Supplementary Material

Photochemistry of Crystalline Chlorodiazirines: The Influence of Conformational Disorder and Intermolecular Cl···N=N Interactions on the Solid State Reactivity of Singlet Chlorocarbenes

Carlos N. Sanrame, Christopher P. Suhrada, Hung Dang and Miguel A. Garcia-Garibay*

Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569.

mgg@chem.ucla.edu

General. NMR spectra were obtained on a Bruker ARX-400 spectrometer. DSC was performed using a Perkin Elmer Pyris 1 differential scanning calorimeter. UV absorptions were measured on a Hewlett-Packard 8453 UV-visible spectrometer. IR spectra were acquired with a Perkin Elmer Paragon 100 FT-IR instrument. EI-HRMS was performed using a VG Autospec (Micromass: Beverly, MA) spectrometer.

α-(4'-Biphenyl)acetamidine hydrochloride (**7b**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.21 (s, 2H); 7.3-7.8 (m, 9H); 8.92 (br s, 2H); 9.47 (br s, 2H). HRMS (EI): Calculated for $C_{14}H_{14}N_2$ (free base), 211.1197; found 211.1191.

α-(4'-Biphenyl)-N-*chloroacetamidine* (**8b**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 2H); 5.18 (br s, 2H); 7.2-7.7 (m, 9H). HRMS (EI): Calculated for $C_{14}H_{13}ClN_2$, 244.0767; found, 244.0772.

General procedure for preparation of chlorodiazirines **4**. In a 50 mL round bottom flask, 1 mmol of **7** was suspended in 12 mL CH_2Cl_2 and 0.2 mmol TBAHS was added. Under *vigorous* magnetic stirring, 12 mL of 1.0 M NaOH(aq) in saturated NaCl(aq) (from dilution of 5 M NaOH with brine) were added. A solution containing 0.5 mL *t*-BuOCl in 2 mL CH_2Cl_2 was then added over a period of *ca*. 45 min until the *N*-chloro intermediate **8** disappeared. The deeply colored biphasic emulsion was separated by decantation and the aqueous layer extracted once with CH_2Cl_2. The combined organic extracts were dried over $CaCl_2$ and passed through a short column of silica gel with CH_2Cl_2 to remove the TBAHS. Purification by column chromatography (SiO_2, pentane) yielded the corresponding chlorodiazirine.

3-(4'-Biphenyl)-3-chlorodiazirine (**4a**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.1-7.7 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.0, 126.4, 127.2, 127.9, 128.9, 134.6, 139.8, 142.3. IR (KBr pellet) 1574, 1485, 1406, 1259, 1034, 1009 cm^{-1}. UV (cyclohexane) 358, 377, 396 nm. M.p. 95 °C (dec.) by DSC. HRMS (EI): Calculated for $C_{13}H_9ClN_2$, 228.0454; found, 228.0452.

3-(4'-Biphenylmethyl)-3-chlorodiazirine (**4b**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (s, 2H); 7.2-7.8 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.3, 48.4, 127.1, 127.5, 127.6, 128.9, 130.0, 131.8, 140.6, 140.8. IR (KBr pellet) 1565, 1488, 1409, 1164, 1123 cm^{-1}. UV (pentane) 340, 349, 357 nm. M.p. 75 °C by DSC. HRMS (EI): Calculated for $C_{14}H_{11}ClN_2$, 242.0611; found, 242.0615.

3-(2-(4'-Biphenyl)ethyl)-3-chlorodiazirine (**4c**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (t, J = 8 Hz) 2H; 2.79 (t, J = 8 Hz) 2H; 7.2 (m, 2H); 7.3 (m, 1H); 7.4 (m, 2H), 7.5-7.6 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.2, 39.1, 48.3, 127.0, 127.2, 127.4, 128.8, 138.2, 139.6, 140.8. IR (KBr pellet) 1567, 1488, 1452, 1407, 1170, 1030 cm^{-1}.

UV (cyclohexane) 342, 349, 360 nm. M.p. 71 °C by DSC. HRMS (EI): Calculated for $C_{15}H_{13}ClN_2$, 256.0767; found 256.0763.

3-(1-(4-Bipheny)-1-methylethyl)-3-chlorodiazirine (**4d**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 6H); 7.36 (m, 1H); 7.45 (m, 2H); 7.62 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.9, 44.5, 55.8, 126.7, 127.1, 127.3, 128.8, 140.1, 140.6, 143.3. IR (KBr pellet) 1568, 1469, 1402, 1368, 1254, 1076, 1006 cm^{-1}. UV (cyclohexane) 343, 349, 360 nm. M.p. 58 °C by DSC. HRMS (EI): Calculated for $C_{16}H_{15}ClN_2$, 270.0924; found, 270.0923.

