

Inorganic Chemistry

including bioinorganic chemistry

Inorg. Chem., 1996, 35(5), 1313-1320, DOI:[10.1021/ic9509140](https://doi.org/10.1021/ic9509140)

Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at <http://pubs.acs.org/page/copyright/permissions.html>



ACS Publications

MOST TRUSTED. MOST CITED. MOST READ.

Copyright © 1996 American Chemical Society

Table S1 ESR Parameters and Concentrations of PhCNSNS[·] at Various Temperatures

temperature		h_{pp}^b	ΔH_{pp}^b	I^b	$[\text{PhCNSNS}^\cdot]^c$
t (°C)	T (°K)	(mm)	(G)		(M)
+20	293	89	1.80	288	0.0380
+5	278	128	1.44	265	0.0350
-10	263	153	1.28	252	0.0335
-25	248	166	1.19	235	0.0310
-40	233	168	1.14	218	0.0290
-55	218	143	1.12	180	0.0237
-70	203	127	1.07	145	0.0191

(a) PhCNSNS[·] was generated by reduction of PhCNSNSAsF₆ (0.0139 g, 0.0376 mmol) with SbPh₃ (0.053 g, 0.15 mmol)/Me₄NCl (0.031 g, 0.28 mmol) in SO₂ (0.055 g)/CFCl₃ (1.417 g) mixture.

(b) The h_{pp} and ΔH_{pp} stand for the peak height (arbitrary unit) and peak-to-peak width (in Gauss) respectively for the most upfield peak of the ESR spectra of PhCNSNS[·] (1:1:1 triplet); the I stands for the intensity of this peak, formulated as

$$I = h_{pp} \times \Delta H_{pp}^2$$

which is directly proportional to the concentration of the PhCNSNS[·] monomer.

(c) The concentrations (C) of PhCNSNS[·] at various temperatures are determined using the formula

$$C = (C_0 I) / I_0$$

C₀ and I₀ stand for the concentration and intensity of ESR spectrum of PhCNSNS[·] at +20 °C respectively. The dimerization of

P-1320-2
~~2~~

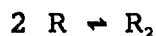
(Table S1 continued)

PhCNSNS· at this temperature (ca. 3%) is reasonably negligible, therefore the initial concentration C_0 can be obtained based on the amount of original PhCNSNSAsF₆ added.

Table S2 Equilibria Constants of the Dimerization^a of PhCNSNS·
at Various Temperatures

temperature T(K)	1/T(10 ³ K ⁻¹)	[PhCNSNS·] (M)	[(PhCNSNS·) ₂] ^a (M)	K ^a	lnK
293	3.41	0.0380	-----	-----	-----
278	3.60	0.0350	0.0015	1.22	0.20
263	3.80	0.0335	0.0023	2.05	0.72
248	4.03	0.0310	0.0035	3.64	1.29
233	4.29	0.0290	0.0045	5.35	1.68
218	4.59	0.0237	0.0072	12.8	2.55
203	4.93	0.0191	0.0095	26.04	3.26

a) There is an equilibrium between PhCNSNS· monomer (R) and dimer (R₂) in solution as follows:



The dimerization equilibrium constant (K) can be formulated as

$$K = [R_2]/[R]^2$$

where $[R_2] = 1/2 ([R]_0 - [R])$, and $[R]_0$ represents the initial concentration of PhCNSNS· radical.

The concentrations of PhCNSNS· monomer [R] at various temperatures were determined by ESR spectroscopy.

The dimerization enthalpy (ΔH_d^0) and entropy (ΔS_d^0) were determined from the slope and intercept of lnK v.s. 1/T plot respectively according to the following equation:

$$\ln K = -\Delta H_d^0/RT + \Delta S_d^0/R$$

The linear relationship of lnK with 1/T (correlation coefficient 0.98) was established by computer regression analysis

(Table S2 continued)

with

$$\text{slope} = -\Delta H_d^0/R = 2.28(2) \times 10^3$$

$$\text{intercept} = \Delta S_d^0/R = -8.00(9)$$

Therefore, $\Delta H_d^0 = -19.0(2)$ kJ/mol and $\Delta S_d^0 = -66.5(7)$ kJ/Kmol.

$$T = 298 \text{ K: } \Delta G_{298}^0 = \Delta H_d^0 - 298\Delta S_d^0 = 817 \text{ J/mol}$$

$$\Delta G_{298}^0 = -298 \ln K_{298} \quad K_{298} = 0.72$$

At 298 K, the percentage of dimerization of 0.02 M PhCNSNS is ca.

