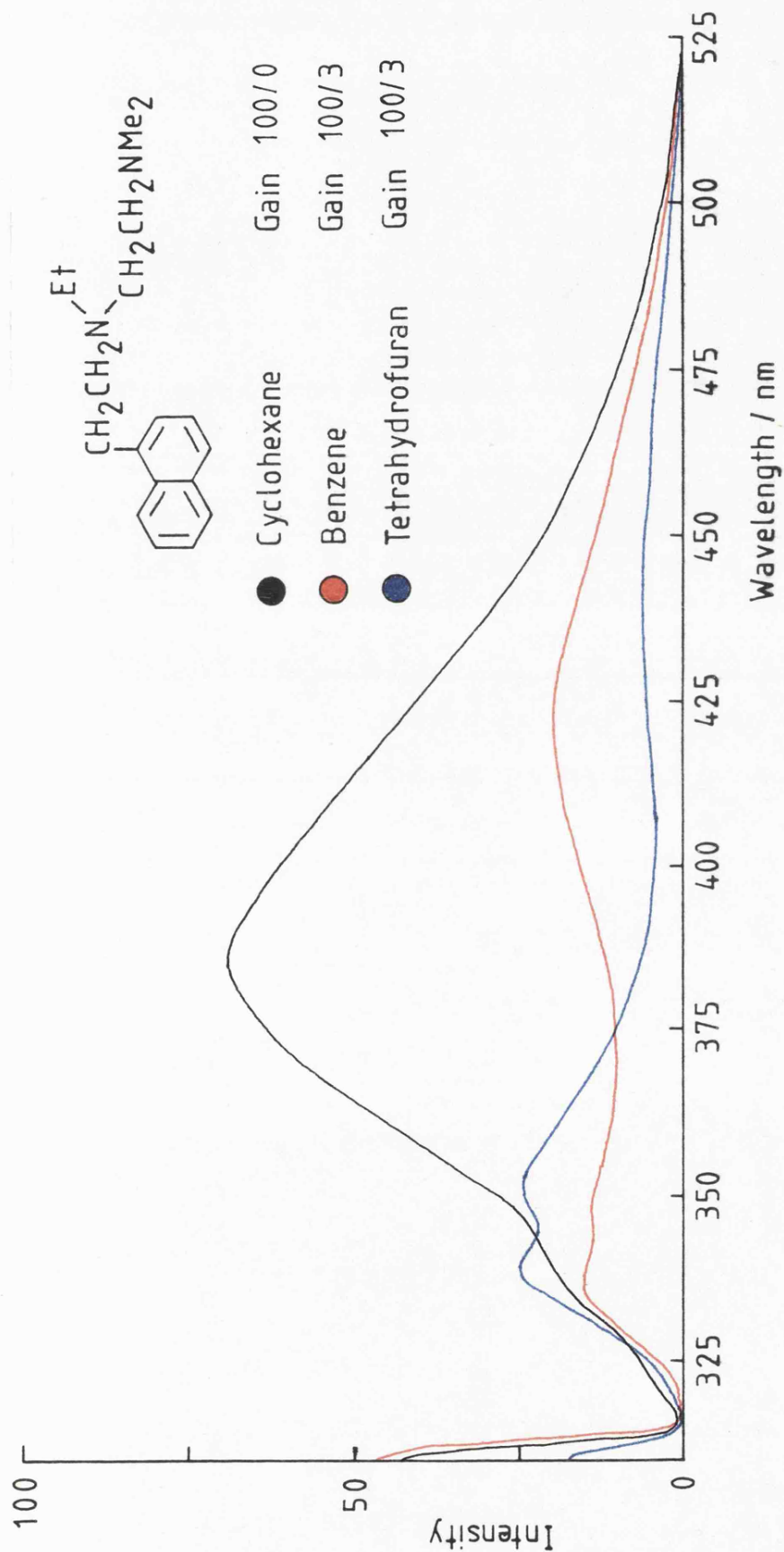


FIGURE 6.(1). Fluorescence Spectra of 1-NpCH₂CH₂N(Et)CH₂CH₂NMe₂ in Degassed Cyclohexane, Benzene and Tetrahydrofuran Solutions at 20°C.

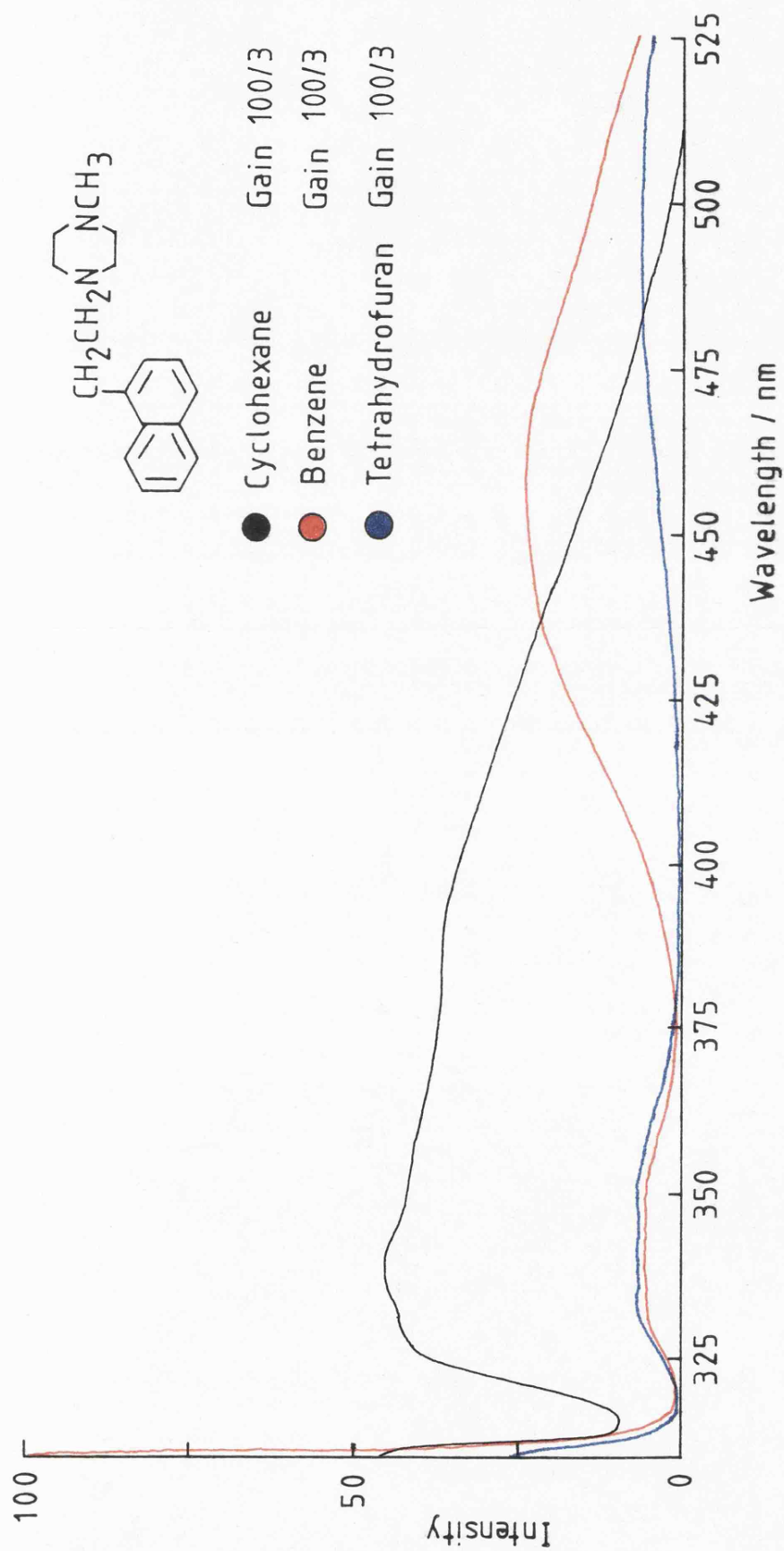


FIGURE 6.(2). Fluorescence Spectra of 1-NpCH₂CH₂NMe in Degassed Cyclohexane, Benzene and Tetrahydrofuran Solutions at 20°C.

COMPOUND	$\lambda_{\max}$ (nm)			
	SOLVENT			
			THF	MeCN
$1\text{-NpCH}_2\text{CH}_2\text{N} \begin{matrix} \text{Et} \\ \text{CH}_2\text{CH}_2\text{NMe}_2 \end{matrix}$	386	420	445	(a)
$1\text{-Np}(\text{CH}_2)_2\text{NEt}_2$	365	408	433	482
$1\text{-Np}(\text{CH}_2)_4\text{NEt}_2$	400	-	-	520
$1\text{-NpCH}_2\text{CH}_2\text{N} \begin{matrix} \text{ } \\ \text{ } \end{matrix} \text{NMe}$	395	485	502	(a)
$1\text{-NpCH}_2\text{CH}_2\text{N}(\text{CH}_2)_5$	360	405	438	488
$1\text{-NpCH}_2\text{CH}_2\text{N} \begin{matrix} \text{ } \\ \text{ } \end{matrix} \text{O}$	340	386	-	465

(a) No exciplex emission observed in acetonitrile solution.

TABLE 6.(1). Fluorescence $\lambda_{\max}$ Values (nm) for
Selected 1-Naphthylethyl Amines and
Diamines in Degassed Cyclohexane, Benzene,
THF and Acetonitrile at 20°C.

tetrahydrofuran and acetonitrile solutions are shown in Figures 6.(1). and 6.(2). respectively, and a visual comparison of the fluorescence spectra of compounds (38), $1\text{-NpCH}_2\text{CH}_2\text{NEt}_2$ and $1\text{-Np}(\text{CH}_2)_4\text{NEt}_2$ in methylcyclohexane solution is made in Figure 6.(3).

Discussion

It has been well established in the literature, that both intramolecular fluorescent excimer and exciplex formation occurs most readily, when the two interacting chromophores are linked together by a flexible hydrocarbon chain comprised of two or three methylene groups. By combining these features together therefore in the synthesis of compound (38), the possibility arose that excitation of the

COMPOUND					SOLVENT		MeCN	
	ϕ_{fM}	ϕ_{fE}	ϕ_{fM}	ϕ_{fE}	THF		ϕ_{fM}	ϕ_{fE}
$1-NpCH_2CH_2N\begin{smallmatrix} \diagup Et \\ \diagdown CH_2CH_2NMe_2 \end{smallmatrix}$	0.002	0.128	0.007	0.028	0.016	0.007	0.005	0.0
$1-Np(CH_2)_2NEt_2$	0.001	0.406	0.001	0.220	0.019	0.097	0.008	0.040
$1-Np(CH_2)_4NEt_2$	0.030	0.034	-	-	-	-	0.009	0.002
$1-NpCH_2CH_2N\begin{smallmatrix} \diagup NMe \\ \diagdown \end{smallmatrix}$	0.019	0.052	0.004	0.031	0.004	0.010	0.014	0.0
$1-NpCH_2CH_2N(CH_2)_5$	0.010	0.236	0.002	0.101	0.025	0.062	0.004	0.029
$1-NpCH_2CH_2N\begin{smallmatrix} \diagup O \\ \diagdown \end{smallmatrix}$	*	0.150	0.002	0.104	-	-	0.003	0.028

* Fluorescence quantum yield for monomer and exciplex emission ($\phi_{fM} + \phi_{fE}$)

TABLE 6.(2). Quantum Yields of Residual Naphthalene Monomer Fluorescence (ϕ_f) and Fluorescent Exciplex Formation (ϕ_{fE}) of a Series of 1-Naphthylethyl Derivatives in Degassed Cyclohexane, Benzene, Tetrahydrofuran and Acetonitrile Solutions at 20°C.

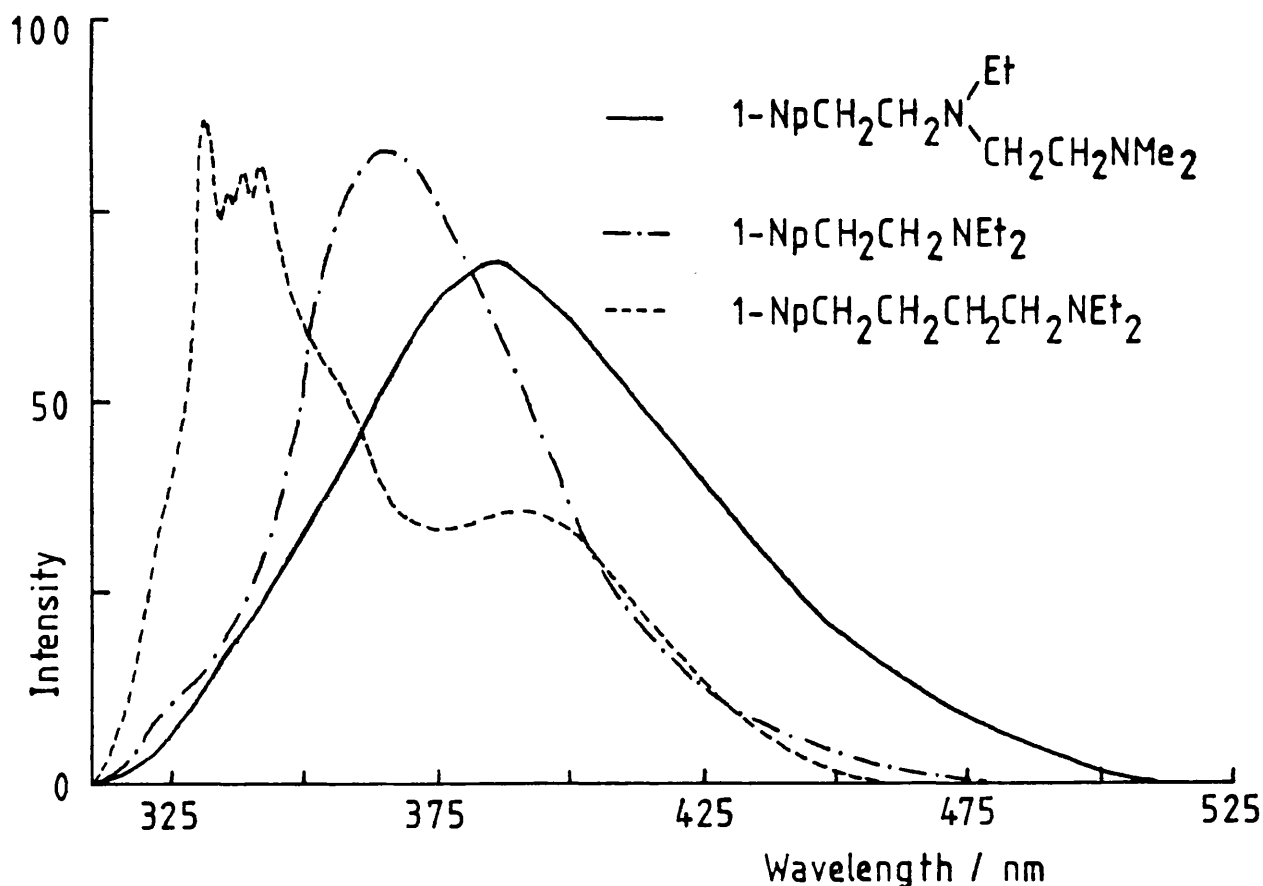
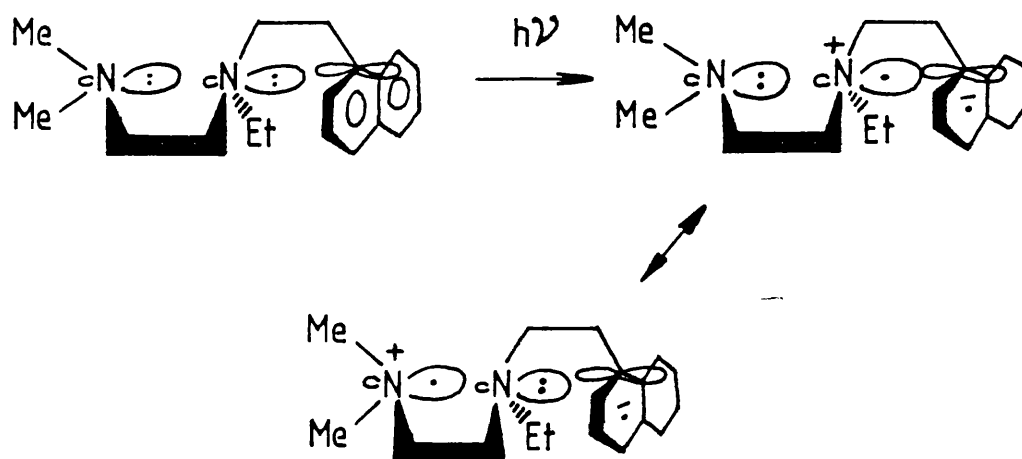


FIGURE 6.(3). The Fluorescence Spectra in Degassed Methylcyclohexane Solution of the Following Compounds: (1) $1\text{-Np}(\text{CH}_2)_2\text{N}(\text{Et})\text{-(CH}_2)_2\text{NMe}_2$, (2) $1\text{-Np}(\text{CH}_2)_2\text{NEt}_2$, (3) $1\text{-Np}(\text{CH}_2)_4\text{NEt}_2$.

aromatic hydrocarbon would lead to the formation of an intramolecular fluorescent ternary excited complex involving both of the amino groups.

As can be seen from the fluorescence data detailed in Tables 6.(1). and 6.(2)., in degassed methylcyclohexane solution, compound (38) gave a broad structureless emission band maximising at 386nm with quantum yields of residual naphthalene fluorescence (ϕ_{f_M}) and fluorescent exciplex formation (ϕ_{f_E}) of 0.002 and 0.128, respectively. Clearly the quenching of the fluorescence from the aromatic hydrocarbon was very efficient in this compound and was accompanied by the formation of an intramolecular exciplex,

but what was the nature of this excited state species? If the singlet excited state naphthalene was only being quenched by an interaction with the nearer of the two amino groups, then one would expect the resultant exciplex emission to closely resemble that of the model compound 1-NpCH₂CH₂NEt₂. This did not appear to be the case however, the diethylamino derivative fluoresced at shorter wavelengths (365nm) and was more efficient at fluorescent exciplex formation with $\phi_{fE} = 0.406$. Likewise if the excited naphthalene entity interacted only with the terminal amino group, the emission should be similar to that of 1-Np(CH₂)₄NEt₂, maximising at ~400nm with quantum yields of $\phi_{fM} = 0.030$ and $\phi_{fE} = 0.034$. (Ideally a comparison should have been made with 1-Np(CH₂)₅NEt₂, but no data was available on this compound). Since neither of these interactions could satisfactorily explain the observed fluorescence behaviour of (38), we attributed the long wavelength emission at ~385nm, to fluorescence from an intramolecular exciplex, involving the simultaneous interaction of both of the amino groups with the excited naphthalene chromophore.



Further evidence supporting the formation of a ternary complex was provided by the fluorescence properties of the diamino derivative in benzene and tetrahydrofuran solution. Although the quenching of the naphthalene fluorescence was still efficient, the emission from the exciplex was very weak and was considerably red-shifted relative to that of 1-NpCH₂CH₂NEt₂. On moving to the highly polar solvent acetonitrile, no emission was observed from (38) other than some very weak residual naphthalene fluorescence. This suggested that in this solvent environment, the quenching of the naphthalene fluorescence was leading to the formation of radical ion pairs, thereby favouring non-radiative decay pathways for the complex.

A similar, though far more pronounced trend was observed in the fluorescence characteristics of compound (39), in which the two amino groups were additionally constrained in a cyclohexyl ring, as shown in Figure 6.(4). The effect of

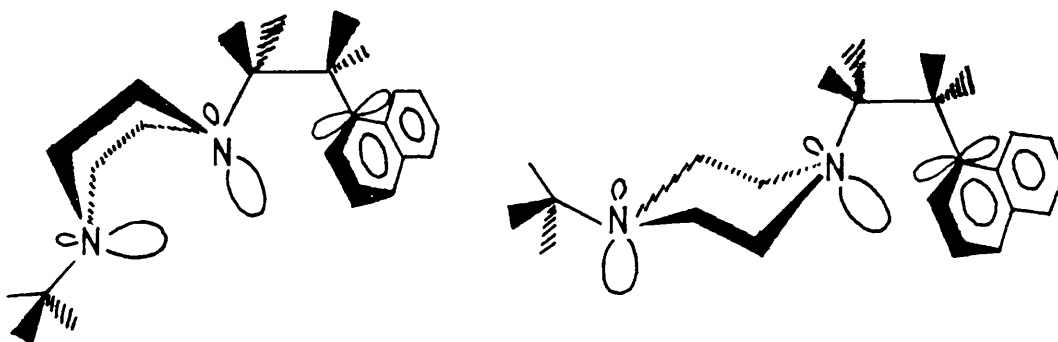


FIGURE 6.(4). Two Possible Conformations for Compound (39) Showing the Chair and Boat Forms of the Diazacyclohexyl Ring.

having a second amino group present in the ring structure was assessed by comparing the fluorescence data of compound (39), with that of the closely related alicyclic derivatives

listed in Tables 6.(1). and 6.(2). Although all three compounds efficiently quenched the naphthalene fluorescence, the diamino derivative was clearly less efficient at forming an intramolecular fluorescent exciplex. Furthermore, for a given solvent, the wavelength maximum of the exciplex formed by (39), was appreciably to the red of those for the exciplexes formed by the other derivatives. This was particularly pronounced in both benzene and tetrahydrofuran solutions, where the red-shifts in the fluorescence spectra were in excess of 50nm, as shown diagrammatically in Figure 6.(5). Our interpretation of these fluorescence results