3%.

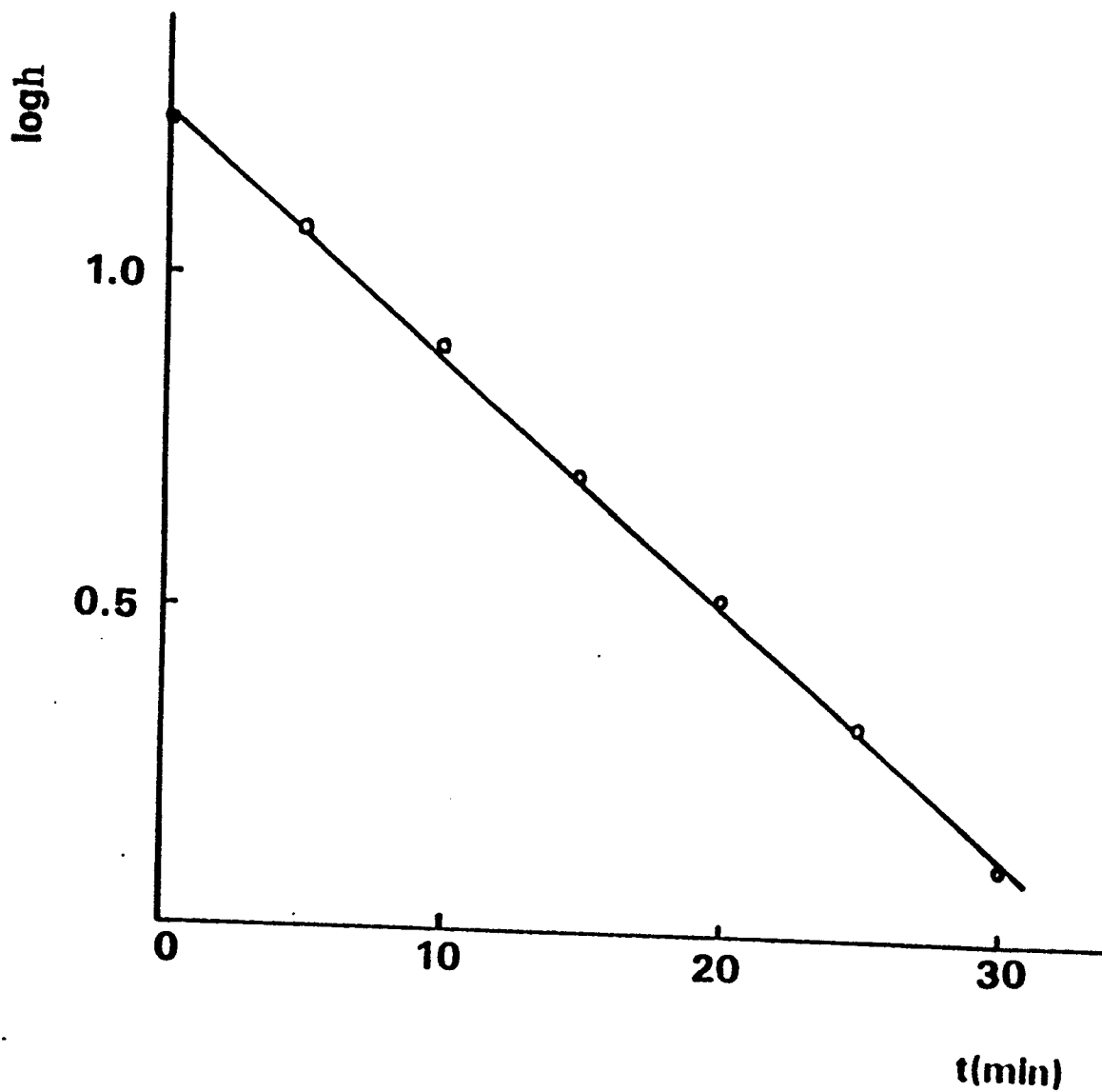


Fig.S1 The change in height (h) of the most upfield peak in ESR spectra of $\text{Bu}^t\overline{\text{CNSNS}}$ with the irradiation (at 254 nm) time.