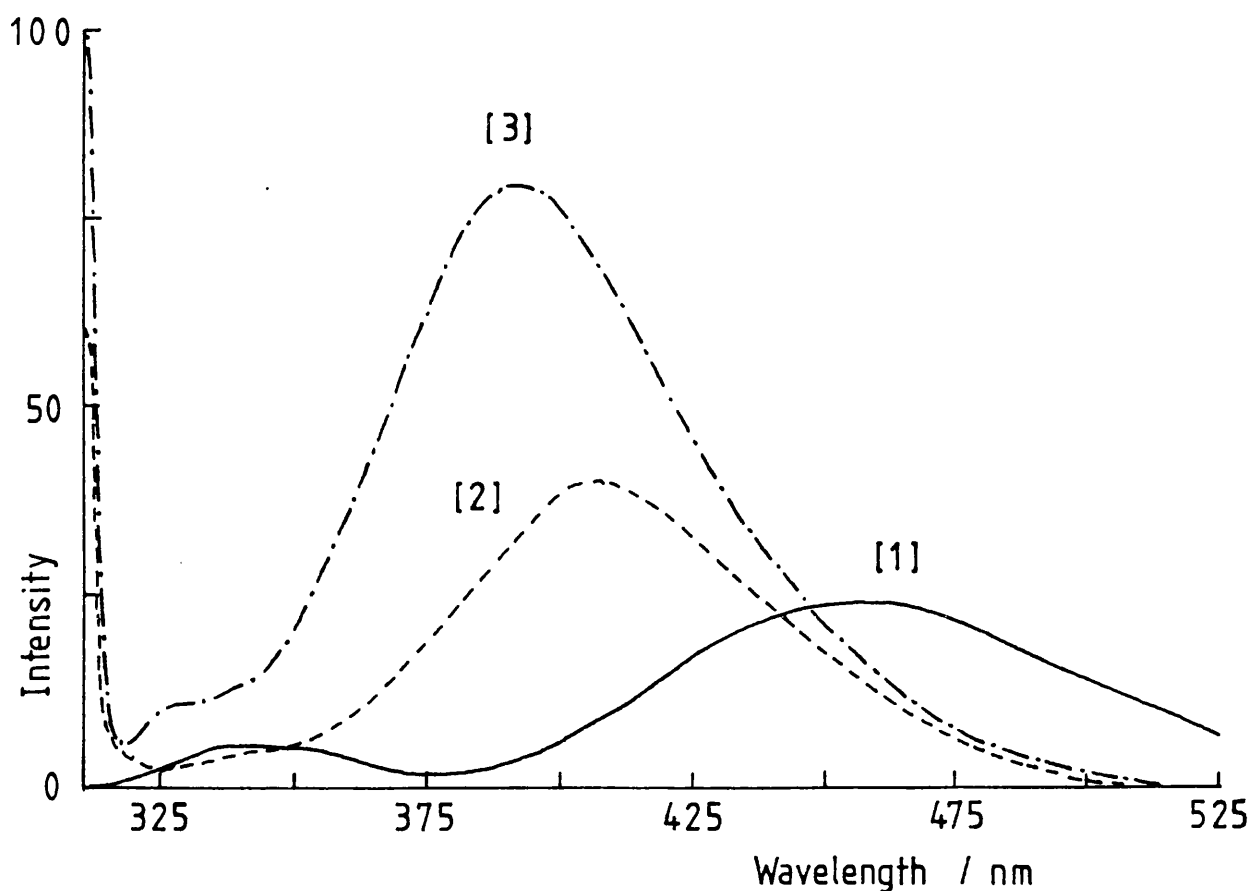
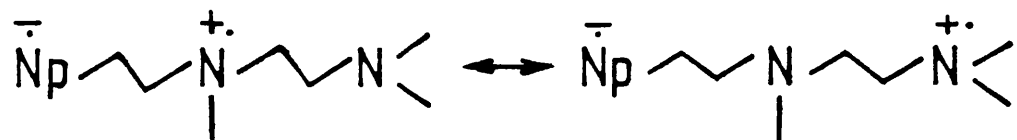


FIGURE 6.(5). Fluorescence Spectra of the Following
1-Naphthylethyl Derivatives in Degassed
Benzene Solutions (OD 0.1 @ 310nm).
(1) 1-NpCH₂CH₂NNMe (2) 1-NpCH₂CH₂N(CH₂)₅
(3) 1-NpCH₂CH₂NO.

was that compound (39) was able to form an intramolecular ternary exciplex, in which the interaction of the two nitrogen atoms was able to stabilise the radical cation. This additional reduction in the energy of the ternary



exciplex relative to that of the more common bichromophoric species formed between the excited aromatic hydrocarbon and a single amino group, accounting for the observed shift to longer wavelengths of the exciplex emission, (assuming that the dissociative ground states of the bi- and tri-chromophoric complexes are of similar energies). The quantum yields of fluorescence from the ternary exciplexes (ϕ_{fE}) decreased as the solvent polarity was increased, demonstrating the increasing importance of non-radiative decay pathways for these systems in the more polar solvents. In fact in acetonitrile solution, we observed only weak residual naphthalene fluorescence, indicating that the polar solvent was favouring the formation of radical ions, rather than a fluorescent exciplex.

A brief mention should also be made here of the fluorescence properties of compound (40). Since the compound contains an electron withdrawing group γ - to the amino unit, one would anticipate this to cause a reduction in the availability of the nitrogen's lone pair for interaction with the excited aromatic hydrocarbon. This appears to be born out in our fluorescence results, where in cyclohexane solution, the fluorescence from compound (40) closely resembled that of a naphthalene chromophore, maximising at

around 340nm. It was difficult to tell whether any of the observed emission was due to an intramolecular exciplex. Increasing the solvent polarity did however appear to lead to the formation of a fluorescent exciplex, as indicated in Tables 6.(1). and 6.(2).

Other examples of fluorescent intramolecular ternary exciplexes are gradually appearing in the literature, again using aromatic hydrocarbon-amine systems. Verhoeven and his co-workers⁽¹⁹⁵⁾ have recently studied a series of trichromophoric systems (41) of the type shown below, and

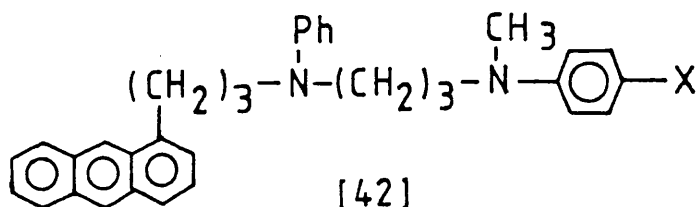


Ar = 1,2 - naphthyl
9 - anthryl

Z = H, 2-OMe, 4-OMe

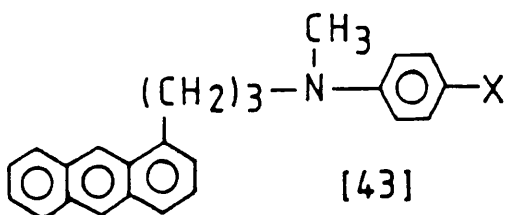
[41]

demonstrated using laser flash photolysis experiments that excitation of the aromatic chromophore is followed by consecutive electron-transfer processes, leading to intramolecular charge separation between the terminal chromophores. Similarly Yang and his colleagues⁽¹⁹⁶⁾ have recently investigated the fluorescence properties of a number of polychromophoric molecules of the general structure (42),



X = H, OMe, Me

[42]



X = H, OMe

[43]

in comparison with those of the anilino derivative (43). On the basis of their fluorescence measurements, they have proposed the formation of an intramolecular ternary exciplex for compound (42), X=OMe, with the alignment shown below in Figure 6.(6).

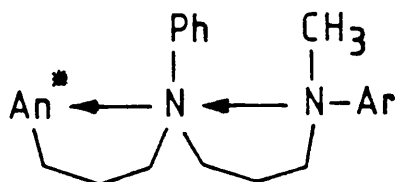
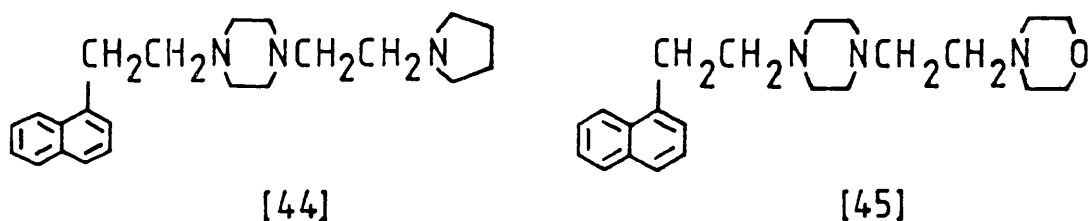


FIGURE 6.(6). Alignment of the Chromophoric Units
Required for Intramolecular Fluorescent
Ternary Exciplex Formation.

6.2.(2).2. Tetrachromophoric Systems.

Our studies on the fluorescence properties of polychromophoric molecules were further extended by the synthesis of compounds (44) and (45) and subsequent investigations into their fluorescence characteristics in a range of different solvents.



Tables 6.(3). and 6.(4). summarise both the fluorescence λ_{max} values and the fluorescence quantum yield data for the two compounds, along with that for compound (39). On the basis of our steady state measurements, it is difficult to tell whether or not the exciplexes formed by (44) and (45) involve the interaction of three or four chromophoric

<u>COMPOUND</u>	$\lambda_{\max}$ (nm)			
	<u>SOLVENT</u>			
			THF	MeCN
1-NpCH ₂ CH ₂ N  NCH ₂ CH ₂ N 	405	460	505	-
1-NpCH ₂ CH ₂ N  NCH ₂ CH ₂ N 	405	455	500	-
1-NpCH ₂ CH ₂ N  NCH ₃	395	458	502	-

TABLE 6.(3). Fluorescence Maxima (nm) for Compounds (39), (44) and (45) in Degassed Cyclohexane, Benzene, Tetrahydrofuran and Acetonitrile Solutions at 20°C.

groups in the excited state. However the quantum yield data and $\lambda_{\max}$ values do appear to support the formation of an exciplex with considerable charge-transfer character and high dipole moment, which one would expect if there was charge separation between the terminal chromophores. Furthermore, the additional 10nm red-shift in the fluorescence of compounds (44) and (45) in cyclohexane solution relative to that of compound (39) may we believe, be attributable to the participation of all three amino groups in the stabilisation of the zwitterionic excited complex. The quantum yields of fluorescent exciplex formation were found to be very low for these systems, presumably reflecting the difficulty in attaining the necessary conformational array of the chromophoric groups, to generate the quaternary excited complex. The nature of the terminal amino group did not appear to have any significant effect on fluorescent exciplex formation.

COMPOUND	SOLVENT							
					THF		MeCN	
	ϕ_{fM}	ϕ_{fE}	ϕ_{fM}	ϕ_{fE}	ϕ_{fM}	ϕ_{fE}	ϕ_{fM}	ϕ_{fE}
1-NpCH ₂ CH ₂ N  NCH ₂ CH ₂ N 	0.008	0.043	0.005	0.036	0.003	0.011	0.005	-
1-NpCH ₂ CH ₂ N  NCH ₂ CH ₂ N 	0.008	0.039	0.006	0.032	0.005	0.013	0.001	-
1-NpCH ₂ CH ₂ N  NCH ₃	0.019	0.052	0.004	0.031	0.004	0.010	0.014	-

TABLE 6.(4). Quantum Yields of Residual Naphthalene Monomer Fluorescence (ϕ_{fM}) and Fluorescent Exciplex Formation (ϕ_{fE}) of Compounds (39), (44) and (45) in Degassed Solutions of Cyclohexane, Benzene, Tetrahydrofuran and Acetonitrile at 20°C.

6.2.(3). Triplet-Triplet Absorption Decays.

Having established that the wavelength of maximal absorption of the naphthalene triplet occurred at 415nm, the decays of the triplet-triplet absorption spectra of both the trichromophoric and tetrachromophoric systems were monitored at this wavelength, using the technique of nano-second laser flash photolysis (detailed in Chapter (7) Section 7.8.(3).). All solutions were thoroughly degassed by repeated freeze-pump-thaw-shake-cycles prior to use and the decay measurements were repeated several times for each sample. The quantum yields of triplet formation of the naphthyl di- and triamino derivatives were evaluated by measuring the maximum absorption at $t=0$ (after extrapolation of the decay curve) and comparing it with that of a standard, 1-methylnaphthalene in cyclohexane solution ($\phi_{TS}=0.48$). The results are summarised in Table 6.(5).

COMPOUND	ϕ_T		
		THF	MeCN
$1\text{-NpCH}_2\text{CH}_2\text{N} \begin{matrix} \text{Et} \\ \text{CH}_2\text{CH}_2\text{NMe}_2 \end{matrix}$	0.25	0.04	0.018
$1\text{-NpCH}_2\text{CH}_2\text{NEt}_2$	0.29	0.33	0.220
$1\text{-NpCH}_2\text{CH}_2\text{N} \begin{matrix} \text{---} \\ \text{NMe} \end{matrix}$	0.43	0.09	0.009
$1\text{-NpCH}_2\text{CH}_2\text{N} \begin{matrix} \text{---} \\ \text{NCH}_2\text{CH}_2\text{N} \end{matrix} \begin{matrix} \text{---} \\ \text{---} \end{matrix}$	0.41	0.05	0.012
$1\text{-NpCH}_2\text{CH}_2\text{N} \begin{matrix} \text{---} \\ \text{NCH}_2\text{CH}_2\text{N} \end{matrix} \begin{matrix} \text{---} \\ \text{O} \end{matrix}$	0.42	0.05	0.008
$1\text{-NpCH}_2\text{CH}_2\text{N} \begin{matrix} \text{---} \\ \text{O} \end{matrix}$	0.50	0.35	0.43
$1\text{-NpCH}_2\text{CH}_2\text{N} \begin{matrix} \text{---} \\ (\text{CH}_2)_5 \end{matrix}$	0.23	0.27	0.43

TABLE 6.(5). Quantum Yields of Triplet Formation (ϕ_T) in Degassed Cyclohexane, Tetrahydrofuran and Acetonitrile Solutions.

COMPOUND			THF			
	k_1 ($\times 10^5 s^{-1}$)	τ_1 (μs)	k_1 ($\times 10^5 s^{-1}$)	τ_1 (μs)	k_2 ($\times 10^5 s^{-1}$)	τ_2 (μs)
1-NpCH ₂ CH ₂ N ^{Et} CH ₂ CH ₂ NMe ₂	1.47	6.8	2.55	3.9	2.18	4.6
1-NpCH ₂ CH ₂ NEt ₂	1.80	5.6	-	-	-	-
1-NpCH ₂ CH ₂ N ^{NMe}	1.13	8.8	1.40	7.2	3.20	3.1
1-NpCH ₂ CH ₂ N ^{NCH₂CH₂N₅}	1.24	8.0	-	-	2.09	4.8
1-NpCH ₂ CH ₂ N ^{NCH₂CH₂N₆}	1.24	8.0	-	-	1.81	5.5
1-NpCH ₂ CH ₂ N ^{NCH₂CH₂N₇}	1.30	7.7	2.61	3.8	4.66	2.2
1-NpCH ₂ CH ₂ N ^{(CH₂)₅}	1.29	7.8	2.62	3.8	5.12	2.0

TABLE 6.(6). Triplet Lifetime Data (τ_T) and Rates of Triplet Decay (k_T) for Selected 1-Naphthyl-ethyl-diamino and -triamino Derivatives in Degassed Solutions of Cyclohexane and THF.

Also included in Table 6.(5)., are the triplet yield data for some structurally related bichromophoric compounds which contain a single amino group. Table 6.(6). summarises the triplet lifetimes (τ_T) and the rates of quenching of the triplet states (k_T) estimated using the procedure detailed in Appendix (I).

Discussion

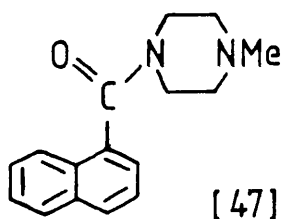
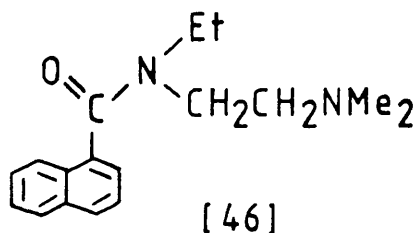
The most apparent feature of the data contained in Table 6.(5)., concerns the dramatic reduction in the quantum yield of triplet formation in both the tri- and tetra-chromophoric systems, upon increasing the solvent polarity. This result was in marked contrast to the trends shown by both the azacycloalkyl derivatives (dealt with in Chapter (2) Section 2.2.(3).) and to a lesser extent the ω -(1-naphthyl)-diethylaminoalkanes, whose ϕ_T values were not particularly dependent on solvent polarity. One possible explanation for the low quantum yields of triplet formation (ϕ_T) and fluorescent exciplex formation (ϕ_{f_E}) for these polychromophoric systems in tetrahydrofuran and acetonitrile solutions, is that the energy of the radical ion pairs formed by these compounds lies below that of the triplet state aromatic hydrocarbon. In this way, radical ion pair formation provides an ideal non-radiative decay pathway for the excited species. As mentioned previously, the ability of the two or three nitrogen atoms to interact should stabilise the radical cation quite considerably in these systems. It should also be noted, that since in cyclohexane solution the triplet quantum yields for the polychromophoric compounds are appreciably higher than the quantum yields of fluorescent exciplex formation, (in some cases by a factor of ten) this suggests that a large proportion of the triplet hydrocarbon

is derived from the initially formed encounter complex and not the fluorescent species. Analysis of the triplet decay profiles of the di- and triamino derivatives in cyclohexane solution, indicated that they followed a first order decay pathway, with triplet lifetimes of the order of 7-8 μ s. In tetrahydrofuran solution however, the situation was complicated by the very low triplet yields in this solvent, which made a detailed analysis of the decay profiles very difficult. It appeared on the basis of our results, that the tri- and tetrachromophoric systems decayed by a first order or mixed first order pathway from the triplet state. The negligible triplet yields for the polychromophoric systems in acetonitrile solutions, rendered a kinetic analysis of the data impractical.

6.2.(4). ^1H Nmr Studies on Selected N-((1-naphthyl)oxo-methyl) Diamino Derivatives.

Introduction

During the synthesis of a number of N-((1-naphthyl)oxo-methyl) diamino derivatives, for use in our fluorescence studies, the ^1H nmr spectra of the intermediate amido-amine derivatives indicated that the compounds were exhibiting restricted bond rotation about the amido linkage. We therefore carried out a detailed analysis of the ^1H nmr spectra of compounds (46) and (47) using both variable temperature and high field techniques.



Results and Discussion

(1) 90MHz ^1H Nmr Spectra.

The spectra of compound (46) run in CDCl_3 contained two signals of equal intensity but different chemical shift for several proton resonances, including those attributable to the terminal dimethylamino group and the N-ethyl substituent. This indicated that in compound (46) there was some hindrance to free rotation of the C-N amide bond, which resulted in there being two distinguishable chemical environments for the substituent alkyl groups, dependent upon whether they were directed towards or away from the carbonyl bond. The positions of the proton resonances are detailed below, along with the suggested origins of the signals.

1.00 δ ;	1.40 δ	(3H,t,NCH ₂ CH ₃)
1.92 δ ;	2.42 δ	(3H,s,NCH ₃)
2.20-2.50 δ		(4H,m,NCH ₂)
2.78 δ		(2H,t,NCH ₂)
3.08-3.32 δ		(2H,m,NCH ₂ -)
3.40-4.20 δ		(4H,br,m,NCH ₂ -)
7.50-8.00 δ		(7H,m,Np)

In a similar fashion, the ^1H nmr spectrum of compound (47) also gave dual signals for the resonance positions of the protons, which we again attributed to hindered rotation about the amido C-N bond.

(2) 220MHz ^1H Nmr Spectra.

In an attempt to clarify the poorly resolved peaks in the spectra of both samples, the 220MHz ^1H Nmr spectra of compounds (46) and (47) were recorded. Unfortunately though, the severe loss of resolution on going to very high field negated any information gained concerning the number of peaks

present in the spectrum.

(3) 90MHz Variable Temperature ¹H Nmr Spectra.

Using a 90MHz instrument, the variable temperature proton Nmr spectrum of compound (46) was recorded in o-dichlorobenzene, increasing the temperature in 10°C intervals from room temperature. A gradual coalescence of the signals was observed as the temperature was elevated, which was complete at 162°C.

The resultant spectrum analysed as given below;

1.08 δ	(3H, t, NCH ₂ CH ₃)
2.12 δ	(6H, s, NMe ₂)
2.52 δ	(2H, t, CH ₂ NMe ₂)
3.24-3.60 δ	(4H, m, NCH ₂)

No further information was derived however from a variable temperature Nmr study on compound (47).

I am grateful to Dr. J.R. Malpass and colleagues in the Department of Chemistry at Leicester University, for the measurement of the variable temperature ¹H nmr spectra of these samples.

6.3. PHENYL DERIVATIVES.

6.3.(1). Fluorescence Spectra.

A number of phenylethyl diamino and triamino derivatives were synthesised analogous to those 1-naphthylethyl- compounds detailed in the previous section and their fluorescence properties investigated briefly. The fluorescence wavelength maxima and quantum yields of fluorescent exciplex formation are detailed in Table 6.(7). where available.

Preliminary studies on the tetrachromophoric systems
 $\text{PhCH}_2\text{CH}_2\text{N} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{NCH}_2\text{CH}_2\text{N} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array}$ and $\text{PhCH}_2\text{CH}_2\text{N} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{NCH}_2\text{CH}_2\text{N} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{O}$ indicated
 that they behaved in a similar manner to $\text{PhCH}_2\text{CH}_2\text{N} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{NMe}$

COMPOUND	SOLVENT		
		THF	MeCN
	$\lambda_{\max}$ (ϕ_{f_E})	$\lambda_{\max}$ (ϕ_{f_E})	$\lambda_{\max}$ (ϕ_{f_E})
$\text{PhCH}_2\text{CH}_2\text{N} \begin{cases} \text{Et} \\ \text{CH}_2\text{CH}_2\text{NMe}_2 \end{cases}$	327	-	(a)
$\text{PhCH}_2\text{CH}_2\text{N} \begin{array}{c} \diagup \\ \text{NMe} \end{array}$	330, 350 (0.053)	395	(a)
$\text{PhCH}_2\text{CH}_2\text{N} \begin{array}{c} \diagup \\ \text{O} \end{array}$	287 (0.137)	357 (0.020)	380 (0.008)

(a) No fluorescent exciplex formation observed in this solvent.

TABLE 6.(7). Fluorescence $\lambda_{\max}$ Values (nm) and Quantum Yields of Fluorescent Exciplex Formation for Selected Phenylethyl Derivatives in Degassed Cyclohexane, Tetrahydrofuran and Acetonitrile at 20°C.

giving a long wavelength emission which we attribute to fluorescence from an intramolecular ternary exciplex. In cyclohexane solution $\text{PhCH}_2\text{CH}_2\text{N} \begin{array}{c} \diagup \\ \text{NMe} \end{array}$ appeared to give a dual emission with maxima at 330 and 350nm, it is possible that this may be due to emission from both a ternary complex (350nm) and a exciplex formed between the phenyl and the nearer of the two amino groups.

CHAPTER SEVEN

Experimental.

7.1. INSTRUMENTATION.

The practical work presented in this thesis was carried out in the Department of Chemistry, The University of Leicester, between October 1978 and September 1980, and in the Department of Chemistry, The City University, London (TCU), between October 1980 and September 1981. Consequently, the site at which certain pieces of apparatus were used is also quoted, where necessary.

7.1.(1). IR Spectra.

These were recorded either as Nujol mulls or as neat films, using a Perkin-Elmer 257 grating spectrophotometer (Leicester), or a Perkin-Elmer 157G grating spectrophotometer (TCU). All $\nu_{\max}$ values are quoted in cm^{-1} units and the following letters used in abbreviating the signal strengths;

br-broad, m-medium, s-strong, v-very, w-weak.

7.1.(2). U/V-Visible Spectra.

Where the spectra were recorded on chart paper, measurements were made, using a Pye-Unicam SP800 u/v-visible spectrophotometer (Leicester) and a Perkin-Elmer 402 u/v-visible spectrophotometer (TCU). Spectra recorded on the 402 instrument were calibrated using a Holmium Oxide glass standard. On occasions where solutions of known optical density at a specific wavelength were required, but their absorption spectra were not needed, the solutions were prepared using a Cecil Instruments CE 272 Linear Readout Ultraviolet Spectrophotometer (TCU).

7.1.(3). ^1H NMR Spectra.