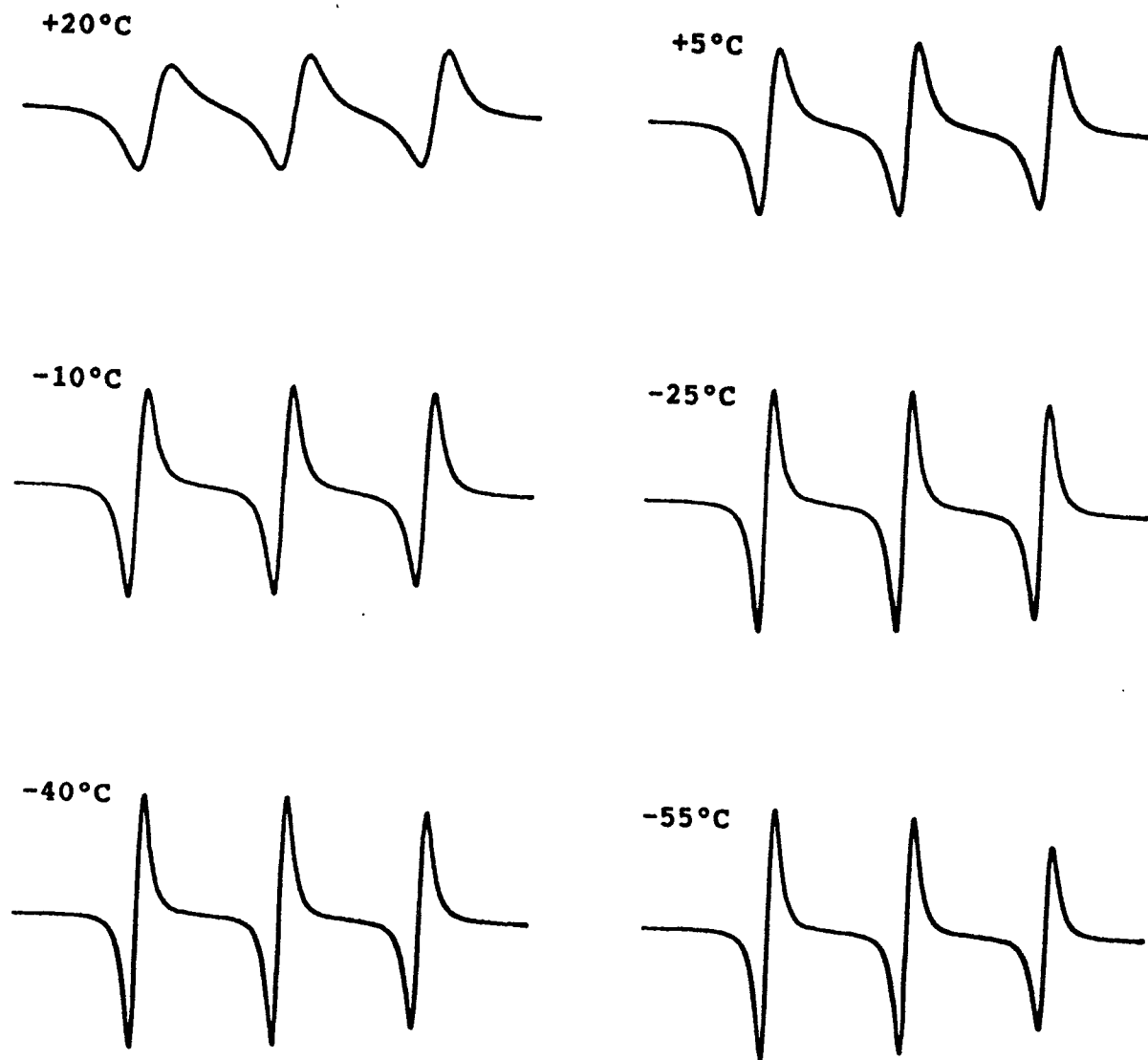


Fig.S2 The ESR spectra of $\text{Ph}\overline{\text{CNSNS}}\cdot$ radical (0.038 M) at various temperatures.