These were measured using a Varian T60 spectrometer, recorded at 60MHz (Leicester) and on a Jeol JNM-MH 100 NMR spectrometer, operated at 100MHz (TCU), utilising an external lock. Tetramethylsilane (TMS) was used as the internal standard, and deuterio-chloroform (CDCl_3), used as the solvent. All spectral chemical shifts are quoted in δ units (ppm), together with

integrated signal intensities. The following abbreviations are utilised in the spectral interpretations;

s-singlet, d-doublet, t-triplet, q-quartet,
m-multiplet, br-broad.

Coupling constants are recorded where necessary in Hz.

7.1.(4). Accurate Mass Spectrometry (AMS).

Measurements were carried out by Mr C. Whitehead, using a Kratos MS 30 Electron Impact (EI) mass spectrometer, linked to a Data System 50 (DS50), at the Department of Chemistry, TCU. Samples were run either at 20eV or 70eV, and deviations from the expected masses are quoted in milli-mass units (mmu). Where possible, the mass peak (M^+) and the base peak (100%) are given.

7.1.(5). Elemental Analysis.

C,H,N, Analyses are quoted in percentages, and for those compounds containing oxygen, the % oxygen content has been determined by difference. Analyses were performed by C,H,N, Analysis Ltd., S. Wigston, Leicester and by Mr P. Hemming (TCU), using a Carlo Erba Model 1106 Elemental Analyser.

7.1.(6). ^{15}N NMR Spectra.

The proton noise decoupled Fourier Transform NMR spectra of some of the amine systems detailed in this thesis, were recorded at 18.24 MHz, by the Physico-Chemical Measurements Unit (PCMU), Harwell, Didcot, Oxon. Samples were run in deutero-chloroform (CDCl_3), in the presence of a paramagnetic relaxation reagent tris-(acetoacetato)chromium III, $\text{Cr}(\text{acac})_3$.

7.1.(7). Melting Points / Boiling Points.

Melting points were recorded using a Kopfler block melting point apparatus and are uncorrected. All compounds prepared as oils, were distilled under reduced pressure, using a Büchi Kugel oven. Boiling points are not corrected.

7.1.(8). Preparative Gas Liquid Chromatography (Prep GLC).

The tertiary alicyclic amines and toluene, were purified by Prep GLC before use. A Pye-Unicam Model 105 Preparative GLC machine was employed, fitted with a 20% Peg A column, using a mixture of 60% ethylene glycol- 40% water and 'cardice' as the coolant. Samples of up to 150 μ l were injected, discarding the material collected under the tails of the major peak. Purified compounds were then sealed into ampoules for long term storage.

7.1.(9). Solvents.

Benzene and diethylether, were dried over sodium wire and tetrahydrofuran was freshly distilled from lithium aluminium hydride before use. Petroleum spirit fractions were distilled to remove any higher boiling impurities.

7.2. PREPARATION OF 1-NAPHTHYL DERIVATIVES.

7.2.(1). Purification of 2-(1'-naphthyl)ethanoic acid (2- α NEA).

Previous work on 1-naphthyl derivatives had demonstrated the need to purify the 2- α NEA, prior to use. 2- α NEA (0.01 mole) was dissolved in chloroform (200cm³) and a cooled solution of 1.2 equivalents of potassium hydroxide (0.12 mole in 200cm³) added. After thorough agitation, the chloroform layer was separated off and discarded. The purified 2- α NEA was liberated by the addition of a 50/50 v/v mixture of concentrated hydrochloric acid and water, with stirring. The material was filtered under suction, washed with water to remove all traces of HCl and dried in a vacuum desiccator, over a fresh sample of P₂O₅. Yield; 18.0g (97%).

7.2.(2). 2-(1'-naphthyl)ethanoyl chloride (2- α NEC).

2- α NEA (0.01 mole) was dissolved in sodium dried benzene

(100cm³) and oxalyl chloride (0.03 mole) added, refluxing the resultant mixture under nitrogen for 2-3 hours. Removal of the solvent and excess oxalyl chloride on a rotary evaporator (Büchi Rotavapor R110), yielded the 2- α NEC ($\sim$ 0.01 mole), as a yellow opaque liquid. The 2- α NEC was not purified or characterised, but was used directly in the next reaction.

7.2.(3). N-(2-(1'-naphthyl)-1-oxo-ethyl)azacyclopentane.

The acid chloride prepared in 7.2.(2). was dissolved in sodium dried ether (50cm³) and added slowly to a stirred solution of azacyclopentane (pyrrolidine) (2.5 equivalents) in sodium dried ether (75cm³), producing large quantities of pyrrolidine hydrochloride. After stirring at room temperature under nitrogen for about 12 hours, water was added (50cm³) and the ether layer separated off from the resultant clear solution. Extracting the aqueous layer with a further portion of ether (50cm³), the combined ether extracts were dried over MgSO₄, filtration and removal of solvent yielding the product as a pale yellow opaque oil. Ensuring that the amide was dry, the sample was characterised, but not purified prior to the next stage.

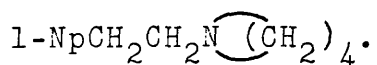


IR(Neat); 3030(m) 2980(s) 2900(s) 1640(s) 1600(m) 1510(m) 1465-1425(s) 810-775(s), ¹H NMR; 1.70-2.04 δ (4H,m,ring CH₂), 3.40 δ (2H,t,CH₂NCO), 3.52 δ (2H,t,CH₂NCO), 4.08 δ (2H,s,NpCH₂CO), 7.24-8.08 δ (7H,m,Np).

7.2.(4). N-(2-(1'-naphthyl)ethyl)azacyclopentane.

The amide produced in 7.2.(3). (0.01 mole), was dissolved in sodium dried ether (50cm³) and added slowly, to an ice-cooled stirred suspension of lithium aluminium hydride (2 molar equivalents) in sodium dried ether (75cm³), under a dry atmosphere of nitrogen. After refluxing the reaction mixture for about 4

hours, it was cooled and the excess lithium aluminium hydride destroyed. By minimising the volume of water added, the alumina produced, remained granular in nature, rather than forming a pasty slurry and facilitated filtration under suction. After washing the residue with water and ether, the ether layers were combined and dried over MgSO_4 . Filtration and removal of the solvent, yielded the amine as a clear pale yellow oil. The amine 7.2.(4). was purified by vacuum distillation and then characterised.



B.pt. $168^\circ\text{-}170^\circ\text{C}$ @ $\sim 0.05\text{mm}$, IR(Neat); 3070(m) 2980(s) 2890(m) 2800(m) 1600(m) 1515(m) 1460(m) 1400(m) 805(s) 785(s), ^1H NMR; 1.60-2.12 δ (4H,m,ring CH_2), 2.33-3.10 δ (6H,m, CH_2N), 3.10-3.67 δ (2H,m, CH_2Np), 7.23-8.33 δ (7H,m,Np), CHN; $\text{C}_{16}\text{H}_{19}\text{N}$, Expected % C 85.28 H 8.50 N 6.22 Actual % C 85.43 H 8.54 N 6.27, AMS; M^+ 225.1465 (0.26%, -5.2mmu), $\text{C}_8\text{H}_{16}\text{N}$ 126.1199 (100%, -8.4mmu), $\text{C}_5\text{H}_{10}\text{N}$ 84.0741 (93.25%, -7.2mmu).

7.2.(5). N-(2-(1'-naphthyl)-1-oxo-ethyl)azacyclohexane.

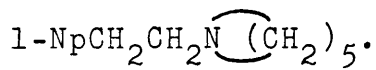
The amide was prepared according to 7.2.(3). using 2- α NEC prepared in 7.2.(2). and azacyclohexane (piperidine). The product was characterised but not purified before use in 7.2.(6).



IR(Neat); 3060(w) 2950(s) 2870(m) 1640(vs) 1600(m) 1500(m) 1440(s) 800(s) 790(s). ^1H NMR; 1.42-1.76 δ (6H,m,ring CH_2), 3.25-3.63 δ (4H,m, NCH_2), 4.12 δ (2H,s, NpCH_2CO), 7.23-8.09 δ (7H,m,Np).

7.2.(6). N-(2-(1'-naphthyl)ethyl)azacyclohexane.

The amine was prepared by lithium aluminium hydride reduction of the amide 7.2.(5). as described in 7.2.(4). and purified by vacuum distillation, prior to use.



B.pt. 172°-173°C @ 0.05mm, IR(Neat); 3060(m) 2950(s) 2870(m) 2780(m) 1600(m) 1510(m) 1470(m) 800(s) 780(s), ¹H NMR; 1.20-1.84 δ (6H,m,ring CH₂), 2.36-2.88 δ (6H,m,CH₂N), 3.16-3.44 δ (2H,m,CH₂Np), 7.20-8.08 δ (7H,m,Np), CHN; C₁₇H₂₁N, Expected % C 85.31 H 8.84 N 5.85 Actual % C84.98 H 8.94 N 6.13, AMS (20eV); M⁺ 239.1685 (0.25%, 1.1mmu), C₆H₁₂N 98.0995 (100%, 2.6mmu).

7.2.(7). N-(2-(1'-naphthyl)-1-oxo-ethyl)azacycloheptane.

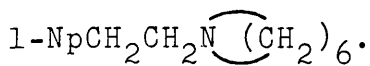
The amide was prepared by the method 7.2.(3)., using an excess of azacycloheptane to trap the HCl generated in the reaction. The material was not purified, but was used directly in the next stage.



IR(Neat); 3040(m) 2920(vs) 2850(s) 1630(vs) 1600(m) 1510(s) 1480-1400(vs) 785(s) 770(s), ¹H NMR; 1.26-1.79 δ (8H,m,ring CH₂), 3.13-3.56 δ (4H,m,NCH₂), 4.00 δ (2H,s,NpCH₂CO), 7.20-8.10 δ (7H,m,Np).

7.2.(8). N-(2-(1'-naphthyl)ethyl)azacycloheptane.

The amine was prepared by reduction of 7.2.(7). using the method outlined in 7.2.(4). The product was purified by preparative thick layer chromatography (Prep TLC), using alumina and 40% diethylether - 60% petroleum spirit (60°-80°C) as the solvent system for developing the plate, to remove the last traces of the amide and then distilled under vacuum.



B.pt. 171°-173°C @ 0.075mm, IR(Neat); 3040(m) 2920(vs) 2850(m) 1600(m) 1510(m) 1470(m) 1395(m) 795(s) 775(s), ¹H NMR; 1.62-1.82 δ (8H,m,ring CH₂), 2.72-3.00 δ (4H,m,NCH₂), 3.18-3.36 δ (2H,m,NpCH₂), 7.20-8.16 δ (7H,m,Np), CHN; C₁₈H₂₃N, Expected %

C 85.32 H 9.15 N 5.53 Actual % C 85.03 H 8.99 N 5.29, AMS; M^+ 253.1867 (0.30%, 1.1mmu), $C_7H_{14}N$ 112.1137 (100%, 1.1mmu).

7.2.(9). N-(2-(1'-naphthyl)-1-oxo-ethyl)azacyclooctane.

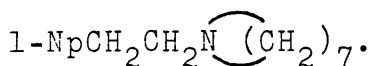
The amide was prepared by method 7.2.(3). and was used in the unpurified form in the next reaction.



IR(Neat); 3060(m) 2960(vs) 2870(s) 1645(vs) 1600(m) 1510(w) 1470-1390(s) 795(s) 785(s), 1H NMR; 1.33-1.93 δ (10H,m,ring CH_2), 3.26-3.69 δ (4H,m, NCH_2), 4.15 δ (2H,s, $NpCH_2CO$), 7.26-8.10 δ (7H,m,Np).

7.2.(10). N-(2-(1'-naphthyl)ethyl)azacyclooctane.

The amide 7.2.(9). was reduced using lithium aluminium hydride by method 7.2.(4). The product was purified by Prep TLC to remove the last traces of the amide, using alumina plates and 25% diethylether - 75% petroleum spirit as the solvent system. The material isolated was further purified by vacuum distillation.



B.pt. 176°-178°C @ ~0.05mm, IR(Neat); 3050(m) 2910(vs) 2850(s) 1600(m) 1510(m) 1480-1440(m) 800(s) 775(s), 1H NMR; 1.40-1.83 δ (10H,m,ring CH_2), 2.53-3.00 δ (6H,m, NCH_2), 3.00-3.43 δ (2H,m, $NpCH_2$), 7.24-8.21 δ (7H,m,Np), CHN; $C_{19}H_{25}N$, Expected % C 85.34 H 9.42 N 5.24 Actual % C 85.19 H 9.54 N 4.99, AMS (70eV); M^+ 267.1899 (0.06%, -8.8mmu), $C_7H_{14}N$ 112.1091 (100%, -3.5mmu), $C_8H_{16}N$ 126.1236 (55.77%, -4.6mmu).

7.2.(11). N-(2-(1'-naphthyl)-1-oxo-ethyl)azacyclononane.

Method 7.2.(3). was modified slightly, by use of equimolar amounts of 2- α NEC and azacyclononane and the addition of triethylamine (2 equivalents), to trap the HCl produced in the reaction. The amide 7.2.(11)., a viscous pale yellow oil, was

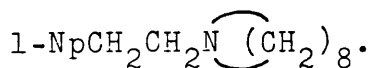
used without purification in reaction 7.2.(12)., but was characterised.



IR(Neat); 3040(m) 2900(vs) 2860(s) 1630(vs) 1600(s) 1510(s) 1480-1400(vs) 1380(s) 795(vs) 780(vs), ¹H NMR; 1.20-2.00 δ (12H,m,ring CH₂), 3.24-3.66 δ (4H,m,NCH₂), 4.17 δ (2H,s,NpCH₂CO), 7.24-8.13 δ (7H,m,Np).

7.2.(12). N-(2-(1'-naphthyl)ethyl)azacyclononane.

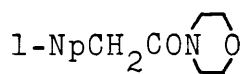
The reduction of amide 7.2.(11). using lithium aluminium hydride, was carried out according to the method used for 7.2.(4). The crude amine was isolated as a fairly viscous clear yellow oil, which was purified by Prep TLC using alumina plates and 10% diethylether - 90% petroleum spirit (60°-80°C), as the solvent system. The amine 7.2.(12). was then vacuum distilled and characterised.



B.pt. 180°-182°C @ 0.05mm, IR(Neat); 3050(m) 2910(vs) 2850(s) 1600(m) 1510(m) 1470(m) 1360(m) 800(s) 775(s), ¹H NMR; 1.33-1.93 δ (12H,m,ring CH₂), 2.45-3.05 δ (4H,m,NCH₂), 3.05-3.50 δ (2H,m,NpCH₂), 7.23-8.23 δ (7H,m,Np), CHN; C₂₀H₂₇N, Expected % C 85.35 H 9.67 N 4.98 Actual C 85.20 H 9.79 N 5.13, AMS (70eV); M⁺ 281.2082 (0.59%, -6.1mmu), C₉H₁₈N 140.1504 (100%, 6.5mmu).

7.2.(13). N-(2-(1'-naphthyl)-1-oxo-ethyl)-1-aza-4-oxacyclohexane.

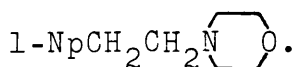
The amide was prepared by the method described in 7.2.(3). using an excess of 1-aza-4-oxacyclohexane (morpholine), to trap the HCl produced. Addition of water however did not result in the dissolution of the solid, which upon filtration and drying over P₂O₅ was characterised as the amide required. The derivative was recrystallised from petroleum spirit (60°-80°C).



M.pt. 106°-108°C, IR(Nujol); 3070(w) 2970(s) 2870(s) 1650(s) 1510(m) 1115(s) 800(s) 775(s), ¹H NMR; 3.35-3.76 δ (4H,m, CONCH₂), 3.80-3.98 δ (4H,m,OCH₂), 4.02 δ (2H,s,NpCH₂CO), 7.10-7.98 δ (7H,m,Np), CHN; C₁₆H₁₇NO₂, Expected % C 75.27 H 6.71 N 5.49 O 12.53 Actual % C 75.35 H 6.79 N 5.63 O 12.23, AMS; M⁺ 255.1343 (78.65%, 8.4mmu), C₅H₈NO₂ 114.0526 (100%, -2.9mmu).

7.2.(14). N-(2-(1'-naphthyl)ethyl)-1-aza-4-oxa-cyclohexane.

The amide 7.2.(13). was insoluble in ether, but was found to dissolve in the presence of sodium dried benzene, apart from this the reaction was carried out as in 7.2.(4). using lithium aluminium hydride for the reducing agent. The amine was isolated as a pale yellow cloudy liquid, which was purified by prep TLC on alumina plates, with 100% diethylether as the solvent system yielding a clear viscous oil, which was distilled under vacuum and then characterised.

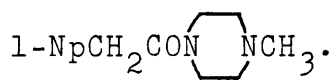


B.pt. 185°-187°C @ ~0.03mm, IR(Neat); 3060(m) 2980(s) 2880(s) 1600(m) 1510(m) 1470(m) 1120(vs) 800(vs) 785(vs), ¹H NMR; 2.40-2.95 δ (6H,m,NCH₂), 3.08-3.48 δ (2H,m,NpCH₂), 3.63-3.92 δ (4H,m,OCH₂), 7.35-8.21 δ (7H,m,Np), CHN; C₁₆H₁₉NO, Expected % C 79.63 H 7.93 N 5.80 O 6.64 Actual % C 79.63 H 8.03 N 5.58 O 7.03, AMS; M⁺ 241.1309 (0.64%, -15.8mmu), C₅H₁₀NO (100%, -19.6mmu).

7.2.(15). N-(2-(1'-naphthyl)-1-oxo-ethyl)N'-methyl-1,4-diazacyclohexane.

The reaction was carried out according to method 7.2.(3)., using an excess of N-methyl-1,4-diazacyclohexane (N-methyl piperazine). Since quaternisation of the terminal amino group of the amide 7.2.(15). was possible, the reaction was basified with potassium hydroxide solution.. The white solid remaining,

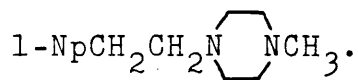
was extracted with several portions of ether (3 X 50cm³), which were then combined with the ether layer from the reaction mixture. After drying and removal of the solvent, the amino-amide 7.2.(15)_, was isolated as a white solid, recrystallised from petroleum spirit (60°-80°C), as white needles and characterised, prior to reduction to the diamino- derivative in the next stage.



M.pt. 116°-118°C, IR(Nujol); 3030(w) 2830(br,s) 1630(s) 1460-1430(s) 1375(s) 780(s), ¹H NMR; 2.20 δ (3H,s,NCH₃), 2.00-2.50 δ (4H,m,NCH₂), 3.26-3.83 δ (4H,m,CONCH₂), 4.08 δ (2H,s, NpCH₂CO), 7.20-8.07 δ (7H,m,Np), CHN; C₁₇H₂₀N₂O, Expected % C 76.09 H 7.51 N 10.44 O 5.96 Actual % C 76.10 H 7.37 N 10.22 O 6.31, AMS; M⁺ 268.1560 (37.16%, -1.6mmu), C₄H₈N 70.0666 (100%, -1.0mmu).

7.2.(16). N-methyl-N'-(2-(1'-naphthyl)ethyl)-1,4-diazacyclohexane.

The reduction of the amino-amide 7.2.(15)_, was carried out using lithium aluminium hydride (3 equivalents), according to the method described in 7.2.(4)_, except that the amino-amide, which was difficult to dissolve in ether, was added as a slurry. The amine 7.2.(16)_, was isolated as a pale yellow slightly opaque oil in >90% yield. Purification was achieved by column chromatography, using alumina (UG1) as the stationary phase, and varying the elutant from 100% petroleum spirit (60°-80°C), to 100% diethylether. After recording a comparative TLC plate, the required fractions were combined and the diamino derivative 7.2.(16)_, was isolated as a slightly coloured opaque liquid. Vacuum distillation yielded a clear yellow oil, which was then characterised.



B.pt. 201°-203°C @ 0.03 mm, IR(Neat); 3040(m) 2920(s) 2840-2740(vs) 1600(s) 1510(s) 1470(s) 800-770(vs), ¹H NMR; 2.30 δ (3H,s,NCH₃), 2.30-2.91 δ (10H,m,NCH₂), 3.03-3.50 δ (2H,m,NpCH₂), 7.23-8.20 δ (7H,m,Np), CHN; C₁₇H₂₂N₂, Expected % C 80.27 H 8.72 N 11.01 Actual % C 80.32 H 8.65 N 11.00, AMS; M⁺ 254.1683 (0.36%, -10.0mmu), C₆H₁₃N₂ 113.0983 (100%, -9.5).

7.2.(17). N-(2-(1'-naphthyl)-1-oxo-ethyl)azacyclotridecane.

The amide 7.2.(17). was prepared by method 7.2.(3). (0.015 mole), using dry triethylamine (0.02 mole), to trap the HCl produced. The white solid in the reaction mixture was filtered off under suction, and thoroughly washed with water, to dissolve the triethylamine-hydrochloride. The residual material was isolated and identified as the required amide. The remainder of the amide was isolated from the ethereal filtrate, after drying. The product was recrystallised from diethylether-petroleum spirit (40°-60°C) mixed solvent, as white needles, and was characterised before reduction.

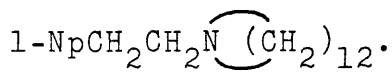


M.pt. 81°-84°C, IR(Nujol); 3050(w) 2930(vs) 2860(s) 1635(vs) 1600(m) 1510(w) 1460-1430(s) 1380(s) 790(s) 770(s), ¹H NMR; 1.00-1.90 δ (20H,m,ring CH₂), 3.10-3.53 δ (4H,m,NCH₂), 4.67 δ (2H,s,NpCH₂CO), 7.20-8.00 δ (7H,m,Np), CHN; C₂₄H₃₃NO, Expected % C 82.00 H 9.46 N 3.99 O 4.55 Actual % C 81.86 H 9.65 N 3.93 O 4.56, AMS (70eV); M⁺ 351.2492 (30.70%, -7.0mmu), C₁₃H₂₄NO 210.1826 (100%, -3.2mmu).

7.2.(18). N-(2-(1'-naphthyl)ethyl)azacyclotridecane.

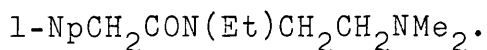
Since the amide 7.2.(17)., was only partially soluble in ether, the reduction with lithium aluminium hydride, was carried out in tetrahydrofuran solution. Although the method used, was

basically that of 7.2.(4)., the reaction mixture was refluxed at a higher temperature ($\sim 75^{\circ}\text{C}$). Since THF and water are miscible, ether was added to the reaction mixture during the work-up, to try and cause a phase separation. Drying and removal of the solvent, yielded a viscous yellow-orange oil, which on characterisation by IR spectroscopy, indicated the presence of a small amount of the amide 7.2.(17). Distillation under vacuum, gave a slightly coloured clear oil, which was then characterised.



B.pt. $164^{\circ}\text{--}167^{\circ}\text{C}$ @ $\sim 0.1\text{mm}$, IR(Neat); 3040(m) 2920(vs) 2850(s) 1600(m) 1510(m) 1460(s) 800(s) 775(s), ^1H NMR; 1.32-1.89 δ (20H,m,ring CH_2), 2.57-2.90 δ (4H,m, CH_2N), 2.98-3.41 δ (2H,m, CH_2Np), 7.20-8.28 δ (7H,m,Np), CHN; $\text{C}_{24}\text{H}_{35}\text{N}$, Expected % C 85.40 H 10.45 N 4.15 Actual % C 84.96 H 10.69 N 4.25, AMS; M^+ 337.2798 (0.19%, 2.9mmu), $\text{C}_{13}\text{H}_{26}\text{N}$ 196.2032 (100%, -3.3mmu).
7.2.(19). N,N-dimethyl-N'-ethyl-N'-(2-(1'-naphthyl)-1-oxo-ethyl)-1,2-diaminoethane.

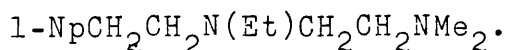
The amide was prepared by the method 7.2.(3). (0.02 mole), using triethylamine (0.03 mole), to trap the HCl produced. The reaction mixture was made basic by the addition of potassium hydroxide, and extracted in the standard way. The amide 7.2.(19). was isolated as a yellow-orange oil (80% yield), and was then characterised.



IR(Neat); 3050(m) 2920(s) 2850(s) 2760(s) 1620(s) 1600(m) 1510(m) 1470-1400(br,s) 1370-1350(s) 780-770(s), ^1H NMR; 1.10 δ , 1.16 δ (3H,t, CH_2CH_3), 2.13 δ , 2.23 δ (6H,s, NCH_3), 2.00-2.67 δ (2H,m, CH_2NMe_2), 3.10-3.69 δ (4H,m, NCH_2), 4.07 δ , 4.13 δ (2H,s, NpCH_2CO), 7.21-8.13 δ (7H,m,Np).

7.2.(20). N,N-dimethyl-N'-ethyl-N'-(2-(1'-naphthyl)ethyl)-1,2-diaminoethane.

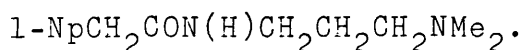
The reduction of the amide 7.2.(19). was carried out using lithium aluminium hydride, following the method of 7.2.(4). The amine 7.2.(20). was isolated as a pale yellow slightly opaque oil, in >90% yield and purified by column chromatography, (alumina UG1, varying the elutant from petroleum spirit (60°-80°C) to diethylether). After running a comparative TLC plate the required fractions were combined and worked up, to yield the amine as a slightly coloured oil (75% yield). After vacuum distillation the amine was characterised.



B.pt. 172°-174°C @ 0.05mm, IR(Neat); 3050(m) 2920(s) 2810(s) 1600(m) 1510(m) 1460(s) 1390(m) 790(s) 770(s), ¹H NMR; 1.10 δ (3H,t,CH₂CH₃), 2.26 δ (6H,s,NMe₂), 2.76 δ (2H,q,CH₂CH₃), 2.20-3.05 δ (6H,m,NCH₂), 3.05-3.46 δ (2H,m,NpCH₂), 7.23-8.16 δ (7H,m,Np), CHN; C₁₈H₂₆N₂, Expected % C 79.95 H 9.69 N 10.36 Actual % C 79.51 H 9.88 N 10.56, AMS; M⁺ C₁₈H₂₆N₂ not detected, C₁₅H₁₈N, 212.1464 (100%, 2.4mmu).

7.2.(21). N,N-dimethyl-N'-(2-(1'-naphthyl)-1-oxo-ethyl)-1,3-diaminopropane.

The reaction was carried out by method 7.2.(3). using an excess of N,N-dimethyl-1,3-diaminopropane. The resultant amino-amide, was isolated as a pale buff coloured material, recrystallised from petroleum spirit (60°-80°C), as white needles and then characterised.



M.pt. 76°-78°C, IR(Nujol); 3100(w) 2940(s) 2870(s) 1635(s) 1565(m) 1465(m) 800(s) 790(s), ¹H NMR; 1.26-1.56 δ (2H,m,CH₂-CH₂CH₂), 1.62 δ (6H,s,NMe₂), 2.00 δ (2H,t,CH₂NMe₂), 3.14-3.32 δ

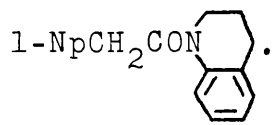
(2H,m,NHCH₂), 3.98 δ (2H,s,NpCH₂CO), 7.28-7.60 δ (4H,m,Np), 7.72-7.98 δ (3H,m,Np), CHN; C₁₇H₂₂N₂O, Expected % C 75.52 H 8.20 N 10.36 O 5.92 Actual % C 75.52 H 8.45 N 10.03 O 6.03 AMS; M⁺ 270.1701 (8.64%, -3.1mmu), C₃H₈N 58.0624 (100%, -3.3mmu), C₆H₁₃N₂O 129.0982 (4.92%, -4.6mmu).

7.2.(22). N,N-dimethyl-N'-(2-(1'-naphthyl)ethyl)-1,3-di-aminopropane.

Attempts were made to reduce the secondary amide 7.2.(21). using both lithium aluminium hydride and sodium borohydride as the reducing agent, but both reactions were unsuccessful.

7.2.(23). N-(2-(1'-naphthyl)-1-oxo-ethyl)-1,2,3,4-tetrahydroquinoline.

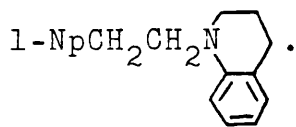
The amide 7.2.(23). was prepared by method 7.2.(3)., using an excess of 1,2,3,4-tetrahydroquinoline to trap the HCl produced. Work-up yielded the amide as a solid, which was recrystallised from ethanol as white needles. The product was then characterised, prior to reduction in the next stage.



IR(Nujol); 3040(w) 2920(s) 2850(s) 1650(s) 1600(m) 1470(s) 1380(s) 780(s) 765(s), ¹H NMR; 1.80 δ (2H,m,CH₂CH₂CH₂), 2.50 δ (2H,t,CH₂Ar), 3.70 δ (2H,t,NCH₂), 4.13 δ (2H,s,NpCH₂-CO), 6.90-7.77 δ (11H,m,Np,Ar).

7.2.(24). N-(2-(1'-naphthyl)ethyl)-1,2,3,4-tetrahydroquinoline.

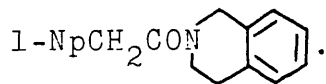
The amide 7.2.(23)., (0.06 mole), was reduced using lithium aluminium hydride by method 7.2.(4). The amine was isolated as a cream coloured solid (89%), recrystallised from petroleum spirit (60°-80°C), as colourless needles and then characterised.



M.pt. 125°-128°C, IR(Nujol); 3060(m) 2920(s) 2850(s) 1600(s) 1510(s) 1465(s) 1355(s) 1200(s) 790(s) 775(s) 740(s) 710(w), ¹H NMR; 1.85 δ (2H,m,CH₂CH₂CH₂), 2.65 δ (2H,t,CH₂Ar), 3.00-3.85 δ (6H,m,CH₂N(4H); CH₂Np(2H)), 6.28-6.95 δ (4H,m,Ar), 7.03-8.06 δ (7H,m,Np), CHN; C₂₁H₂₁N, Expected % C 87.76 H 7.37 N 4.87 Actual % C 87.50 H 7.42 N 4.59, AMS; M⁺ 287.1642 (7.88%, -3.2mmu), C₁₀H₁₂N 146.0885 (100%, -8.4mmu).

7.2.(25). N-(2-(1'-naphthyl)-1-oxo-ethyl)-1,2,3,4-tetrahydro-isoquinoline.

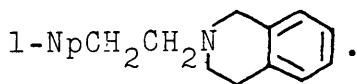
The amide was prepared as in 7.2.(3) ., using an excess of 1,2,3,4-tetrahydro-isoquinoline, to trap the HCl generated. The product 7.2.(25) ., was isolated as an orange viscous oil, characterised and then used without further purification in the reduction 7.2.(26).



IR(Neat); 3040(m) 2970(m) 2860(m) 1630(s) 1600(m) 1510(m) 1450-1420(s) 1370(m) 785(s) 770(s) 750(s), ¹H NMR; 2.33-3.00 δ (2H,m,CH₂CH₂Ar), 3.26-4.00 δ (2H,m,CH₂CH₂NCO), 4.05 δ (2H,s,NpCH₂CO), 4.33-4.80 δ (2H,m,ArCH₂NCO), 6.56-8.10 δ (11H,m,NpAr).

7.2.(26). N-(2-(1'-naphthyl)ethyl)-1,2,3,4-tetrahydro-isoquinoline.

The reduction was carried out by method 7.2.(4) ., yielding the amine 7.2.(26) . as a yellow viscous oil. After purification by Prep TLC (alumina, 50% petroleum spirit (60°-80°C) - 50% diethylether), the amine, a clear yellow viscous oil, was then characterised.



IR(Neat); 3040(s) 2960(s) 2760(s) 1600(s) 1510(s) 1395(s)

800(s) 775(s) 745(s), AMS; M^+ $C_{21}H_{21}N$ 287.1539 (0.53%, -13.5mmu), $C_{10}H_{12}N$ 146.0795 (100%, -17.5mmu).

7.2.(27). N-(2-(1'-naphthyl)-1-oxo-ethyl)-N'-(2-azacyclopentyl-2-oxo-ethyl)-1,4-diazacyclohexane.

The diamido compound 7.2.(27). was synthesised according to method 7.2.(3)., but using equimolar quantities of 2- α NEC and N-(2-azacyclopentyl-2-oxo-ethyl)-1,4-diazacyclohexane. The HCl generated, was trapped by triethylamine (2 equivalents). The white solid remaining after addition of water, was filtered under suction, washed and then dried over P_2O_5 , in a vacuum desiccator, (79%). Characterisation revealed that the solid was the required diamide 7.2.(27).

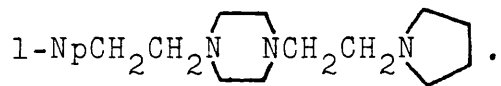


IR(Nujol); 3040(w) 2920(vs) 2860(s) 1640(s) 1600(m) 1470-1450(s) 805(s) 790(m), 1H NMR; 1.72-2.06 δ (4H,m,ring CH_2), 2.34-2.72 δ (4H,m, $\underline{CH_2}$ NCH₂CO), 3.10 δ (2H,s,NCH₂CON), 3.28-3.88 δ (8H,m,C(O)NCH₂), 4.16 δ (2H,s,NpCH₂C(O)), 7.22-8.04 δ (7H,m,Np), AMS; M^+ 365.2151 (26.81%, 4.8mmu), $C_{17}H_{19}N_2O$ 267.1210 (100%, -28.7mmu).

7.2.(28). N-(2-(1'-naphthyl)ethyl)-N'-(2-(azacyclopentyl)-ethyl)-1,4-diazacyclohexane.

The reduction was carried out as in 7.2.(4)., using lithium aluminium hydride (0.025 mole), but the diamide (0.006 mole), had to be added as a slurry in freshly distilled tetrahydrofuran. After work-up, the ether was added to the THF filtrate, to displace some of the water from the organic phase. The crude product, was obtained as a pale yellow, opaque viscous oil (63%), purified by vacuum distillation and then characterised. The material solidified on cooling. A

lower boiling fraction was identified as N-(2-(azacyclopentyl)ethyl)-1,4-diazacyclohexane, derived from the initial amino-amide.



M.pt. 46°-49°C, B.pt. 164°-166°C @ ~0.01mm, IR(Nujol);
3050(m) 2960(vs) 2800(vs) 1600(m) 1510(m) 1460(s) 1160-1120(s)
800(vs) 780(vs), ¹H NMR; 1.68-1.88 δ (4H,m,ring CH₂), 2.44-
2.80 δ (18H,m,NCH₂), 3.16-3.38 δ (2H,m,NpCH₂), 7.28-7.54 δ
(4H,m,Np), 7.64-7.88 δ (2H,m,Np), 7.96-8.10 δ (1H,m,Np),
CHN; C₂₂H₃₁N₃, Expected % C 78.29 H 9.26 N 12.45 Actual %
C 78.09 H 9.43 N 12.34, AMS (70eV); M⁺ 337.2465 (0.89%,
-5.3mmu), C₁₇H₂₁N₂ 253.1659 (100%, -4.5mmu).

7.2.(29). N-(2-(1'-naphthyl)-1-oxo-ethyl)-N'-(2-(1-aza-4-oxa-cyclohexyl)-2-oxo-ethyl)-1,4-diazacyclohexane.

The reaction was performed as in 7.2.(27)., following the method of 7.2.(3). The white solid remaining after addition of water was filtered, washed with water and dried over P₂O₅ in a vacuum desiccator and identified as the required diamide 7.2.(29). (80%).

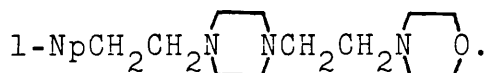


M.pt. 176°-178°C, IR(Nujol); 3050(w) 2960-2920(vs) 2860(s)
1640(s) 1600(m) 1510(m) 1470-1450(vs) 1380(s) 795,790(s)
770(s), ¹H NMR; 2.28-2.58 δ (4H,m,CH₂NCH₂CO), 3.16 δ (2H,s,
NCH₂CO), 3.42-3.82 δ (12H,m,OCH₂,CONCH₂), 4.18 δ (2H,s,NpCH₂-
CO), 7.30-7.64 δ (4H,m,Np), 7.78-8.04 δ (3H,m,Np), AMS; M⁺,
C₂₂H₂₇N₃O₃, 381.1931 (18.23%, -12.1mmu), C₁₇H₁₉N₂O 267.1337
(100%, -16.1mmu).

7.2.(30). N-(2-(1'-naphthyl)ethyl)-N'-(2-(1-aza-4-oxa-cyclohexyl)ethyl)-1,4-diazacyclohexane.

The diamide 7.2.(29)., was reduced as in 7.2.(28)., using

the method of 7.2.(4). Work-up yielded the required amine as a slightly coloured viscous oil, which was purified by vacuum distillation. A lower boiling fraction was identified as the reduction product of the initial amino-amide. The amine 7.2.(30)., solidified after distillation and was further purified by recrystallisation from petroleum spirit (60°-80°C) as white needles, prior to characterisation.



B.pt. 175°-179°C @ ~0.02mm, M.pt. 52°-55°C, IR(Nujol); 3050(m) 2950(vs) 2810(vs) 1600(m) 1510(m) 1450(s) 1160-1120(vs) 870(s) 800(vs) 780(vs), ¹H NMR; 2.44-2.84 δ (18H,m,NCH₂), 3.20-3.40 δ (2H,m,NpCH₂), 3.68-3.84 δ (4H,m,CH₂O), 7.28-7.60 δ (4H,m,Np), 7.68-7.92 δ (2H,m,Np), 8.00-8.16 δ (1H,m,Np), CHN; C₂₂H₃₁N₃O, Expected % C 74.75 H 8.84 N 11.89 O 4.52 Actual % C 74.51 H 9.12 N 11.72 O 4.65, AMS; M⁺ 353.2411 (1.37%, -5.6mmu), C₁₇H₂₁N₂ 253.1468 (100%, -23.6mmu), C₁₁H₂₂-N₃O 212.1627 (26.13%, -13.5mmu).

7.2.(31). 1-Naphthoyl chloride (1-NC).

The acid chloride 7.2.(31)., was prepared according to method 7.2.(2)., using oxalyl chloride. Although 1-naphthoic acid was only partially soluble in benzene, the product was soluble and therefore the normal work-up procedure was followed, giving the 1-naphthoyl chloride (1-NC), as a green slightly opaque solution. No attempt was made either to purify or characterise the product, which was used in the next stage.

7.2.(32). N-(1-(1'-naphthyl)-1-oxo-methyl)azacyclopentane.

The procedure followed was that of method 7.2.(3)., reacting 1-NC with azacyclopentane (2 equivalents), in sodium dried ether. Work-up yielded the amide 7.2.(32)., as a pale

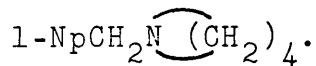
yellow fairly viscous oil, which was characterised, but then used without any purification in reaction 7.2.(33).



IR(Neat); 3050(m) 2970(s) 2880(s) 1625(vs) 1595(s) 1510(s) 1470-1430(vs) 800(s) 785(s), ¹H NMR; 1.66-2.11 δ (4H,m,ring CH₂), 3.10 δ (2H,t,CH₂NCO), 3.80 δ (2H,t,CH₂NCO), 7.24-7.60 δ (4H,m,Np), 7.72-7.94 δ (3H,m,Np).

7.2.(33). N-((1'-naphthyl)methyl)azacyclopentane.

The amide 7.2.(32)., was reduced using lithium aluminium hydride following method 7.2.(4). The product, isolated as a clear yellow oil (90%), was purified by vacuum distillation, to leave a clear colourless oil, which was then analysed.



B.pt. 101°-103°C @ ~0.01mm, IR(Neat); 3050(m-s) 2970(vs) 2880(s) 2800(vs) 1600,1510(s) 1460(s)1350(s) 800,780(vs), ¹H NMR; 1.64-1.92 δ (4H,m,ring CH₂), 2.46-2.74 δ (4H,m,NCH₂), 4.09 δ (2H,s,NpCH₂N), 7.42-7.70 δ (4H,m,Np), 7.78-8.02 δ (2H,m,Np), 8.30-8.52 δ (1H,m,Np), CHN; C₁₅H₁₇N, Expected % C 85.26 H 8.11 N 6.63 Actual % C 85.21 H 7.96 N 6.72, AMS; M⁺ 211.1319 (56.91%, -4.2mmu), C₁₁H₉ 141.0779 (91.32%, 7.4mmu), C₅H₁₀N 84.0430 (66.08%, -38.3mmu).

7.2.(34). N-(1-(1'-naphthyl)-1-oxo-methyl)azacyclohexane.

The amide was prepared as in 7.2.(32)., using an excess of azacyclohexane (2 equivalents), and was isolated as a pale cream coloured solid (~95%). The material was characterised, and then reduced to the required amine in the next stage.

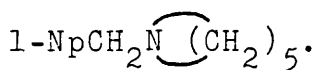


M.pt. 91°-93°C, IR(Nujol); 3040(w) 2960(s) 2930(vs) 1630, 1620(vs) 1595(m) 1475-1450(s) 820,805(s) 790(m-s), ¹H NMR; 1.22-1.90 δ (6H,m,ring CH₂), 3.10 δ (2H,t,CH₂NCO), 3.88 δ

(2H,m,CH₂NCO), 7.30-7.56 δ (4H,m,Np), 7.70-7.98 δ (3H,m,Np),
CHN; C₁₆H₁₇NO, Expected % C 80.30 H 7.16 N 5.85 O 6.69
Actual % C 80.25 H 7.21 N 5.71 O 6.83, AMS; M⁺ 239.1280
(26.67%, -3.0mmu), C₁₁H₇O 155.0408 (27.06%, -8.9).

7.2.(35). N-((1'-naphthyl)methyl)azacyclohexane.

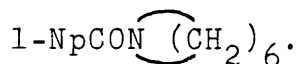
The amide 7.2.(34)_, was reduced by method 7.2.(4)_, to
yield the required amine as a clear yellow oil (>95%). The
material was purified by vacuum distillation, to give a clear
colourless oil, which was subsequently characterised.



B.pt. 97°-99°C @ ~0.01mm, IR(Neat); 3050(m-s) 2940(vs)
2860(s) 2760(s) 1600(m-s) 1510(s) 1390-1255(series,s) 800,785
(vs) 770(vs), ¹H NMR; 1.40-1.68 δ (6H,m,ring CH₂), 2.36-2.56
δ (4H,m,NCH₂), 3.88 δ (2H,s,NpCH₂N), 7.36-7.58 δ (4H,m,Np),
7.66-7.88 δ (2H,m,Np), 8.24-8.38 δ (1H,m,Np), CHN; C₁₆H₁₉N,
Expected % C 85.28 H 8.50 N 6.22 Actual % C 85.11 H 8.65
N 6.28, AMS; M⁺ 225.1565 (43.66%, 4.7mmu), C₁₁H₉ 141.0671
(74.65%, -3.3mmu).

7.2.(36). N-(1-(1'-naphthyl)-1-oxo-methyl)azacycloheptane.

The method of 7.2.(3)_, was followed in this preparation,
to yield the amide 7.2.(36)_, as a slightly coloured solid.
After recrystallisation from pet. spirit (60°-80°C), as
white micro-needles (66%), the amide was characterised.

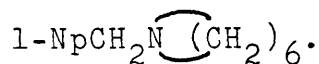


IR(Nujol); 3050(w) 2930(vs) 2860(s) 1630(vs) 1595(m) 1470(vs)
1380(s) 805(s) 785(s), ¹H NMR; 1.44-2.08 δ (8H,m,ring CH₂),
3.12-3.32 δ (2H,m,CONCH₂), 3.68-4.00 δ (2H,m,CONCH₂), 7.26-
7.64 δ (4H,m,Np), 7.72-7.96 δ (3H,m,Np), CHN; C₁₇H₁₉NO,
Expected % C 80.60 H 7.56 N 5.53 O 6.31 Actual % C 80.49
H 7.65 N 5.38 O 6.48, AMS; M⁺ 253.1330 (39.58%, -13.7mmu),

$C_{11}H_7O$ 155.0410 (100%, -8.7mmu), $C_{10}H_7$ 127.0491 (77.60%, -5.7mmu).

7.2.(37). N-((1'-naphthyl)methyl)azacycloheptane.

The recrystallised amide 7.2.(36)_, was reduced using lithium aluminium hydride (2.5 equivalents), by method 7.2.(4). to yield the amine as a clear yellow-orange oil (>90%). Purification by vacuum distillation, afforded 7.2.(37)_, as a clear slightly coloured oil (82%), which was characterised.



B.pt. 109°-112°C @ ~0.01mm, IR(Neat); 3050(m-s) 2930(vs) 2860(s) 2780(s) 1600(m-s) 1510(s) 1470-1455(s) 1360(s) 790(vs) 775(vs), 1H NMR; 1.54-1.74 δ (8H,m,ring CH_2), 2.62-2.80 δ (4H,m, NCH_2), 4.04 δ (2H,s, $NpCH_2N$), 7.28-7.58 δ (4H,m, Np), 7.68-7.88 δ (2H,m, Np), 8.28-8.44 δ (1H,m, Np), CHN; $C_{17}H_{21}N$, Expected % C 85.31 H 8.84 N 5.85 Actual % C85.10 H 8.93 N 5.72, AMS; M^+ 239.1568 (26.27%, -10.6mmu), $C_{11}H_9$ 141.0677 (100%, -2.7mmu), $C_6H_{12}N$ 98.0897 (62.92%, -7.2mmu).

7.2.(38). N-((1'-naphthyl)-1-oxo-methyl)azacyclooctane.

The amide 7.2.(38)_, was prepared by the basic method of 7.2.(3). but equimolar amounts of the 1-naphthoyl chloride and azacyclooctane were used, and the HCl produced, was trapped by triethylamine (2 molar equivalents). Work-up gave the amide as a solid, which recrystallised from pet. spirit (60°-80°C), as slightly coloured micro-needles, (78%), and was then fully characterised.