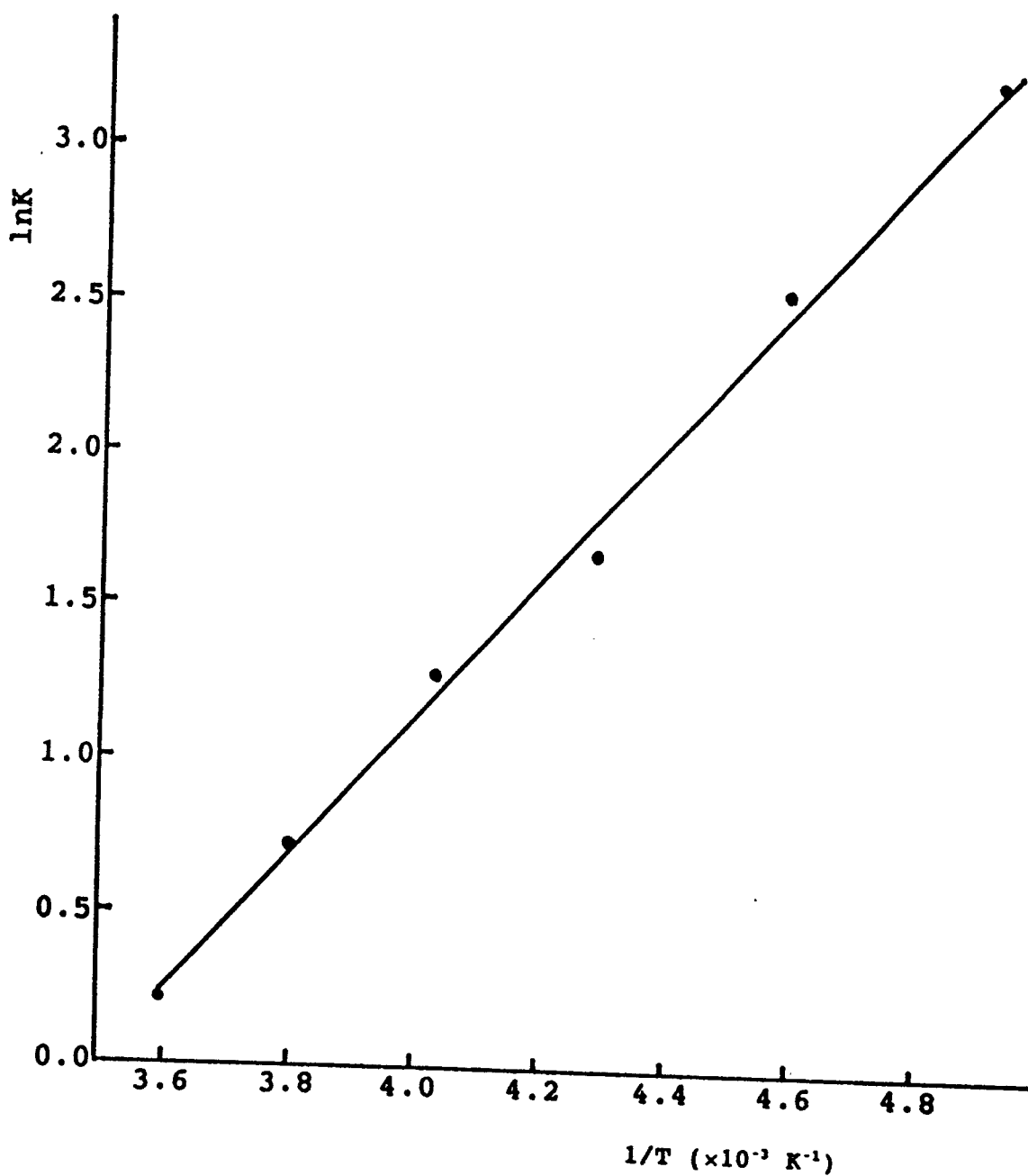


Fig. 3 The plot of logarithm of the equilibrium constant (K) of PhCNSNS dimerization against the reciprocal of the absolute temperature.