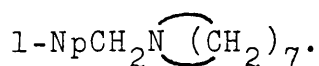


IR(Nujol); 3050(w) 2960,2930(vs) 2860(s) 1625(vs) 1590(w-m) 1470(s) 815(s) 800(s) 790(s), 1H NMR; 1.24-2.40 δ (10H,m, ring CH_2), 3.06-3.28 δ (2H,m, $CONCH_2$), 3.28-3.74 δ (1H,m, $CON-CH_2$), 3.84-4.36 δ (1H,m, $CONCH_2$), 7.36-7.64 δ (4H,m, Np), 7.72-

8.00 δ (3H,m,Np), CHN; $C_{18}H_{21}NO$, Expected % C 80.86 H 7.92
N 5.24 O 5.98 Actual % C 80.61 H 8.03 N 5.32 O 6.24, AMS;
 M^+ 267.1607 (56.22%, -1.6mmu), $C_{11}H_7O$ 155.0446 (100%, -5.1mmu).

7.2.(39). N-((1'-naphthyl)methyl)azacyclooctane.

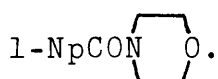
Reduction of the amide 7.2.(38)., and work-up as outlined
in method 7.2.(4)., yielded the amine as a clear yellow-
orange oil (87%). Vacuum distillation afforded amine 7.2.(39).
as a clear slightly coloured oil (74%), which was fully
characterised.



B.pt. 112°-113.5°C @ ~0.01mm, IR(Neat); 3050(m-s) 2920(vs)
2860(s) 2780(s) 1600(m) 1510(m-s) 1470-1440(m-s) 795(vs) 780
(vs), 1H NMR; 1.36-1.68 δ (10H,m,ring CH_2), 2.48-2.72 δ
(4H,m, NCH_2), 3.98 δ (2H,s, $NpCH_2N$), 7.32-7.56 δ (4H,m,Np),
7.64-7.88 δ (2H,m,Np), 8.28-8.44 δ (1H,m,Np), CHN; $C_{18}H_{23}N$,
Expected % C 85.32 H 9.15 N 5.53 Actual % C 85.06 H 9.29 N
5.57, AMS; M^+ 253.1837 (14.88%, 0.6mmu), $C_{11}H_9$ 141.0687
(100%, -1.7mmu), C_7H_{14} 112.1042 (90.10%, -8.4mmu).

7.2.(40). N-((1'-naphthyl)-1-oxo-methyl)-1-aza-4-oxa-cyclo-
hexane.

The amide 7.2.(40)., was synthesised by following the
method outlined in 7.2.(3)., utilising an excess of the
1-aza-4-oxa-cyclohexane (2.5 equivalents), in order to trap
the HCl produced. Work-up led to the isolation of the product
as a viscous opaque pale yellow oil (>90%), which was charac-
terised and then used without purifying in the next reaction.

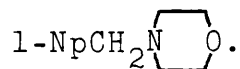


IR(Neat); 3060(m) 2970(s) 2860(s) 1640(vs) 1600(s) 1510(s)
1470-1440(vs) 1120(s) 800(vs) 780(vs), 1H NMR; 3.04-3.28 δ
(2H,m, $CONCH_2$), 3.34-3.60 δ (2H,m, $CONCH_2$), 3.70-4.04 δ (4H,m,

CH_2OCH_2), 7.32-7.60 δ (4H,m,Np), 7.70-7.96 δ (3H,m,Np).

7.2.(41). N-((1'-naphthyl)methyl)-1-aza-4-oxa-cyclohexane.

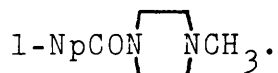
The amide was reduced using lithium aluminium hydride (2.5 equivalents), by method 7.2.(4).., to give the amine as a pale yellow oil (>95%). After vacuum distillation, the purified amine, a clear colourless oil (75%), was fully characterised.



B.pt. 107°-108.5°C @ ~0.01mm, IR(Neat); 3050(m-s) 2960(vs) 2860(vs) 1600(m-s) 1510(s) 1455(s) 1395(s) 1120(vs) 795-790(vs) 775(vs), ¹H NMR; 2.48 δ (4H,t,NCH₂CH₂O), 3.66 δ (4H,t,NCH₂-CH₂O), 3.88 δ (2H,s,NpCH₂N), 7.30-7.56 δ (4H,m,Np), 7.66-7.86 δ (2H,m,Np), 8.18-8.34 δ (1H,m,Np), CHN; C₁₅H₁₇NO, Expected % C 79.26 H 7.54 N 6.16 O 7.04 Actual % C 78.96 H 7.72 N 5.96 O 7.36, AMS; M⁺ 227.1324 (26.57%, 1.4mmu), C₁₁H₉ 141.0523 (100%, -18.1mmu), C₄H₈NO 86.0650 (45.51%, 4.4mmu).

7.2.(42). N-((1'-naphthyl)-1-oxo-methyl)-N'-methyl-1,4-diazacyclohexane.

The preparation of amide 7.2.(42).., by method detailed in 7.2.(3).., yielded a pale yellow opaque, very viscous oil (>90%). The product was vacuum distilled, to give a very viscous translucent material, which was characterised.



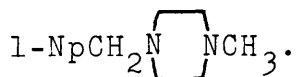
B.pt. 155°-159°C @ ~0.01mm, IR(Neat); 3060(m) 2940(vs) 2800(vs) 1635(vs) 1595(s) 1510(s) 1470-1430(vs) 805(vs) 780 (vs), ¹H NMR; 2.20-2.44 δ (2H,m,NCH₂), 2.38 δ (3H,s,NMe), 2.56-2.76 δ (2H,m,NCH₂), 3.24-3.40 δ (2H,m,CONCH₂), 4.00-4.24 δ (2H,m,CONCH₂), 7.56-7.80 δ (4H,m,Np), 7.96-8.16 δ (3H,m,Np), AMS; C₁₆H₁₈N₂O, M⁺ 254.1431 (8.00%, 1.2mmu), C₁₁H₇O 155.0430 (7.17%, -6.7mmu), C₁₃H₁₁NO 197.0771 (1.55%, -6.9mmu).

The ¹H Nmr spectrum of this amide shows a variable

temperature dependence. A more detailed discussion of the Nmr data is given in Section 6.(2)., consequently the NCH_2 -signals are referred to as multiplets at this stage.

7.2.(43). N-(1'-naphthylmethyl)-N'-methyl-1,4-diazacyclohexane.

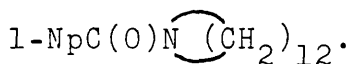
The diamine was prepared by reduction of the amide 7.2.(42)., using lithium aluminium hydride (3 equivalents), by the method outlined in 7.2.(4). Work-up in the usual way yielded the product as a clear colourless oil (88%). The diamine 7.2.(43)., was then purified by vacuum distillation and fully characterised.



B.pt. 114°-116°C @ 0.01mm, IR(Neat); 3050(m-s) 2960(vs) 2800(vs) 1600,1510(m-s) 1455(s) 800-790,775(vs), ¹H NMR; 2.22 δ (3H,s,NMe), 2.26-2.64 δ (8H,m,NCH₂CH₂N), 3.88 δ (2H,s,NpCH₂N), 7.26-7.56 δ (4H,m,Np), 7.62-7.86 δ (2H,m,Np), 8.18-8.36 δ (1H,m,Np), CHN; C₁₆H₂₀N₂, Expected % C79.96 H 8.39 N 11.65 Actual % C 79.97 H 8.38 N 11.51, AMS; M⁺ 240.1612 (100%, -1.4mmu), C₁₁H₉ 141.0607 (28.43%, -9.7mmu), C₅H₁₁N₂ 99.0830 (28.53%, -9.2mmu).

7.2.(44). N-((1'-naphthyl)-1-oxo-methyl)azacyclotridecane.

The amide 7.2.(44)., was prepared by reacting equimolar amounts of 1-NC and azacyclotridecane, trapping the HCl produced, with triethylamine (2 molar equivalents). The amide was isolated initially as a very viscous, opaque oil (90%), but this was induced to crystallise, and the product subsequently recrystallised from pet. spirit (60°-80°C), as a colourless material, (71%), which was then fully characterised.

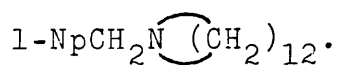


M.pt. 88°-90°C, IR(Nujol); 3060(m) 2930(vs) 2860(s) 1635(s)

1600,1510(m-s), 1470-1425(vs) 1380(s) 805(vs) 785(vs),
¹H NMR; 1.08-2.08 δ (20H,m,ring CH₂), 3.00-3.20 δ (2H,t,CON-
 CH₂), 3.60-3.80 δ (2H,t,CONCH₂), 7.32-7.68 δ (4H,m,Np), 7.76-
 8.00 δ (3H,m,Np), CHN; C₂₃H₃₁N₂O, Expected % C 81.85 H 9.26
 N 4.15 O 4.74 Actual % C 81.90 H 9.36 N 4.17 O 4.57, AMS;
 M⁺ 337.2488 (32.06%, 8.2mmu), C₁₁H₇O 155.0553 (54.39%, 5.6mmu).

7.2.(45). N-((1'-naphthyl)methyl)azacyclotridecane.

The amide 7.2.(44)..^o, was reduced according to method
 7.2.(4)..^o, using lithium aluminium hydride (3 molar equivalents)
 to yield the crude amine as a slightly opaque colourless oil
 (>90%). Purification by vacuum distillation afforded the
 amine 7.2.(45)..^o, as a clear colourless oil (83%), which was
 fully characterised.

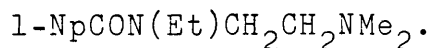


B.pt. 145^o-147^oC @ 0.01mm, IR(Neat); 3050(m) 2940(vs)
 2860(s) 1600(m) 1510(m-s) 1460(s) 795(vs) 780(vs), ¹H NMR;
 1.22-1.54 δ (20H,m,ring CH₂), 2.34-2.52 δ (4H,t,NCH₂ ring),
 3.92 δ (2H,s,NpCH₂N), 7.42-7.56 δ (4H,m,Np), 7.72-7.90 δ (2H,
 m,Np), 8.38-8.52 δ (1H,m,Np), CHN; C₂₃H₃₃N, Expected % C
 85.39 H 10.28 N 4.33 Actual % C 85.54 H 10.17 N 4.34, AMS;
 M⁺ 323.2661 (40.38%, 4.9mmu), C₁₂H₂₄N 182.1887 (100%, -2.2mmu),
 C₁₁H₉ 141.0719 (63.8%, 1.5mmu).

7.2.(46). N,N-dimethyl-N'-ethyl-N'-((1'-naphthyl)-1-oxo-
 methyl)-1,2-diaminoethane.

The amide was synthesised according to the method of
 7.2.(3)..^o, but using equimolar quantities of 1-NC and N,N-
 dimethyl-N'-ethyl-1,2-diaminoethane. The HCl produced, being
 trapped by triethylamine (2 equivalents). Addition of water
 and work-up in the usual manner, yielded the amide 7.2.(46)..^o,
 as an opaque pale yellow viscous oil, which could not be

induced to crystallise (~95%). The material was purified by vacuum distillation, giving a clear colourless oil, and was characterised (61%).

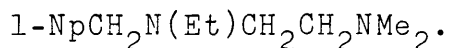


B.pt. 129°-134°C @ ~0.01mm, IR(Neat); 3060(m) 2980(s) 2860(s) 2770(s) 1635(vs) 1600(m) 1510(m-s) 1470-1430(vs) 805 (vs) 785(vs), CHN; C₁₇H₂₂N₂O, Expected % C 75.52 H 8.20 N 10.36 O 5.92 Actual % C 75.35 H 8.38 N 10.43 O 5.84, AMS; M⁺ 270.1675 (0.79%, -5.7mmu), C₃H₇N₂ 71.0648 (37.67%, 3.9mmu), C₃H₈N 58.0601 (100%, -5.6mmu).

The ¹H Nmr spectrum of the amide was recorded in both CDCl₃ and C₆D₆. In each solvent, the spectra indicated that an exchange process was taking place between two distinct conformers. A detailed interpretation of the ¹H Nmr data is given in Section 6.(2). The failure of D₂O to exchange with any of the peaks in the spectrum (even when left overnight), indicated the absence of any unreacted N,N-dimethyl-N'-ethyl-1,2-diaminoethane.

7.2.(47). N,N-dimethyl-N'-ethyl-N'-((1'-naphthyl)methyl)-1,2-diaminoethane.

The amine 7.2.(47). was synthesised by reduction of the amide, using lithium aluminium hydride, according to method 7.2.(4). Work-up yielded the crude amine, as a slightly coloured clear oil (91%), which was characterised, after purification by vacuum distillation, (75%).



B.pt. 110°-113°C @ 0.05mm, IR(Neat); 3040(m) 2960(s) 2850(s) 2810(vs) 1600(m) 1510(m-s) 1460(s) 1380(m-s) 790(vs) 770(vs), ¹H NMR; 1.08 δ (3H,t,CH₂CH₃), 2.20 δ (6H,s,NMe₂), 2.28-2.76 δ (6H,m,NCH₂), 4.06 δ (2H,s,NpCH₂N), 7.40-7.68 δ

(4H,m,Np), 7.76-7.96 δ (2H,m,Np), 8.38-8.50 δ (1H,m,Np),

CHN; $C_{17}H_{24}N$, Expected % C 79.64 H 9.43 N 10.93 Actual %
C 79.54 N 9.33 N 10.80, AMS; M^+ 256.1857 (2.93%, -8.3mmu),
 $C_{14}H_{16}N$ 198.1240 (100%, -4.3mmu), $C_{11}H_9$ 141.0610 (5.52%,
-9.5mmu).

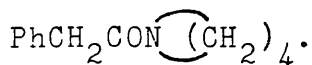
7.3. PHENYL DERIVATIVES.

7.3.(1). 2-Phenylethanoyl chloride (2-PEC).

2-PEC was prepared by refluxing 2-phenylethanoic acid (0.01 mole), with oxalyl chloride (0.03 mole), in sodium dried benzene (100cm³), for about 2 hours under nitrogen. Removal of the solvent and excess oxalyl chloride, yielded the 2-PEC, as a yellow cloudy liquid (>95%), which was used without purification or characterisation in the next reaction.

7.3.(2). N-(2-phenyl-1-oxo-ethyl)azacyclopentane.

The amide was prepared by reacting the 2-PEC, with 2 equivalents of azacyclopentane (pyrrolidine), in sodium dried ether, under nitrogen. Addition of water and work-up as in 7.2.(3)., yielded the product as a clear yellow oil, which was characterised, prior to reduction to the amine, but not purified.

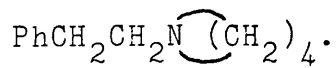


IR(Neat); 3050(m) 2990(s) 2890(s) 1640(vs) 1500(s) 1460(vs)
750(s) 730(s) 715,705(s) ¹H NMR; 1.70-2.00 δ (4H,m,ring
CH₂), 3.28-3.60 δ (4H,m,NCH₂), 3.62 δ (2H,s,PhCH₂CO), 7.26 δ
(5H,m,Ph).

7.3.(3). N-(2-phenylethyl)azacyclopentane.

An ethereal solution of the amide 7.3.(2). (75cm³), was added to an ice-cooled, stirred slurry of lithium aluminium hydride (2.5 equivalents), in sodium dried ether (75cm³).

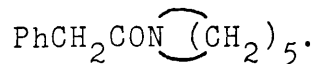
After refluxing for several hours under nitrogen, work-up yielded the amine as a pale yellow oil. Purification by Prep TLC (alumina, 75% petroleum spirit (60°-80°C)-25% diethyl-ether), followed by vacuum distillation, gave a clear pale yellow oil, which was then characterised.



B.pt. 105°-107°C @ ~0.1mm, IR(Neat); 3020(m) 2970(s) 2870(m) 2780(s) 1600(m) 1500(s) 1450(s) 750(s) 700(s), ¹H NMR; 1.67-2.00 δ (4H,m,ring CH₂), 2.36-2.67 δ (4H,m,NCH₂ ring), 2.72 δ (4H,m,NCH₂CH₂Ph), 7.20 δ (5H,m,Ph), CHN; C₁₂H₁₇N, Expected % C 82.23 H 9.78 N 7.99 Actual % C 82.00 H 9.96 N 8.18, AMS; M⁺ 171.1162 (1.40%, -19.9mmu), C₅H₁₀N 84.0782 (100%, -3.1mmu).

7.3.(4). N-(2-phenyl-1-oxo-ethyl)azacyclohexane.

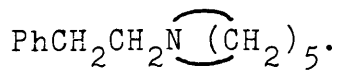
The amide was prepared, according to the method of 7.3.(2). and isolated as a yellow oil. It was used without purification in the next reaction, but was characterised.



IR(Neat); 3050(m) 2960(s) 2880(s) 1635(vs) 1585(s) 1500(s) 1450(s) 1260(s) 1025(s) 735(s) 705(s), ¹H NMR; 1.36-1.64 δ (6H,m,ring CH₂), 3.24-3.40 δ (2H,m,CH₂NCO), 3.44-3.60 δ (2H,m,CH₂NCO), 3.70 δ (2H,s,PhCH₂CO), 7.08-7.28 δ (5H,m,Ph).

7.3.(5). N-(2-phenylethyl)azacyclohexane.

Amide 7.3.(4)., was reduced using lithium aluminium hydride, by method 7.3.(3). Work-up yielded the crude amine as a pale yellow opaque oil, purified first by column chromatography, (alumina, 90% petroleum spirit (60°-80°C)-10% di-ethylether), then by vacuum distillation. The amine 7.3.(5), a clear colourless oil, was then characterised.



B.pt. 112°-114°C @ 0.15mm, IR(Neat); 3020(s) 2920(s) 2850(s) 2750(s) 1600(m) 1500(s) 1450(s) 1370(s) 740(s) 695(s), ¹H NMR; 1.38-1.81 δ (6H,m,ring CH₂), 2.31-3.00 δ (8H,m,NCH₂, PhCH₂), 7.13 δ (5H,m,Ph), CHN; C₁₃H₁₉N, Expected % C 82.48 H 10.12 N 7.40 Actual % C 82.33 H 10.32 N 7.31, AMS (70eV); M⁺ 189.1429 (0.11%, -8.8mmu).

7.3.(6). N-(2-phenyl-1-oxo-ethyl)azacycloheptane.

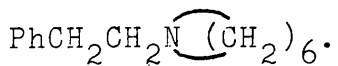
The amide was prepared by method 7.3.(2). and isolated as a clear yellow oil, which was analysed and used directly in the next reaction.



IR(Neat); 3030(m) 2920(vs) 2850(s) 1630(vs) 1600(s) 1500(m) 1450(vs) 1380(s) 1150(s) 725(vs) 700(s), ¹H NMR; 1.42-1.78 δ (8H,m,ring CH₂), 3.30-3.58 δ (4H,m,CH₂NCO), 3.70 δ (2H,s, PhCH₂CO), 7.10-7.34 δ (5H,m,Ph).

7.3.(7). N-(2-phenylethyl)azacycloheptane.

The amide was reduced by the usual method, giving the crude product as a slightly coloured oil, which was purified by prep TLC, (alumina, 80% petroleum spirit (60°-80°C) - 20% diethylether) to give a clear colourless oil and then analysed.



B.pt. 119°-120°C @ 0.025mm, IR(Neat); 3030(m) 2920(vs) 2850(s) 1600(m) 1500(s) 1455(s) 1360(s) 1130(s) 750(s) 700(s) ¹H NMR; 1.53-1.83 δ (8H,m,ring CH₂), 2.60-2.90 δ (8H,m,NCH₂ (6H),PhCH₂, (2H),), 7.12 δ (5H,m,Ph), CHN; C₁₄H₂₁N, Expected % C 82.70 H 10.41 N 6.89 Actual % C 82.79 H 10.45 N 6.82, AMS (70eV); M⁺ 203.1601 (0.96%, -7.3mmu), C₇H₁₄N 112.1067 (100%, -6.0mmu).

7.3.(8). N-(2-phenyl-1-oxo-ethyl)azacyclooctane.

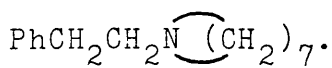
The preparation was carried out as in method 7.3.(2). giving the crude amide as a clear yellow oil, used without purification in the next reaction, once it had been analysed.



IR(Neat); 3030(m) 2920(vs) 2860(s) 1640(vs) 1600(s) 1500(s) 1470(vs) 1380(s) 725(vs) 700(s), ¹H NMR; 1.21-1.91 δ (10H, m, ringCH₂), 3.28-3.54 δ (4H, m, NCH₂), 3.71 δ (2H, s, PhCH₂CO), 7.28 δ (5H, m, Ph).

7.3.(9). N-(2-phenylethyl)azacyclooctane.

The amide was reduced as in 7.3.(3). using lithium aluminium hydride, work-up yielding the amine as a pale yellow oil. Purification by column chromatography (alumina, 90% pet. spirit (60°-80°C) - 10% diethylether), followed by vacuum distillation, gave a clear colourless oil, which was then characterised.



B.pt. 117°-118°C @ 0.025mm, IR(Neat); 3030(s) 2920(vs) 2850(s) 2770(s) 1600(m) 1500(s) 1475(s) 1360(s) 750(s) 700(s) ¹H NMR; 1.43-1.81 δ (10H, m, ring CH₂), 2.46-2.80 δ (4H, m, NCH₂), 2.70 δ (4H, m, PhCH₂CH₂N), 7.17 δ (5H, m, Ph), CHN; C₁₅H₂₃N, Expected % C 82.89 H 10.67 N 6.44 Actual % C 83.15 H 10.66 N 6.41, AMS (70eV); M⁺ 217.1846 (0.54%, -1.6mmu), C₈H₁₆N 126, 1151 (100%, 11.2mmu).

7.3.(10). N-(2-phenyl-1-oxo-ethyl)azacyclononane.

The amide 7.3.(10). was prepared by method 7.3.(2). except that equimolar amounts of 2-PEC and azacyclononane were used and the HCl produced in the reaction was trapped by triethylamine (2 equivalents). Work-up yielded the amide as a clear yellow oil which was characterised and used

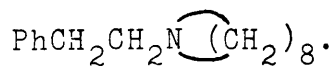
without purification in the next reaction.



IR(Neat); 3020(m) 2900(vs) 2850(s) 1635(vs) 1600(m) 1500(s) 1480-1410(vs) 1380(s) 1150(s) 705,695(vs), ¹H NMR; 1.20-2.00 δ (12H,m,ring CH₂), 3.26-3.63 δ (4H,m,NCH₂ ring), 3.73 δ (2H,s,PhCH₂CO), 7.28 δ (5H,m,Ph).

7.3.(11). N-(2-phenylethyl)azacyclononane.

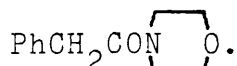
The amide 7.3.(10) was reduced using lithium aluminium hydride, by method 7.3.(3), to give the required amine as a clear yellow oil. After Prep TLC purification (alumina, 90% petroleum spirit (60°-80°C) - 10% diethylether), the amine, a clear colourless oil, was characterised.



IR(Neat); 3030(s) 2910(vs) 2800(s) 1600(m) 1500(s) 1455(s) 1355(s) 750(s) 700(s), ¹H NMR; 1.36-1.76 δ (12H,m,ring CH₂), 2.36-2.73 δ (4H,m,NCH₂ ring), 2.70 δ (4H,m,PhCH₂CH₂N), 7.07 δ (5H,m,Ph), CHN; C₁₆H₂₅N, Expected % C 83.06 H 10.89 N 6.05 Actual % C 82.94 H 11.00 N 5.89, AMS; M⁺ 231.1817 (0.38%, -16.9mmu), C₉H₁₈N 140.1441 (100%, 0.2mmu).

7.3.(12). N-(2-phenyl-1-oxo-ethyl)-1-aza-4-oxa-cyclohexane.

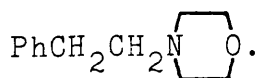
The reaction was carried out according to method 7.3.(2), using an excess of 1-aza-4-oxa-cyclohexane (morpholine), to trap the HCl produced. The amide was obtained as a yellow oil, which on cooling, crystallised to a pale yellow solid. The material was characterised and used in the next reaction, without purification.



IR(Nujol); 3060(w) 2970(vs) 2860(s) 1645(s) 1460(s) 1120(s) 740(s) 710(s), ¹H NMR; 3.43 δ (4H,m,NCH₂), 3.60 δ (4H,m,OCH₂), 3.70 δ (2H,s,PhCH₂CO), 7.24 δ (5H,m,Ph).

7.3.(13). N-(2-phenylethyl)-1-aza-4-oxa-cyclohexane.

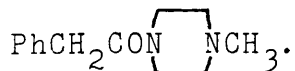
The amide was reduced as in 7.3.(3)., yielding the amine as a clear almost colourless oil. After purification by Prep TLC (alumina, 90% petroleum spirit (60°-80°C) - 10% diethylether), the amine 7.3.(13)., a clear colourless oil, was then characterised.



IR(Neat); 3030(s) 2940(vs) 2860(s) 2740(m) 1600(m) 1500(s) 1455(s) 1360(s) 1110(vs) 750(s) 705,700(s), ¹H NMR; 2.40-3.00 δ (8H,m,PhCH₂CH₂N), 3.63-3.83 δ (4H,m,OCH₂), 7.20 δ (5H,m,Ph), CHN; C₁₂H₁₇NO, Expected % C 75.35 H 8.96 N 7.32 O 8.37 Actual % C 75.05 H 9.11 N 7.31 O 8.53, AMS; M⁺ 191.1483 (0.16%, 17.3mmu), C₅H₁₀NO 100.0805 (100%, 4.3mmu).

7.3.(14). N-(2-phenyl-1-oxo-ethyl)-1,4-diazacyclohexane.

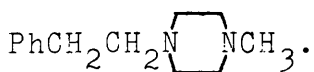
The amide 7.3.(14)., was prepared by method 7.3.(2). and isolated as a yellow oil, it was used without purification, in the next stage, after characterisation.



IR(Neat); 3040(m) 2960(s) 2870(m-s) 1645(vs) 1600(m) 1500(s) 1465(vs) 740(s) 705(s),. ¹H NMR; 2.10 δ (3H,s,MeN), 1.94-2.34 δ (4H,m,MeNCH₂), 3.18-3.64 δ (4H,m,CH₂NCO), 3.54 δ (2H,s,PhCH₂-CO), 7.10 δ (5H,m,Ph).

7.3.(15). N-(2-phenylethyl)-1,4-diazacyclohexane.

Reduction of the crude amide, with lithium aluminium hydride, afforded the amine 7.3.(15)., as a pale yellow cloudy oil. Purification by Prep TLC (alumina, 90% pet. spirit (60°-80°C) - 10% diethylether), yielded a colourless oil, which was then characterised.



B.pt. 120°-122°C @ 0.05mm, IR(Neat); 3040(m) 2950(s) 2890(s)

1600(m) 1500(s) 1460(s) 1375(s) 1140(s) 755(s) 705(s), ¹H NMR;
2.23 δ (3H,s,NMe), 2.26-2.90 δ (12H,m,NCH₂,PhCH₂), 7.10 δ (5H,
m,Ph), CHN; C₁₃H₂₀N₂, Expected % C 76.42 H 9.87 N 13.71,
Actual % C 76.40 H 9.94 N 13.68, AMS; M⁺ 204.1609 (0.31%,
-1.8mmu), C₄H₈N 70.0733 (100%, 7.7mmu), C₆H₁₃N₂ 113.1125
(30.7%, 14.6mmu).

7.3.(16). N-(2-phenyl-1-oxo-ethyl)azacyclotridecane.

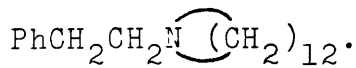
The amide was prepared by method 7.3.(2) ., except that
equimolar amounts of 2-PEC and azacyclotridecane were used,
and the HCl produced, was trapped by triethylamine (2 equi-
valents). The product was isolated as a yellow oil (91%),
characterised and then reduced in the next stage.



IR(Neat); 3030(m) 2930(vs) 2860(s) 1640(vs) 1600(m) 1500(s)
1455(vs) 1375(s) 730(s) 700(s), ¹H NMR; 1.16-1.76 δ (20H,m,
ring CH₂), 3.12-3.44 δ (4H,m,NCH₂ ring), 3.64 δ (2H,s,PhCH₂CO),
7.12 δ (5H,m,Ph).

7.3.(17). N-(2-phenylethyl)azacyclotridecane.

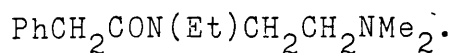
Reduction of the amide 7.3.(16) ., by method 7.3.(3) ., gave
the amine as a pale yellow oil (>95%), which was characterised
after vacuum distillation.



B.pt. 118.5°-119.5°C @ ~0.01mm, IR(Neat); 3030(s) 2930(vs)
2860(s) 1600(m) 1500(m) 1460(s) 1375(m) 730(m) 700(s), ¹H NMR;
1.22-1.58 δ (20H,m,ring CH₂), 2.22-2.82 δ (6H,m,NCH₂), 2.94-
3.46 δ (2H,m,PhCH₂), 7.26 δ (5H,m,Ph), CHN; C₂₀H₃₃N, Expected
% C 83.56 H 11.57 N 4.87 Actual % C 83.50 H 11.69 N 5.13,
AMS (70eV); M⁺ 287.2536 (0.19%, -7.7mmu), C₁₃H₂₆N 196.1952
(100%, -11.4mmu), C₇H₇ 91.0551 (3.09%, 0.3mmu).

7.3.(18). N,N-dimethyl-N'-ethyl-N'-(2-phenyl-1-oxo-ethyl)-1,2-diaminoethane.

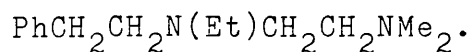
The reaction was carried out according to the method of 7.3.(2)., using an excess of N,N-dimethyl-N'-ethyldiaminoethane, to trap the HCl produced. The amide 9.3.(18)., was isolated as a clear yellow oil, characterised and then reduced without purification.



IR(Neat); 3030(m-s) 2940(vs) 2860,2770(s) 1630(vs) 1600(m) 1500(s) 1470-1420(vs) 1380-1360(m) 730(s) 700(s), ^1H NMR; 1.06 δ (3H,t, CH_2CH_3), 2.15 δ (6H,s, NMe_2), 2.20-2.80 δ (2H,m, CH_2NMe), 3.05-3.53 δ (2H,m, CH_2NCO), 3.28 δ (2H,q, $\text{CH}_3\text{CH}_2\text{NCO}$), 3.56 δ (2H,s, PhCH_2CO), 7.12 δ (5H,m,Ph).

7.3.(19). N,N-dimethyl-N'-ethyl-N'-(2-phenylethyl)-1,2-diaminoethane.

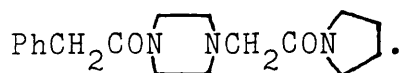
Reduction of the amide 7.3.(18)., by method 7.3.(3)., yielded the required amine as a clear slightly coloured oil. The material was purified by Prep TLC (alumina, 60% pet. spirit (60°-80°C) - 40% diethylether), giving a clear colourless oil, which was then characterised.



IR(Neat); 3030(m) 2940(vs) 2860(s) 2760(s) 1600(m) 1500(m-s) 1455(s) 1385(m) 745(s) 700(s), ^1H NMR; 1.00 δ (3H,t, CH_2CH_3), 2.10 δ (6H,s, NMe_2), 2.17-2.60 δ (6H,m, NCH_2), 2.63 δ (4H,m,Ph- $\text{CH}_2\text{CH}_2\text{N}$), 7.07 δ (5H,m,Ph), CHN; $\text{C}_{14}\text{H}_{24}\text{N}_2$, Expected % C 76.31 H 10.98 N 12.71 Actual % C 76.22 H 11.05 N 12.42, AMS; M^+ 220.2029 (0.38%, +8.9 mmu), $\text{C}_{11}\text{H}_{16}\text{N}$ 162.1589 (100%, +30.6 mmu).

7.3.(20). N-(2-phenyl-1-oxo-ethyl)-N'-(2-azacyclopentyl-2-oxo-ethyl)-1,4-diazacyclohexane.

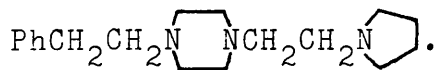
The diamide 7.3.(20).., was prepared by method 7.3.(2).., using equimolar amounts of 2-PEC and N-(azacyclopentyl-2-oxo-ethyl)-1,4-diazacyclohexane. Triethylamine (2 equivalents), was added to trap the HCl. The product was only partially soluble in ether, so extraction with dichloromethane (3 X 50 cm³) was necessary, to yield a pale yellow opaque viscous oil (80%). This was characterised and then reduced.



IR(Neat); 3040(m) 2980(s) 2880(s) 2810(s) 1640(vs) 1500(s) 1450(s) 730,700(s), ¹H NMR; 1.70-2.14 δ (4H,m,ring CH₂), 2.26-2.70 δ (4H,m,CH₂NCH₂), 3.08 δ (2H,s,NCH₂CO), 3.28-3.68 δ (6H,m,CH₂NCO), 3.52-3.88 δ (2H,m,CH₂NCO), 3.74 δ (2H,s,Ph-CH₂CO), 7.26 δ (5H,m,Ph).

7.3.(21). N-(2-phenylethyl)-N'-(2-azacyclopentyl-ethyl)-1,4-diazacyclohexane.

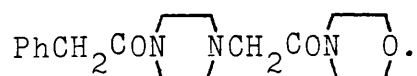
The amine was prepared by the reduction of the diamide 7.3.(20).., in freshly distilled tetrahydrofuran, using lithium aluminium hydride (3 equivalents), according to method 7.3.(3). The crude material, a clear yellow oil, was purified by vacuum distillation to give a clear colourless oil, which crystallised completely upon cooling.



B.pt. 129⁰-132⁰C @ ~0.01mm, IR(Neat); 3040(m-s) 2950(vs) 2880(s) 2800(vs) 1600(m) 1500(s) 1455(s) 1160-1130(s) 750(s) 700(s), ¹H NMR; 1.64-1.92 δ (4H,m,ring CH₂), 2.42-2.80 δ (20H,m,NCH₂,PhCH₂), 7.24 δ (5H,m,Ph), CHN; C₁₈H₂₉N, Expected % C 75.21 H 10.17 N 14.62 Actual % C 75.00 H 10.16 N 14.42, AMS; M⁺ 287.2346 (0.45%, -1.6mmu), C₁₃H₁₉N₂ 203.1511 (100%, -3.7mmu).

7.3.(22). N-(2-phenyl-1-oxo-ethyl)-N'-(2-(1-aza-4-oxa-cyclohexyl)-2-oxo-ethyl)-1,4-diazacyclohexane.

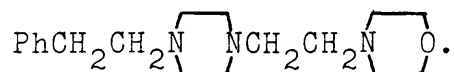
The diamide was prepared as in 7.3.(20)., following the method of 7.3.(2)., but the material was only partially soluble in ether, and had to be extracted using dichloromethane (3 X 50 cm³). The crude product, isolated as a pale yellow opaque oil (75%) was characterised but used without purification, in the next stage.



IR(Neat); 3040(m) 2960(s) 2860(s) 2760(m) 1640(vs) 1500(s) 1470-1450(s) 1370(m) 735(s) 700(s), ¹H NMR; 2.22-2.82 δ (4H, m, CH₂NCH₂), 3.14 δ (2H, s, NCH₂CO), 3.34-3.98 δ (12H, m, CH₂NCO, CH₂OCH₂), 3.74 δ (2H, s, PhCH₂CO), 7.28 δ (5H, m, Ph).

7.3.(23). N-(2-phenylethyl)-N'-((1-aza-4-oxa-cyclohexyl)ethyl)-1,4-diazacyclohexane.

The crude amide 7.3.(22). was reduced according to method 7.3.(3)., using lithium aluminium hydride (3 molar equivalents) with tetrahydrofuran as the solvent. Work-up yielded the required amine as a clear yellow oil, which was purified by vacuum distillation to give a slightly coloured clear oil. The amine crystallised on cooling and was then characterised.



B.pt. 135°-138°C @ 0.01mm, IR(Neat); 3030(m) 2940(vs) 2860, 2800(vs) 1600(m) 1500(m-s) 1460(s) 1160-1120(vs) 780(m) 750(s), ¹H NMR; 2.42-2.94 δ (20H, m, PhCH₂, NCH₂), 3.66-3.82 δ (4H, m, CH₂OCH₂), 7.18-7.38 δ (5H, m, Ph), CHN; C₁₈H₂₉N₃O, Expected % C 71.25 H 9.63 N 13.85 O 5.27 Actual % C 71.12 H 9.58 N 13.76 O 5.54, AMS; M⁺ 303.2289 (0.20%, -2.1mmu), C₁₃H₁₉N₂ 203.1338 (100%, -21.0mmu), C₅H₁₀NO 100.0655 (15.23%, -10.7mmu).

7.4. PREPARATION OF N-ALKYL AMINES.

7.4.(1). N-methyl azacycloheptane.

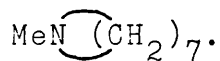
The N-methylated amine 7.4.(1)., was prepared according to the method of Eschweiler and Clark⁽¹⁹⁷⁾. 90% Formic acid (0.52 mole), was cooled in ice and azacycloheptane (0.10 mole) slowly added, with continuous stirring, followed by a 40% w/v solution of formaldehyde (0.22 mole), added dropwise. The reaction mixture was then refluxed at 125°C for 18 hours, stirring throughout. After cooling, concentrated HCl (36% w/v HCl; 1.0 mole) was slowly added to ensure that the amine was present as the hydrochloride salt, and the excess formaldehyde and formic acid were removed by rotary evaporation. The residue was basified with concentrated potassium hydroxide solution and extracted with several portions of ether. Drying and work-up yielded the crude amine as a pale yellow oil (72%), which was purified by distillation to give a slightly coloured oil (58%). The amine was then characterised, and later purified further by prep GLC, see Section 7.6. for details.



IR(Neat); 2910(vs) 2850(vs) 2780(vs) 1470,1385(s), ¹H NMR; 1.53-1.85 δ (8H,m,ring CH₂), 2.27 δ (3H,s,NMe), 2.40-2.67 δ (4H,m,NCH₂).

7.4.(2). N-methyl azacyclooctane.

The amine was prepared by the method detailed in 7.4.(1)., but working on a smaller scale (0.03 mole), and was isolated as a clear pale yellow oil (68%). Purification by Kugel distillation gave the amine 7.4.(2)., as a clear very pale yellow oil (60%), which was then characterised. As in 7.4.(1). a sample was further purified by prep GLC, see Section 7.6.



B.pt. 149° - 152°C @ 760mm. IR(Neat); 2920(vs) 2780,2760(vs)

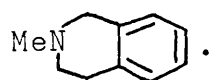
1475(s) 1380(s), ^1H NMR; 1.40-1.77 δ (10H,m,ring CH_2), 2.25 δ (3H,s,NMe), 2.30-2.60 δ (4H,m, NCH_2).

7.4.(3). N-methyldiethylamine.

Diethylamine (0.5 mole) was N-methylated to give the amine 7.4.(3). by the method detailed in 7.4.(1).., but in the work-up the amount of potassium hydroxide solution used was kept to a minimum, to reduce the loss of product into the aqueous phase. After ether extraction, the ether was removed by distillation using a Dufton fractionation column, but the amine appeared to co-distil with the solvent. Therefore, the amine was purified by using Prep GLC to separate the solvent.

7.4.(4). N-methyl-1,2,3,4-tetrahydroisoquinoline.

1,2,3,4-tetrahydroisoquinoline was N-methylated by method 7.4.(1).., and after removal of excess reagents, work-up gave the crude amine as a clear orange oil. Purification by vacuum distillation, gave a clear colourless oil which was analysed.

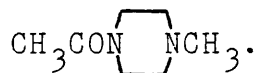


B.pt. 62° - 63°C @ ~2mm, IR(Neat); 3030(m) 2960(s) 2880(s) 2780(m) 1600(s) 1500(m) 1470(s) 1390(s) 780(s) 765(s), ^1H NMR (CCl_4); 2.30 δ (3H,s,NMe), 2.40-2.93 δ (4H,m, $\text{NCH}_2\text{CH}_2\text{Ar}$), 3.42 δ (2H,s, NCH_2Ar), 6.70-7.03 δ (4H,m,Ph), CHN; $\text{C}_{10}\text{H}_{13}\text{N}$, Expected % C 81.59 H 8.90 N 9.51 Actual % C 81.54 H 8.82 N 9.72, AMS; M^+ 147.1028 (48.32%, -2.0mmu), $\text{C}_{10}\text{H}_{12}\text{N}$ 146.0971 (100%, 0.2mmu).

7.4.(5). N-oxo-ethyl-N'-methyl-1,4-diazacyclohexane.

A solution of ethanoyl chloride (0.05 mole) in sodium dried ether (50cm³), was added slowly to a stirred solution of N-methyl-1,4-diazacyclohexane (0.125 mole) in sodium dried ether (50cm³), under a nitrogen atmosphere. The reagents were stirred for about 24 hours at room temperature then water

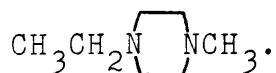
added to dissolve the hydrochloride salt, and work-up of the ether layer yielded the crude amido-amine as a clear yellow oil (95%). The product was purified by vacuum distillation to give a clear colourless oil (87%) and then characterised.



B.pt. 90°-92°C @ 0.1mm. IR (Neat); 2940-2840(vs) 2790(vs) 1665-1625(vs) 1470(vs) 1380(s) 1175(s), ¹H NMR (CDCl₃); 1.95 δ (3H,s,NMe), 2.20 δ (3H,s,CH₃CON), 2.17-2.40 δ (4H,m,CH₂NMe), 3.30-3.55 δ (4H,m,CH₂NCO).

7.4.(6). N-ethyl-N'-methyl-1,4-diazacyclohexane.

The N-oxo-ethyl-N'-methyl-1,4-diazacyclohexane 7.4.(6)., (0.035 mole) was reduced using lithium aluminium hydride (0.07 mole) in sodium dried ether (~50cm³). Work-up of the reaction mixture, minimising the amount of water added, yielded an ethereal solution which was distilled using a Dufton fractionation column to remove the ether. Problems were encountered with co-distillation, and the material had to be purified by Prep GLC, see Section 7.6. for details.

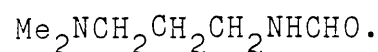


¹H NMR; 1.07 δ (3H,t,CH₂CH₃), 2.27 δ (3H,s,NMe), 2.42 δ (2H,q,NCH₂CH₃), 2.40-2.52 δ (8H,m,NCH₂CH₂N).

7.4.(7). N,N-dimethyl-N'-oxo-methyl-1,3-diaminopropane.

The N-formylated diamine 7.4.(7). was prepared according to the method of Krapcho, Turk and Pribyl⁽¹⁹⁸⁾. N,N-dimethyl-1,3-diaminopropane (0.4 mole), was added portionwise to formic acid (1.2 mole) and the resultant pink coloured mixture was refluxed for 24 hours, giving a clear colourless oil. After removing the excess formic acid by vacuum distillation, the residue was cooled treated with sodium hydroxide solution and extracted with ether containing a small amount of chloroform.

Work-up yielded a slightly coloured oily material, which was transferred to a Vigreux flask and distilled under vacuum to give a clear colourless oil (32%).



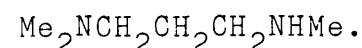
B.pt. 126°-128°C @ 15mm, IR(Neat); 3250(br,vs) 2980(vs)

2860(vs) 1700-1655(br,vs) 1550-1535(vs) 1470(s) 1390(s),

^1H NMR; 1.70 δ (2H,q, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.26 δ (6H,s, NMe_2), 2.38 δ (2H,t, $\text{Me}_2\text{NCH}_2\text{CH}_2$), 2.80 δ (1H,s,NH), 3.42 δ (2H,q, $\text{CH}_2\text{CH}_2\text{NHCHO}$), 8.20 δ (1H,s,NHCHO).

7.4.(8). N,N,N'-trimethyl-1,3-diaminopropane.

The formylated diamine 7.4.(7)., was reduced using lithium aluminium hydride (1.5 molar equivalents), but in the work-up the minimum amount of water was used due to the water solubility of the product. The diamine 7.4.(8)., was isolated as a slightly coloured oil in low yield, despite attempts to salt out the amine and employing continuous ether extraction.

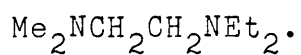


IR(Neat); 2940(vs) 2860,2780(vs) 1690(m) 1465(vs) 1380(m),

^1H NMR;

7.4.(9). N,N-diethyl-N',N'-dimethyl-1,2-diaminoethane.

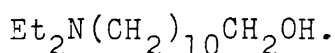
N,N-dimethyl-bromoethylamine hydrobromide, a cream coloured solid (0.02 mole), was added to a large excess of diethylamine (0.4 mole) and the resultant mixture refluxed under nitrogen, at 115°C for about 72 hours. Large quantities of a white solid, diethylamine hydrobromide, were deposited during the reaction and dissolved upon the addition of water. Ether extraction and work-up yielded the crude N,N-diethyl-N',N'-dimethyl-1,2-diaminoethane, as a dark orange oily material, purified by distillation at atmospheric pressure.



IR(Neat); 2960(vs) 2820(vs) 1470(s) 1380(s), ^1H NMR; 1.02 δ (6H,t, CH_2CH_3), 2.21 δ (6H,s, NMe_2), 2.30-2.70 δ (4H,t, $\text{NCH}_2\text{CH}_2\text{N}$, 4H,q, NCH_2CH_3).

7.4.(10). N,N-diethyl-11-amino-undecan-1-ol.

11-Bromo-undecan-1-ol (0.01 mole) was added to diethylamine (0.5 mole) and the resultant pale orange clear solution refluxed for 72 hours. The hydrobromide formed during the reaction, was filtered off and removal of the excess diethylamine from the filtrate, yielded the crude amino-alcohol as an orange red oil. Purification by vacuum distillation gave the product as a clear pale yellow oil (66%), which was analysed.