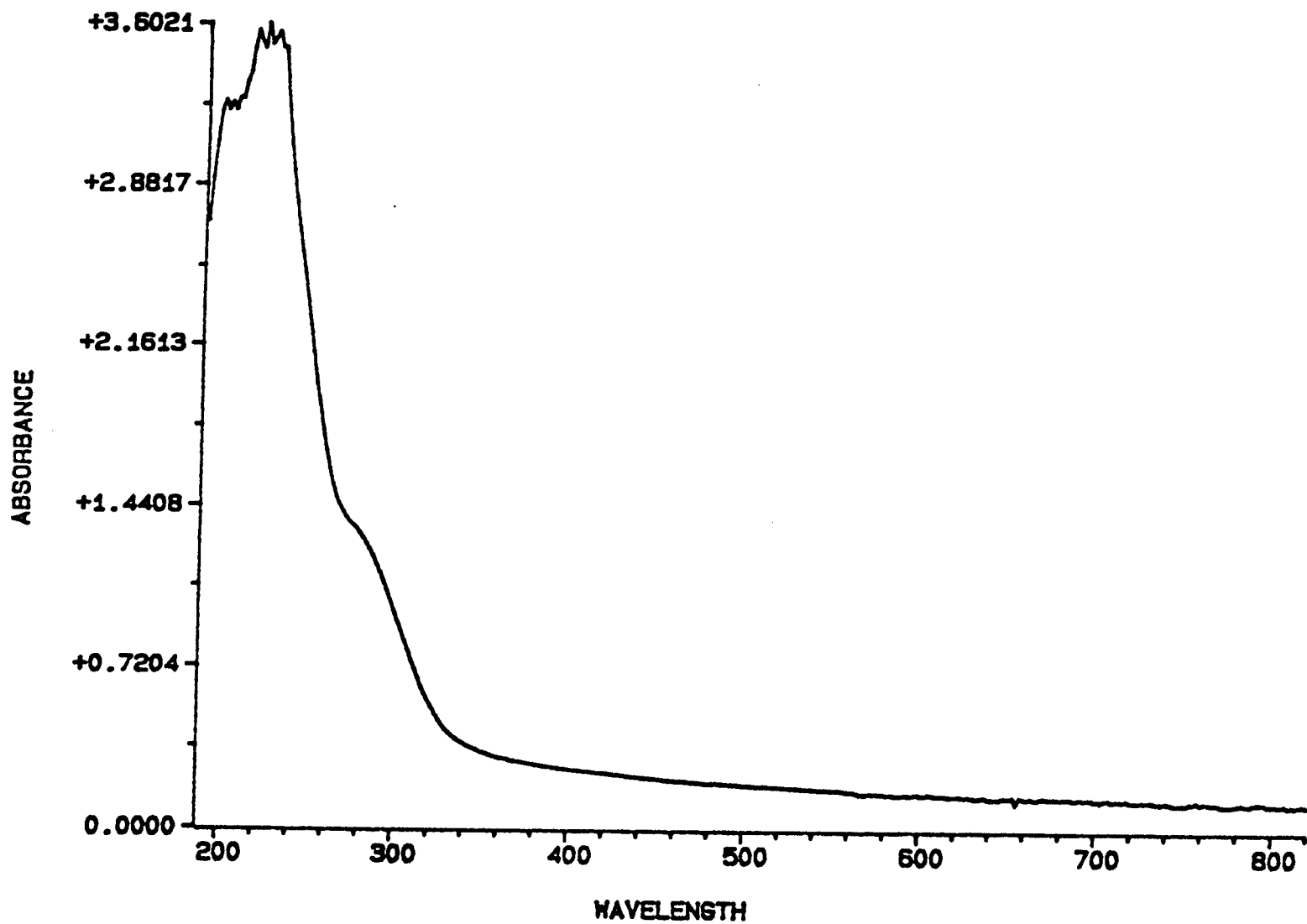


Fig.S4 The UV-Visible spectrum of pure PhC(NSSN) in CFCl_3 (ca. 0.04 M).