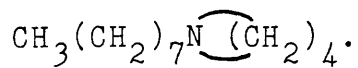


B.pt. 112°-115°C @ 0.02mm, IR(Neat); 3400-3300(br,vs) 2930 (vs) 2820(vs) 1470(s) 1380(s) 1065(br,s), ^1H NMR; 1.04 δ (6H,t, CH_3CH_2), 1.20-1.72 δ (18H,m,chain CH_2), 2.16 δ (1H,s,OH), 2.36-2.68 δ (2H,q, NCH_2CH_3 , 2H,t, NCH_2CH_2), 3.68 δ (2H,t, $\text{CH}_2\text{CH}_2\text{OH}$), CHN; $\text{C}_{15}\text{H}_{33}\text{NO}$, Expected % C 74.01 H 13.67 N 5.75 O 6.57 Actual % C 73.85 H 13.87 N 5.77 O 6.51, AMS; M^+ 243.2750 (0.37%, 18.8mmu), $\text{C}_5\text{H}_{12}\text{N}$ 86.1064 (100%, 9.5mmu).

7.4.(11). N-octyl-azacyclopentane.

Freshly powdered potassium hydroxide pellets (0.10 mole) were added to dry dimethylsulphoxide, DMSO (50cm³), and stirred under nitrogen for about 30 minutes. Azacyclopentane (0.05 mole) was added, stirring for about 45 minutes, to generate the azacyclopentyl anion. Finally a solution of 1-bromooctane (0.05 mole) in dry DMSO (50cm³) was added dropwise, and the resultant mixture stirred under nitrogen at room temperature, for about 18 hours. After adding water (300cm³) and stirring thoroughly, the reaction mixture was extracted with ether

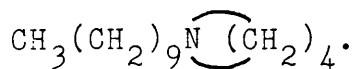
(4 X 100 cm³), backwashing each portion with water to remove traces of DMSO. Drying of the combined ether layers and work-up yielded the crude amine as a yellow oil (83%), purified by vacuum distillation to give a clear colourless oil (77%), which was subsequently characterised.



B.pt. 97°-99°C @ 0.15mm, IR(Neat); 2920(vs) 2850(vs) 2780 (vs) 1470(s) 1390(m) 1150(s), ¹H NMR; 0.70-1.02 δ (3H,m, chain CH₂), 1.02-1.52 δ (12H,m,chain CH₂), 1.52-1.85 δ (4H,m, ring CH₂), 2.17-2.57 δ (6H,m,NCH₂), CHN; C₁₂H₂₅N, Expected % C 78.61 H 13.74 N 7.64 Actual % C 78.80 H 13.59 N 7.88, AMS; M⁺ 183.2030 (2.31%, 4.4mmu), C₆H₁₂N 84.0845 (100%, -9.4mmu).

7.4.(12). N-decylazacyclopentane.

The N-decylazacyclopentane was prepared (0.05 mole) by method 7.4.(11)., (using equimolar quantities of azacyclopentane and 1-bromodecane (0.05 mole), dry DMSO (100cm³) and powdered potassium hydroxide (0.10 mole)). After reacting for 18 hours, work-up yielded the crude amine as a yellow oil (57%), purified by vacuum distillation to give a clear colourless oil (48%) and then characterised.

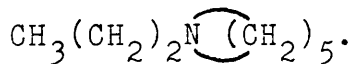


B.pt. 110°-112°C @ 0.15mm, IR(Neat); 2920(vs) 2850(vs) 2870 (vs) 1470(s) 1380(m), ¹H NMR; 0.70-1.03 δ (3H,m,chain CH₃), 1.03-1.57 δ (16H,m,chain CH₂), 1.60-1.83 δ (4H,m,ring CH₂), 2.17-2.53 δ (6H,m,NCH₂), CHN; C₁₄H₂₉N, Expected % C 79.55 H 13.82 N 6.62 Actual % C 79.46 H 13.96 N 6.35, AMS; M⁺ 211.2314 (2.30%, 1.4mmu), C₅H₁₀N 84.0786 (100%, -2.7mmu).

7.4.(13). N-propylazacyclohexane.

The N-alkylated amine 7.4.(13)., was prepared by reacting 1-bromopropane (0.1 mole) with an excess of azacyclohexane

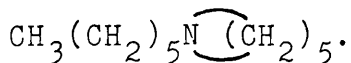
(0.25 mole), and heating at 100°C for about 30 minutes. Addition of water caused dissolution of the white solid present and the reaction mixture was extracted with ether, to give the crude amine as a clear pale yellow oil (75%) which was purified by distillation.



B.pt. 108°-110°C @ 760mm, IR(Neat); 2920(br,vs) 2850(vs) 2800(vs) 2370(s) 1470(s) 1380(s), ¹H NMR; 0.70-1.04 δ (3H,t, chain CH₃), 1.04-1.87 δ (8H,m,ring CH₂, CH₂CH₃), 2.07-2.50 δ (6H,m,NCH₂), CHN; C₈H₁₇N, Expected % C 75.52 H 13.67 N 11.01 Actual % C 75.60 H 13.39 N 10.91 AMS; M⁺ 127.1330 (5.89%, -3.1mmu), C₆H₁₂N 98.0937 (100%, -3.3mmu).

7.4.(14). N-hexylazacyclohexane.

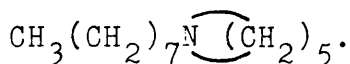
The N-hexyl derivative of azacyclohexane was prepared according to the method of 7.4.(11). Work-up yielded the crude product as a pale yellow oil (87%), purified by reduced pressure distillation to give a clear colourless oil which was characterised (72%).



B.pt. 75°-77°C @ 2mm, IR(Neat); 2920(vs) 2850(vs) 2760(s) 2680(m) 1470(vs) 1380(s), ¹H NMR; 0.73-1.05 δ (3H,m,chain CH₃), 1.05-1.78 δ (14H,m,chain CH₂) 2.05-2.40 δ (6H,m,ring NCH₂).

7.4.(15). N-octylazacyclohexane.

The N-alkylated amine 7.4.(15)., was prepared by method 7.4.(11)., yielding the crude product as a pale yellow oil (83%), purified by vacuum distillation, to give a clear colourless oil and characterised.

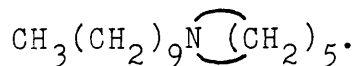


B.pt. 87°-89°C @ 2mm, IR(Neat); 2920(vs) 2860(s) 2760(s)

2690(m) 1470(s) 1380(s) 1155(s), ^1H NMR; 0.75-1.02 δ (3H,m, chain CH_3), 1.10-1.75 δ (18H,m,ring CH_2 , chain CH_2), 2.00-2.40 δ (6H,m, NCH_2), CHN; $\text{C}_{13}\text{H}_{27}\text{N}$, Expected % C 79.11 H 13.78 N 7.10 Actual % C 78.89 H 14.08 N 6.94, AMS; M^+ 197.2199 (1.76%, 5.5mmu), $\text{C}_6\text{H}_{12}\text{N}$ 98.0980 (100%, 1.0mmu).

7.4.(16). N-decylazacyclohexane.

The amine 7.4.(16).., was prepared by the method detailed in 7.4.(11).., using equimolar amounts of 1-bromodecane and azacyclohexane. Work-up in the usual way, yielded the crude N-decylazacyclohexane, as a pale yellow oil (67%), which was purified by vacuum distillation and then analysed.

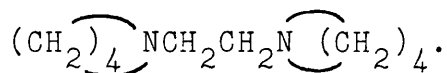


B.pt. 109 $^\circ$ -112 $^\circ$ C @ 0.075mm, IR(Neat); 2920(vs) 2850(vs) 2760(s) 1470(s) 1380(s) 1155(s), ^1H NMR; 0.70-1.05 δ (3H,m, chain CH_3), 1.05-1.75 δ (22H,m,chain CH_2 , ring CH_2), 2.03-2.40 δ (6H,m, NCH_2), CHN; $\text{C}_{15}\text{H}_{31}\text{N}$, Expected % C 79.93 H 13.86 N 6.21 Actual % C 79.79 H 14.02 N 6.05, AMS; M^+ 225.2482 (1.41%, 2.5mmu), $\text{C}_6\text{H}_{12}\text{N}$ 98.0922 (100%, -4.8mmu).

7.5. PREPARATION OF α,ω -DIAMINOALKANES.

7.5.(1). 1,2-bis-(azacyclopentyl)ethane.

The α,ω -diaminoalkane 7.5.(1).., was synthesised by using the procedure detailed in 7.4.(11).., reacting azacyclopentane (0.10 mole) with 1,2-dibromoethane (0.05 mole). Work-up in the usual way, yielded the crude diamine as a pale yellow clear oil (60%). Purification by vacuum distillation gave 7.5.(1). as a clear slightly coloured oil, which was analysed.

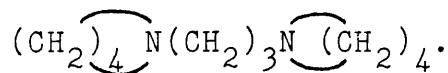


B.pt. 70.5 $^\circ$ -72 $^\circ$ C @ ~0.02mm, IR(Neat); 2940(vs) 2870(s) 2780(vs) 1460(m) 1340(m) 1140(m), ^1H NMR; 1.61-2.00 δ (8H,

m,ring CH₂), 2.38-2.77 δ (12H,m,NCH₂), CHN; C₁₀H₂₀N₂,
 Expected % C 71.38 H 11.98 N 16.65 Actual % C 71.64 H 11.70
 N 16.40, AMS; M⁺ 168.1584 (1.32%, -4.2mmu), C₅H₁₀N 84.0812
 (100%, 0.0mmu).

7.5.(2). 1,3-bis-(azacyclopentyl)propane.

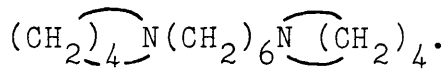
The diamine 7.5.(2). was prepared according to the method detailed in 7.4.(11).., using azacyclopentane (0.1 mole) and 1,3-dibromopropane (0.05 mole). Work-up yielded the crude product as a pale yellow clear oil after extracting the reaction mixture with both ether and chloroform. Purification by vacuum distillation yielded the product as a clear colourless oil (68%).



B.pt. 190°-192°C @ ~30mm, IR(Neat); 2950(vs) 2870(s) 2800
 (vs) 1480(m) 1355(s) 1160(s), ¹H NMR; 1.60-2.00 δ (10H,m,
 ring CH₂, NCH₂CH₂CH₂N), 2.30-2.67 δ (12H,m,NCH₂), CHN;
 C₁₁H₂₂N₂, Expected % C 72.47 H 12.16 N 15.37 Actual % C 72.20
 H 11.98 N 15.32, AMS; M⁺ 182.1637 (2.29%, -14.6mmu),
 C₅H₁₀N 84.0754 (100%, -5.9mmu).

7.5.(3). 1,6-bis-(azacyclopentyl)hexane.

The diamine 7.5.(3).., was prepared by method 7.5.(1).., and isolated in the crude form as a yellow oil (60%). Vacuum distillation gave the product as a clear colourless oil (49%), which was then analysed.

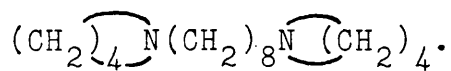


B.pt. 205°-210°C @ 30mm, IR(Neat); 2960(vs) 2870(s) 2780
 (vs) 1460(s) 1350(s) 1140(s), ¹H NMR; 1.27-1.53 δ (8H,m,
 NCH₂(CH₂)₄CH₂N), 1.65-1.97 δ (8H,m,ring CH₂), 2.27-2.63 δ
 (12H,m,NCH₂), CHN; C₁₄H₂₈N₂, Expected % C 74.94 H 12.58
 N 12.48 Actual % C 74.78 H 12.77 N 12.56, AMS; M⁺ 224.2199

(0.98%, -5.3mmu), $C_5H_{10}N$ 84.0728 (100%, -3.3mmu).

7.5.(4). 1,8-bis-(azacyclopentyl)octane.

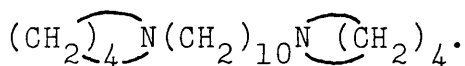
The diamine 7.5.(4)., was synthesised as in 7.5.(1). and isolated as a clear yellow oil (85%). Purification by vacuum distillation afforded the required diamine as a clear colourless oil (73%), which was characterised.



B.pt. 116°-118°C @ 0.05mm, IR(Neat); 2960(vs) 2860(s) 2780(vs) 1460(s) 1350(s) 1150(s), ¹H NMR; 1.22-1.51 δ (12H, m, chain CH₂), 1.65-1.98 δ (8H, m, ring CH₂), 2.32-2.64 δ (12H, m, NCH₂), CHN; C₁₆H₃₂N₂, Expected % C 76.12 H 12.78 N 11.10 Actual % C 75.84 H 12.92 N 10.88, AMS; M⁺ 252.2604 (5.08%, 3.9mmu), $C_5H_{10}N$ 84.0930 (100%, 11.7mmu).

7.5.(5). 1,10-bis-(azacyclopentyl)decane.

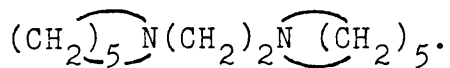
The diamine 7.5.(5). was prepared by the route given in 7.4.(11). The crude material was purified by vacuum distillation, to give a clear colourless oil (52%), which partially solidified at room temperature.



B.pt. 121°-123°C @ 0.05mm, IR(Neat); 2970(vs) 2860(vs) 2780(vs) 1460(s) 1350(s) 1150(s), ¹H NMR; 1.16-1.48 δ (16H, m, chain CH₂), 1.70-1.90 δ (8H, m, ring CH₂), 2.34-2.62 δ (12H, m, NCH₂), AMS; M⁺ 280.2853 (0.89%, -2.5mmu), $C_5H_{10}N$ 84.0870 (100%, 5.7mmu).

7.5.(6). 1,2-bis-(azacyclohexyl)ethane.

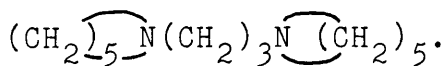
The diamine 7.5.(6). was synthesised according to method 7.5.(1). Work-up of the reaction mixture yielded the crude material (50%), distilled under vacuum to give a clear colourless oil and then analysed.



B.pt. 80°-82°C @ 0.02mm, IR(Neat); 2950(vs) 2860(s) 2760(s) 1460(s) 1390(s) 1280(s) 1130(vs), ¹H NMR; 1.44-1.78 δ (12H, m, ring CH₂), 2.42-2.64 δ (12H, m, NCH₂), CHN; C₁₂H₂₄N₂, Expected % C 73.41 H 12.32 N 14.27 Actual % C 73.40 H 12.28 N 14.36, AMS; M⁺ 196.1904 (0.53%, -3.6mmu), C₆H₁₂N (100%, -4.7mmu).

7.5.(7). 1,3-bis-(azacyclohexyl)propane.

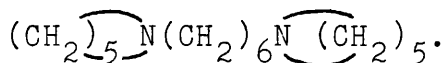
Reaction of azacyclohexane (0.1 mole) with 1,3-dibromopropane (0.05 mole), according to the method 7.4.(11)., gave the crude diamino- derivative as a yellow oil (89%). Purification by vacuum distillation yielded a clear colourless oil, which was characterised.



B.pt. 100°-102°C @ 0.03mm, IR(Neat); 2940(vs) 2860(s) 2740(vs) 1470(s) 1380(s) 1260(s), ¹H NMR; 1.40-1.88 δ (14H, m, ring CH₂, NCH₂CH₂CH₂N), 2.28-2.56 δ (12H, m, NCH₂), CHN; C₁₃H₂₆N₂, Expected % C 74.22 H 12.46 N 13.32 Actual % C 74.04 H 12.56 N 13.07, AMS; M⁺ 210.2212 (4.38%, 11.6mmu), C₆H₁₂N 98.1000 (100%, 3.0mmu).

7.5.(8). 1,6-bis-(azacyclohexyl)hexane.

Preparation of 7.5.(8). by method 7.5.(1)., yielded the crude material as a pale yellow clear oil (90%), which was purified by vacuum distillation as a clear colourless oil (78%) and analysed.

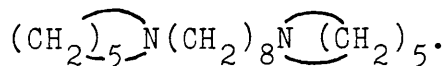


B.pt. 112°-114°C @ 0.02mm, IR(Neat); 2940(vs) 2860(s) 2760(vs) 1470(s) 1380(s) 1120(vs) 1040(s), ¹H NMR; 1.26-1.78 δ (20H, m, ring CH₂, chain CH₂), 2.26-2.54 δ (12H, m, NCH₂), CHN; Expected % C 76.12 H 12.78 N 11.10 Actual % C 76.04

H 12.99 N 11.08, AMS; M^+ 252.2465 (2.03%, -10.0mmu),
 $C_6H_{12}N$ 98.0923 (100%, -4.7mmu).

7.5.(9). 1,8-bis-(azacyclohexyl)octane.

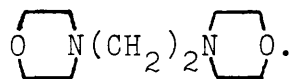
The diamine 7.5.(9)., was synthesised by the method outlined in 7.5.(1). Work-up gave the crude product as a pale yellow oil (76%), purified by vacuum distillation to give a clear colourless oil (70%), which was then analysed.



B.pt. 118°-120°C @ 0.02mm, IR(Neat); 2940(vs) 2860(s) 2760
 (vs) 1470(s) 1380(s) 1260(s) 1160(s), ^1H NMR; 1.22-1.78 δ
 (24H,m,ring CH_2 , chain CH_2), 2.22-2.54 δ (12H,m, NCH_2), CHN;
 $C_{18}H_{36}N_2$, Expected % C 77.07 H 12.94 N 9.99 Actual % C 76.88
 H 13.14 N 9.89, AMS; M^+ 280.2819 (1.77%, -6.0mmu), $C_6H_{12}N$
 98.0939 (100%, -3.1mmu).

7.5.(10). 1,2-bis-(1-aza-4-oxacyclohexyl)ethane.

The diamino- derivative 7.5.(10)., was prepared by the addition of 1,2-dibromoethane to an excess of 1-aza-4-oxacyclohexane, refluxing the resultant mixture at 100°C for about 4 hours under nitrogen. After removal of the excess amine, the solid residue was mixed with ground potassium hydroxide and heated under reduced pressure in the presence of a small amount of water. The material was taken up in ether, dried and then redistilled under vacuum, yielding 7.5.(10). as a clear colourless oil which crystallised upon cooling.

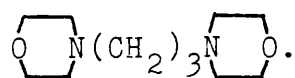


B.pt. 80°-81°C @ 0.05mm, M.pt. 65°-68°C, IR(Nujol);
 2940(vs) 2860(vs) 2800(s) 1460(s) 1380(m) 1120(vs) 1010(s),
 ^1H NMR; 2.40-2.60 δ (12H,m, NCH_2), 3.60-3.82 δ (8H,m, OCH_2),
CHN; $C_{10}H_{20}N_2O_2$, Expected % C 59.97 H 10.06 N 13.99 O 15.98

Actual % C 59.78 H 10.02 N 13.91 O 16.29, AMS; M^+ 200.1644 (0.21%, 11.9mmu), $C_5H_{10}NO$ (60.06%, -10.7mmu).

7.5.(11). 1,3-bis-(1-aza-4-oxacyclohexyl)propane.

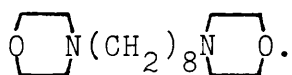
The compound was prepared by the method outlined in 7.5.(10)., reacting 1-aza-4-oxacyclohexane (~0.20 mole) with 1,3-dibromopropane (0.01 mole). Work-up of the reaction mixture yielded the crude diamine 7.5.(11)., as a pale yellow oil, purified by vacuum distillation, to give a clear colourless oil.



B.pt. 91°-93°C @ ~0.05mm, IR(Neat); 2950(vs) 2850(vs) 2800 (vs) 1460(s) 1375(m) 1270(s) 1120(vs) 1070(s), ^1H NMR; 1.50-1.84 δ (2H,m,NCH₂CH₂CH₂N), 2.28-2.52 δ (12H,m,NCH₂), 3.60-3.78 δ (8H,m,OCH₂), CHN; $C_{11}H_{22}N_2O_2$, Expected % C 61.65 H 10.35 N 13.07 O 14.93 Actual % C 61.52 H 10.44 N 13.10 O 14.94, AMS; M^+ 214.1561 (0.42%, -12.0mmu), $C_5H_{10}NO$ 100.0683 (100%, -7.9mmu).

7.5.(12). 1,8-bis-(1-aza-4-oxacyclohexyl)octane.

The diamino- derivative 7.5.(12)., was prepared by the reaction of 1,8-dibromooctane (0.007 mole) with an excess of 1-aza-4-oxacyclohexane (~0.20 mole), but in the work-up the hydrobromide was filtered off. Removal of excess amine from the filtrate, yielded an oil, which solidified upon cooling. The material was purified by vacuum distillation to give a colourless solid on cooling.



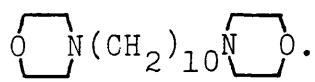
B.pt. 126°-128°C @ ~0.05mm, M.pt. 38.5°-42°C, IR(Nujol); 2940(vs) 2860(vs) 2760(s) 1460(vs) 1375(m) 1120(vs), ^1H NMR; 1.20-1.60 δ (12H,m,NCH₂(CH₂)₆CH₂N), 2.22-2.52 δ (12H,m,NCH₂), 3.64-3.82 δ (8H,m,OCH₂), CHN; $C_{16}H_{32}N_2O_2$, Expected % C 67.56

H 11.34 N 9.85 O 11.25 Actual % C 67.38 H 11.34 N 9.90 O 11.38, AMS; M^+ 284.2502 (5.75%, 3.8mmu), $C_5H_{10}NO$ 100.0717 (100%, -4.6mmu).

7.5.(13). 1,10-bis-(1-aza-4-oxacyclohexyl)decane.

Following the method outlined in 7.5.(12)., the crude diamino derivative, was isolated as a yellow solid, after removal of the excess 1-aza-4-oxacyclohexane from the filtrate.

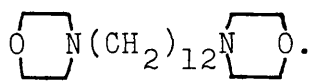
Purification by vacuum distillation yielded the product as a clear colourless oil which solidified upon cooling.



B.pt. 148°-150°C @ ~0.05mm, M.pt. 37°-39°C, IR(Nujol); 2920(vs) 2850(vs) 1465(s) 1380(m) 1120(vs), ^1H NMR; 1.24-1.52 δ (16H,m,NCH₂(CH₂)₈CH₂N), 2.24-2.58 δ (12H,m,NCH₂), 3.62-3.82 δ (8H,m,OCH₂), CHN; $C_{18}H_{36}N_2O_2$, Expected % C 69.18 H 11.61 N 8.97 O 10.24 Actual % C 68.90 H 11.55 N 8.93 O 10.62, AMS; M^+ 312.2761 (2.74%, -1.5mmu), $C_5H_{10}NO$ 100.0735 (100%, -2.7mmu).

7.5.(14). 1,12-bis-(1-aza-4-oxacyclohexyl)dodecane.

The diamino compound 7.5.(14)., was prepared according to the method outlined in 7.5.(10)., but after adding water to dissolve the hydrobromide salt, the resultant white precipitate was filtered and dried in vacuo, over NaOH pellets, to yield the crude product. After purification, the sample was analysed.