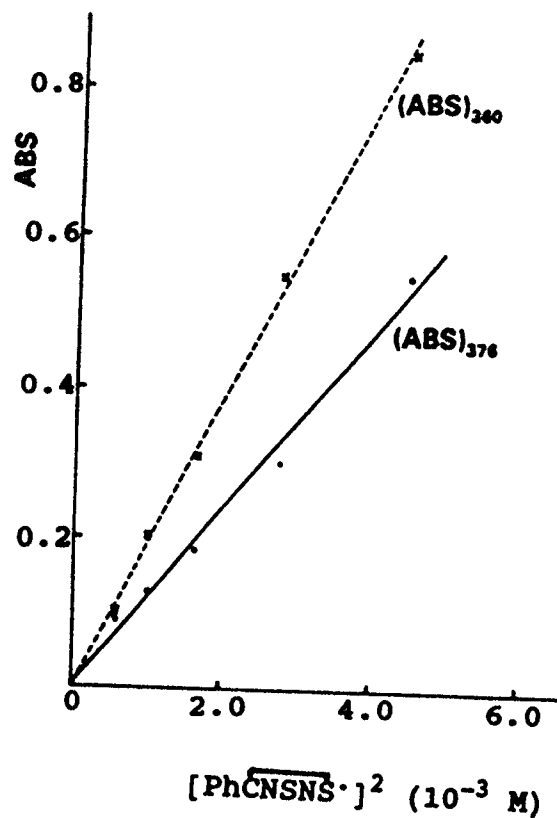
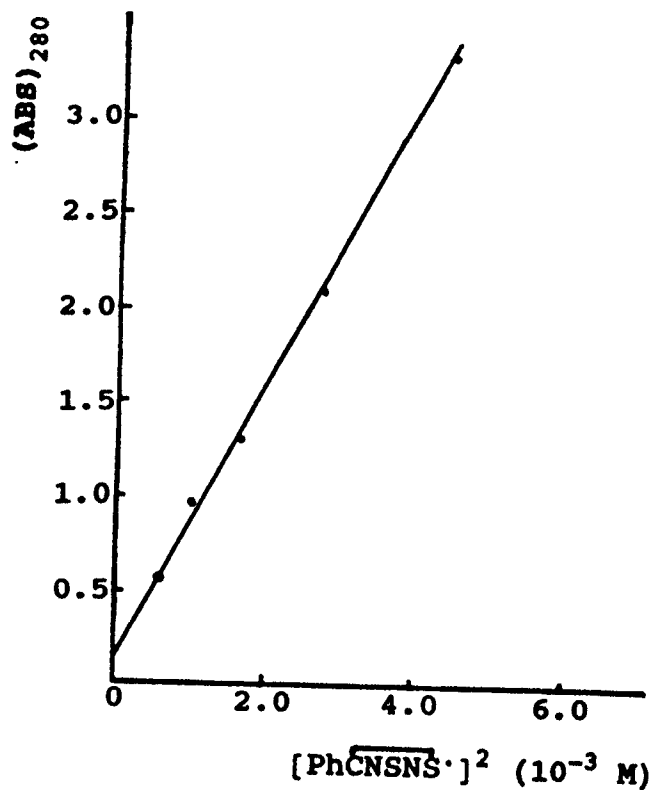


Fig. 5 The relationship between the absorbances of bands (at 280, 360 and 376 nm) in the simulated UV-Vis spectra of $\text{PhCNSNS}\cdot$ and the square of the initial concentration of $\text{PhCNSNS}\cdot$ (A) monomer $[\text{A}]^2$.

P-1320-9