M.pt. 44°-46°C, IR(Nujol); 2920(vs) 2850(vs) 2820(s) 1465 (vs) 1380(m) 1115(vs), ^1H NMR; 1.24-1.52 δ (20H,m,NCH₂(CH₂)₁₀-CH₂N), 2.36-2.56 δ (12H,m,NCH₂), 3.70-3.84 δ (8H,m,OCH₂), CHN; $C_{20}H_{40}N_2O_2$, Expected % C 70.59 H 11.76 N 8.24 O 9.41 Actual % C 70.55 H 11.68 N 8.15 O 9.62, AMS; M^+ 340.3060 (10.47%, -2.9mmu), $C_5H_{10}NO$ 100.0499 (100%, -26.3mmu).

Amine	Oven Temp. (°C)	Attenuation	Chart Speed (mm/hr)	Sample Size (μ l)	N ₂ Flow (psi)	Outlet Heater (°C)	Retention Time (min)
$\text{MeN}(\text{CH}_2)_7$	144	10×10^4	600	150	8	175	2.10-3.40
$\text{MeN}(\text{CH}_2)_6$	139	10×10^4	600	150	8	175	1.90-3.10
$\text{MeN}(\text{CH}_2)_5$	99	10×10^4	600	150	8	125	2.00-3.50
$\text{MeN}(\text{CH}_2)_4$	74	10×10^4	600	150	8	90	2.10-3.50
NEt_3	81	10×10^4	600	150	8	100	1.30-2.30
MeNEt_2	50	5×10^4	600	150	8	75	1.00-3.00
$\text{MeN} \begin{array}{ c } \hline \text{NMe} \\ \hline \end{array}$	124	10×10^4	600	150	8	150	2.90-5.30
$\text{MeN} \begin{array}{ c } \hline \text{NEt} \\ \hline \end{array}$	136	5×10^4	600	100	8	150	4.25-6.75
$\text{MeN} \begin{array}{ c } \hline \text{O} \\ \hline \end{array}$	104	5×10^4	600	100	8	125	6.20-8.30
Toluene	100	10×10^4	600	150	8	125	3.90-5.70

TABLE 7.(1). Experimental conditions used in Prep GLC purification of selected tertiary amines.

7.6. PURIFICATION OF MATERIALS BY PREPARATIVE GAS LIQUID CHROMATOGRAPHY (PREP GLC).

The tertiary saturated amines and toluene used in our fluorescence studies were purified by distillation, followed by Prep GLC. The experimental conditions employed for each system are listed in Table 7.(1)., along with the observed retention times. The purified samples were then sealed in glass ampoules for long-term storage.

7.7. SOURCES OF MATERIALS USED.

7.7.(1). Spectroscopic Solvents.

These were obtained from the following suppliers and used without further purification:

Aldrich Chemical Co. Ltd. - Acetonitrile (99.5%) and methanol (99.9%) (spectrophotometric grade, GOLD LABEL).

B.D.H. - Tetrahydrofuran.

Eastman-Kodak Co. - Methylcyclohexane.

Goss Scientific Instruments Ltd. - Methanol-OD (99.5%).

Hopkin and Williams - Cyclohexane, dichloromethane and hexane fraction (Spectrosol^R), benzene (scintillator grade).

E. Merck - Benzene and acetonitrile (Uvasol^R).

7.7.(2). Reagents.

The following reagents were supplied as detailed below:

Aldrich Chemical Co. Ltd. - 1-naphthylethanoic acid (1-NEA), 1-naphthoic acid, oxalyl chloride, azacyclopentane (pyrrolidine) N-methylazacyclopentane, azacyclohexane (piperidine), N-methylazacyclohexane, azacycloheptane, azacyclooctane, azacyclononane, azacyclotridecane, 1,4-diazacyclohexane (piperazine), N-methyl-1,4-diazacyclohexane, N,N'-dimethyl-1,4-diazacyclohexane, 1-aza-4-oxacyclohexane (morpholine), N-methyl-1-aza-4-oxacyclohexane, diethylamine, triethylamine, 2-phenylethyl-

amine, N,N-dimethyl-N'-ethyl-1,2-diaminoethane, 1,2,3,4-tetrahydroquinoline, 1,2,3,4-tetrahydroisoquinoline, N-(2-azacyclopentyl-2-oxoethyl)-1,4-diazacyclohexane, N-(2-(1-aza-4-oxacyclohexyl-2-oxoethyl)-1,4-diazacyclohexane, bromo-hexane, -octane and -decane, 1,2-dibromoethane, 1,3-dibromopropane, 1,6-dibromohexane, 1,8-dibromooctane, 1,10-dibromodecane, 1,12-dibromododecane.

B.D.H. - 2-phenylethanoic acid (2-PEA), N,N-dimethyl-(2-hydroxyethyl)amine, N-methyl-N,N-bis-(2-hydroxyethyl)amine, N,N,N-tris-(2-hydroxyethyl)amine, bromopropane, toluene (analar), dimethylsulphoxide (DMSO).

Koch-Light Laboratories Ltd. - 1-naphthylethanoic acid (1-NEA), oxalyl chloride, 1-aza-4-oxacyclohexane.

Fisons Ltd. - DMSO.

R. Emanuel - N,N-dimethyl-1,3-diaminopropane.

7.8. PHOTOPHYSICAL MEASUREMENTS.

7.8.(1). Fluorescence Studies.

All fluorescence measurements were made using an uncorrected Perkin-Elmer MPF-4 Fluorescence Spectrophotometer. Solvents used were of high purity spectrophotometric grade where available, as outlined in Section 7.7.(1). Solvent blanks were recorded in each case, to check that they showed negligible emission, at maximum sensitivity, over the wavelength ranges being monitored. Solutions were made up in 1cm path length quartz rectangular fluorimeter cells, to an OD of 0.1 at the following excitation wavelengths: 310nm (1-naphthyl derivatives), 265nm (phenyl derivatives), 240,250 and 265nm (tertiary aliphatic amines). Degassing was achieved either by (i) thoroughly flushing the solution with a fine stream of dry 'white spot' nitrogen (oxygen free) or argon

(research grade) for about 5-6 minutes and stoppering the cell or (ii) using three consecutive freeze-pump-thaw-shake-cycles (FPTSC). It was found in our work that removal of oxygen from the solutions during degassing cycles was enhanced by taking the closed cell off the vacuum line and vigorously shaking the contents during thawing. On each occasion, the degassing cell was evacuated to a pressure of 10^{-3} mm or less.

Quantum yields of fluorescence (ϕ_F) were determined relative to that from a degassed solution of a standard of known absolute quantum yield, either toluene or 1-methyl naphthalene ($\phi_{F_s} = 0.14, 0.21$ resp.)⁽¹⁵¹⁾, depending upon the system being dealt with. Quantum yields were calculated, by weighing the areas bounded by the spectra of the compound, and comparing them with the weights of the areas enclosed by the standard, recorded under similar conditions (same gain settings and slit widths). Quantum yields derived from a range of sensitivity settings, were averaged out.

7.8.(2). Fluorescence Lifetime Measurements.

The fluorescence lifetimes of the alicyclic amine systems in both cyclohexane and tetrahydrofuran solutions, were recorded using the pulse-sampling technique⁽¹⁸⁸⁾. Whilst not as accurate or sensitive overall as the time-correlated single-photon counting methods (SPC), it provides a simple method for measuring fluorescent lifetimes longer than ~ 2 ns. The diagrammatical representation of the apparatus used, is shown in Figure 7.(1).

Excitation was provided by the discharge from a free-running nanosecond flash lamp (Applied Photophysics Model 311) giving repetition rates up to ~ 10 kHz (depending upon the applied voltage, gas pressure and electrode gap), with a discharge duration of 1-2 ns. Emission from the sample was then

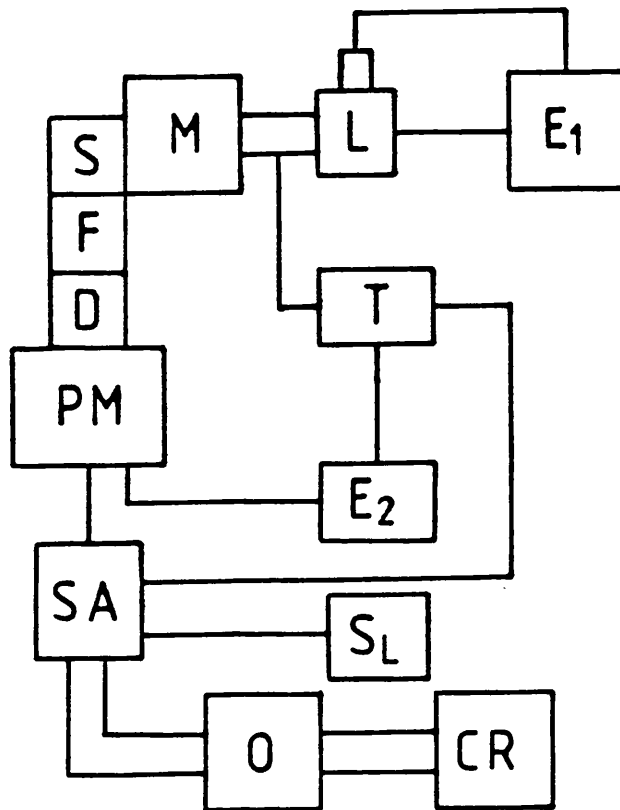


FIGURE 7.(1). Pulse Sampling Apparatus.

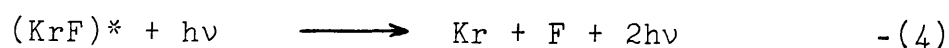
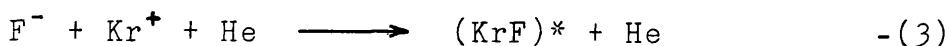
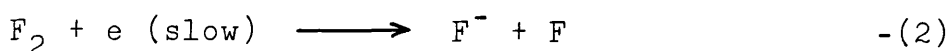
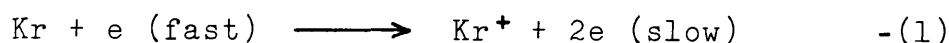
- L Applied Photophysics nanosecond flash lamp (Model 311)
- M Bausch and Lomb 1200mm grating monochromator
- S Sample compartment
- F Neutral density filter
- D Iris diaphragm (manually operated)
- PM Signal photomultiplier tube EMI type 9813 KB
- T Phototrigger - Model 931A photomultiplier tube
- E₁ Brandenburg regulated power supply (0-30kV)
- E₂ Farnell Instruments Ltd. Type E2 stabilised EHT power supply (for PM tube)
- SA Bradley Electronics Sampling Adaptor Type 158
- S_L Ramp generator
- O Telequipment oscilloscope DM64
- CR Advance Model HR-100 X-Y chart recorder

filtered to remove any scattered excitation light, attenuated using an adjustable iris diaphragm and detected with a sensitive end window PM tube (EMI Type 9813 QKB). The time profile of the signal output from the PM tube was detected by a sampling adaptor, whose output was in turn displayed on an oscilloscope or X-Y chart recorder. A second PM tube (Model 931A) linked to the lamp by a fibre-optic cable provided the electrical trigger pulse for the sweep of the sampling adaptor synchronised with the flashing of the lamp.

7.8.(3). Triplet-Triplet Absorption Spectra.

The triplet-triplet absorption spectra of a series of 1-naphthyl derivatives were studied using the technique of nanosecond laser flash photolysis, monitoring the absorption decays at 415nm. Details of the instrumentation used are given below.

Laser Characteristics. The excitation pulse was provided by an Oxford Lasers Ltd., Model KX2 Rare Gas-Halide Excimer Laser using krypton fluoride as the lasing gas. The transitions occurring in this type of laser are characterised by having bound excited molecular levels and weakly bound or even repulsive lower levels. Hence the emission of a photon is followed by rapid dissociation of the molecule ($<1\text{ps}$), preventing a build-up in the lower level. Though complex, the excitation mechanisms of the rare gas-halide lasers are thought to involve the following reactions shown in Scheme 7.(1).



Scheme 7.(1). Excitation Mechanisms in KrF Excimer Laser.

The efficiency of the system is attributed to the very efficient formation of Kr^+ and the fact that $\sim 30\%$ of the energy stored in Kr^+ reappears in the emitted photon. It is also important for stage (3) to proceed very rapidly to create significant populations of the excited $(\text{KrF})^*$, ($\tau \sim 6.5\text{ns}$).

One of the advantages of this type of laser is the ability to adjust the emission wavelength, simply by changing the gas mixture in the laser. Details of the laser output are given in Table 7.(2).⁽¹⁹⁹⁾.

Lasing Molecule	Wavelength (nm)	Peak Power (MW)	Pulse Length (ns)	Pulse Energy (mJ)
ArF	193	10	17	174
KrF	249	10	27	260
XeCl	308	3	25	>100
XeF	353	5	23	114
N_2^+	428	-	-	1
N_2	337	-	-	1
KrCl	222	0.5	20	10

TABLE 7.(2). Characteristics of the Rare Gas-Halide Laser Head Output.

Our present work has involved the use of KrF as the lasing mixture, generating high energy u/v radiation at 249nm. The following gases were used: krypton (BOC Speciality Gases research grade), 2% fluorine - 98% helium (BOC) as the halogen source and helium (research grade) as the buffer gas. Nitrogen or compressed air (better) was supplied to the spark-gap at 30psi, to give reliable triggering.

The gas pressures used in the laser operation for optimal performance are detailed in Table 7.(3). -(Data reproduced by kind permission of Oxford Lasers Ltd.⁽¹⁹⁹⁾).

Lasing Molecule	Wavelength (nm)	Active Gas (mbar)	Halogen Donor (mbar)	Helium (psig)
ArF	193	133	9	20
KrF	249	30	7	20
XeF	353	9	7	20
KrCl	222	33	3	20
XeCl	308	9	4	20
N ₂ ⁺	428	4	-	20
N ₂	337	80	-	-

TABLE 7.(3). Gas Pressures for Optimal Laser Performance.

The halogen donor can be changed from F₂ to HCl, but this involves depassivating and repassivating of the laser interior, a process by which the halogen donors react with the laser electrodes and flanges, covering them with a protective coating of reaction products.

Monitoring System for Transients. The monitoring light source was provided by a 75W Xenon lamp, linked to an arc lamp pulsing unit. It was found to be necessary to instal an isolating switch between the capacitor charging mechanism and the fire button, to prevent premature firing of the lamp from the electrical noise generated in switching. A diagrammatic representation of the laser flash photolysis system is shown in Figure 7.(2).

The laser was used in single-shot mode and triggered by a synchronous signal from the arc lamp pulsing unit, employing a variable delay of 0.2-2.0 μ s. All solutions were made up to an OD=1.0 at the operational wavelength of the laser and were thoroughly degassed by repeated freeze-pump-thaw-shake-cycles. Two shutters, manually operated by the activation of solenoid coils, were utilised to prevent either the laser pulse or xenon monitoring light from falling on the sample compartment. The xenon lamp shutter (SH2), could be left permanently open

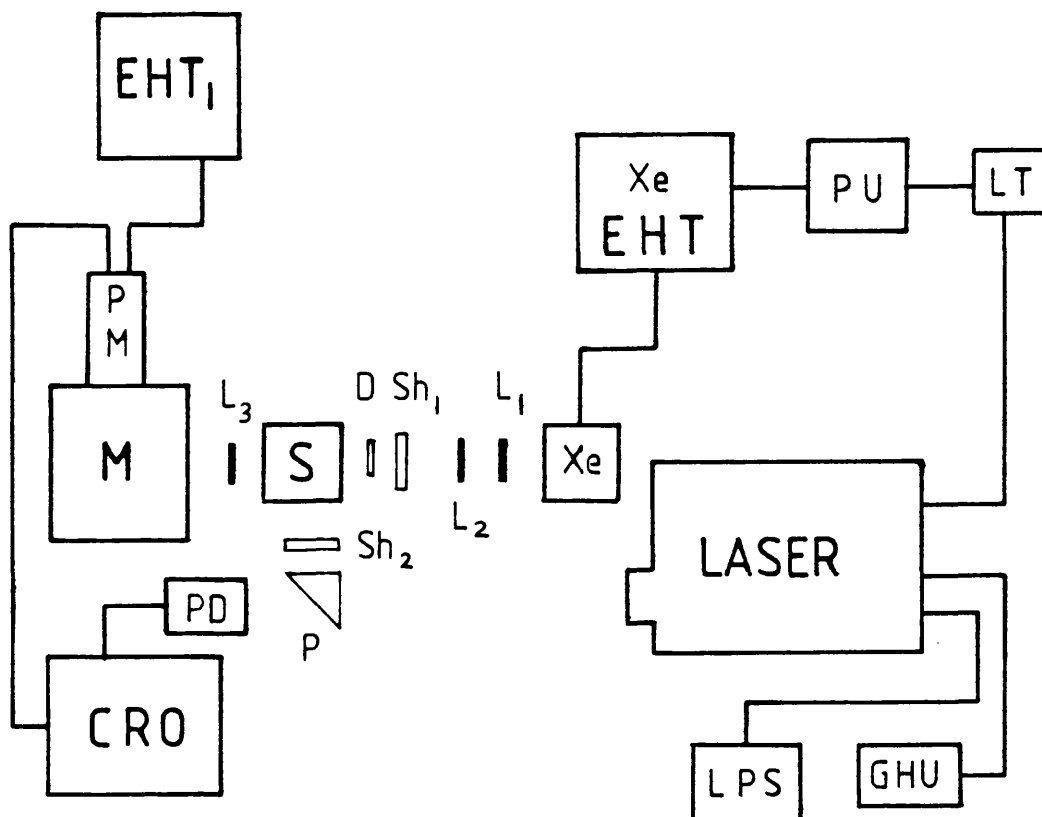


FIGURE 7.(2). Diagrammatic Representation of the Laser Flash Photolysis System.

LPS	Laser power supply
GHU	Laser gas handling unit
Xe	75W xenon lamp
LT	Laser trigger unit
Xe EHT	Xenon lamp power supply
PU	Arc lamp pulsing unit
L_1-L_3	Lenses
D	Diaphragm
SH_1	Xenon lamp shutter
SH_2	Laser pulse shutter
P	Prism
PD	Photodiode
M	Monochromator
PM	Photomultiplier tube (Hamamatsu TV Co. Ltd. Type R928)
EHT_1	PM tube power supply
CRO	Tektronix storage oscilloscope Model 466

when the pulsing unit was in use, as the higher pulse intensity, enabled the use of minimum slit widths on the monochromator inlet and outlet and no problems were encountered with PM tube saturation (Hamamatsu TV Co. Ltd., Type R928). Having set the monochromator at the wavelength of maximal absorption of the triplet species produced, the signal from the PM tube was transmitted to a storage oscilloscope (Tektronix 466) and the decay of the triplet-triplet absorption spectrum displayed on the screen using variable time base settings. The information was recorded on Polaroid 667 black and white land film, using a Shackman Model 7000 oscilloscope camera. The data was then analysed according to the procedure detailed in Appendix (I).

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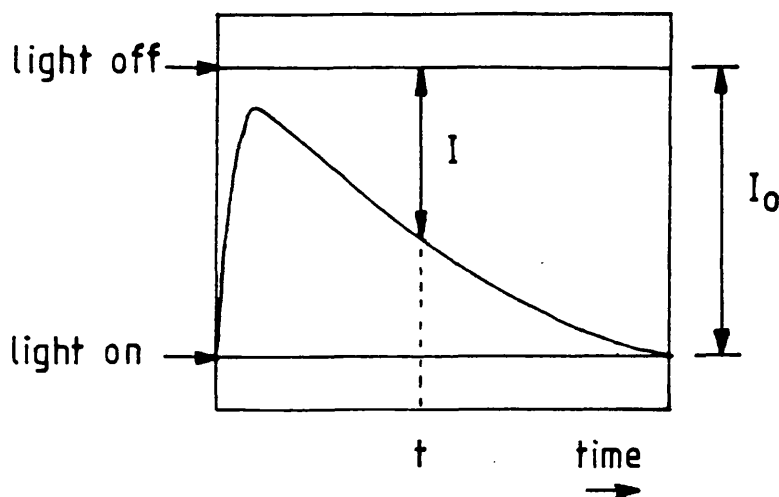
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APPENDIX (I)

ANALYSIS OF TRIPLET-TRIPLET ABSORPTION DECAY CURVES.

With reference to the simplified decay trace shown below, the following procedure was utilised in the analysis of the triplet-triplet absorption decay curves.



(1) Measure I_0 (the difference between the light on and light off levels) and values of I for various values of time ' t ' after flash photolysis.

(2) For First Order Decay Analysis.

(a) Divide I_0 by I for various values of ' t '

(b) Take $\log_{10} \frac{I_0}{I}$ for various values of ' t '

(c) Take $\log_{10}$ values of $\log_{10} \frac{I_0}{I}$

(d) Plot values $\log_{10} \left[\log_{10} \frac{I_0}{I} \right]$ versus time ' t '

(e) If this is a straight line, then slope = $2.303 \times$ rate constant (k_T).

(3) For Second Order Decays.

(a) Divide I_0 by I for various values of ' t '

(b) Take $\log_{10} \frac{I_0}{I}$ for various values of ' t '

(c) Take reciprocal of $\log_{10} \frac{I_0}{I}$ for various values

of 't'

(d) Plot $\left[\log_{10} \frac{I_0}{I} \right]^{-1}$ versus time

(e) For a straight line plot, slope = $\frac{k_T}{\epsilon \times l}$

where k_T = rate constant, ϵ = triplet-triplet molar extinction coefficient, l = path length of cell (cm).

(4) If required the triplet-triplet absorption spectrum of the intermediate may be obtained by plotting values of optical density of transient at $t=t_1$ versus wavelength. In the case of 1-methylnaphthalene, the triplet-triplet absorption was found to maximise at 418nm, whilst naphthalene maximised at 415nm.

STUDIES ON PHOTO-EXCITED COMPLEX FORMATION. - R.A. BEECROFT.

The aims of this project were to investigate the influence of tertiary amine structure upon both intramolecular and intermolecular fluorescent exciplex formation with simple aromatic hydrocarbons and to probe the photophysical properties of a number of polychromophoric systems. In the latter, interest centred upon the possible formation of intramolecular fluorescent exciplexes involving the interaction of more than two chromophoric units.

A series of 2-(1-naphthyl)ethyl- and 2-(phenylethyl)-azacycloalkanes were studied and results indicated that the extent of intramolecular exciplex formation, was influenced by the amine ring size. In the intermolecular interaction between benzene and a series of N-methylated azacycloalkanes in cyclohexane solution, the quenching of the aromatic hydrocarbon fluorescence was found in several cases, to be accompanied by energy transfer to the amino unit, which subsequently fluoresced. Variable temperature studies ruled out the intermediacy of a fluorescent exciplex in the energy transfer process.

Further studies utilising high concentrations of benzene were found to favour the formation of intermolecular fluorescent exciplexes, in which solvation by benzene plays a part. These results indicated that the energy of the amine and solvation of the exciplex were relevant to the pathway taken by the process. The photophysical and nitrogen-15 Nmr properties of the N-methylated azacycloalkanes and closely related α,ω -diaminoalkanes were examined.

Finally our studies into the behaviour of polychromophoric systems containing an aromatic hydrocarbon and two amine groups indicated quite clearly the formation of an intramolecular exciplex involving all three groups.