General procedure for solution photolysis. Approximately 10 mg of chlorodiazirine **4** was dissolved in 0.7 mL C_6D_6 in an NMR tube. The sample was placed behind a λ > 350 nm filter and wrapped in foil to exclude adventitious light, then photolyzed for *ca*. 2 h before a 400 W Hanovia medium pressure quartz mercury vapor lamp.

General procedure for solid state photolysis. A sample of approximately 10 mg of chlorodiazirine **4** was ground into a powder and sandwiched as a very thin layer between Pyrex microscope slides. The slides were placed behind a λ > 350 nm filter and wrapped in foil to exclude adventitious light, then photolyzed before a 400 W Hanovia medium pressure quartz mercury vapor lamp.

Solution photolysis of **4a**. Upon photolysis, a white solid precipitated from the C_6D_6 solution. The solid was collected by filtration and identified as 1,4-(bis-4'-biphenyl)-1,4-dichloro-2,3-diaza-1,3-butadiene (**9a**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (m, 2H); 7.48 (m, 4H); 7.69 (m, 8H); 8.22 (m, 4H). Due to the low solubility of **9a** in $CDCl_3$ and all other solvents tested, it was not feasible to obtain a ^{13}C NMR spectrum. IR (KBr pellet) 1595, 1484, 1403, 1201 cm^{-1}. UV (chloroform) 359 nm. M.p. ca. 280 °C. HRMS (EI): Calculated for $C_{26}H_{18}Cl_2N_2$, 428.0847; found, 428.0848.

Solid state photolysis of **4a**. After 6 h photolysis, a solid product was collected. This product failed to dissolve to an appreciable extent in ether, but TLC analysis of the ether supernatant confirmed the near-total absence of starting material **4a**. The solid was identified as **9a** by comparison of characterization data (*v.s.*).

Solution photolysis of **4b**. Prior to photolysis, the following ^{1}H NMR spectrum was obtained for chlorodiazirine **4b** (400 MHz, C_6D_6): δ 2.74 (s, 2H); 6.90 (m, 2H); 7.05-7.25 (m, 3H); 7.32 (m, 2H); 7.39 (m, 2H). After 2 h photolysis, the following products and ratios were assigned on the basis of the following signals (residual **4b** = 12 %).
(Z)-1-Chloro-2-(4'-biphenyl)ethene ((*Z*)-**6b**) (18 %): δ 5.84 (d, J = 8 Hz, 1H); 6.19 (d, J = 8 Hz, 1H).
(E)-1-Chloro-2-(4'-biphenyl)ethene ((*E*)-**6b**) (70 %): δ 6.27 (d, J = 14 Hz, 1H); 6.63 (d, J = 14 Hz, 1H).

Solid state photolysis of **4b**. The solid photolysis product mixture was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR (400 MHz). Products were identified and ratios assigned based on the following major signals.
(Z)-1-Chloro-2-(4'-biphenyl)ethene ((*Z*)-**6b**): δ 6.29 (d, J = 8 Hz, 1H); 6.67 (d, J = 8 Hz, 1H).
(E)-1-Chloro-2-(4'-biphenyl)ethene ((*E*)-**6b**): δ 6.69 (d, J = 13 Hz, 1H); 6.87 (d, J = 13 Hz, 1H).
1,6-Bis(4'-biphenyl)-2,5-dichloro-3,4-diaza-2,4-hexadiene (**9b**): δ 4.02 (s, 4H).
Minor impurities in the sample were removed by passing the product mixture through a short column of silica gel and eluting with 1:1 CH_2Cl_2-pentane. Thus was obtained a pure mixture whose ^{1}H NMR spectrum showed signals for (*Z* + *E*)-**6b** and **9b**; MS analysis on this sample produced corresponding M^+ peaks:
6b HRMS (EI): Calculated for $C_{14}H_{11}Cl$, 214.0549; found, 214.0554.
9b HRMS (EI): Calculated for $C_{28}H_{22}Cl_2N_2$, 456.1160; found, 456.1165.

Solution photolysis of **4c**. Prior to photolysis, the following ^{1}H NMR spectrum was obtained for chlorodiazirine **4c** (400 MHz, C_6D_6): δ 1.73 (t, J = 8 Hz, 2H); 2.34 (t, J = 8 Hz, 2H); 6.80 (m, 2H); 7.14 (m, 1H); 7.22 (m, 2H); 7.37 (m, 2H); 7.47 (m, 2H). After 135 min photolysis, the following products and ratios were assigned on the basis of the following signals (residual **4c** = 3 %).
(Z)-1-Chloro-3-(4'-biphenyl)propene ((*Z*)-**6c**) (72 %): δ 3.41 (dd, J_d = 7 Hz, J_d = 1 Hz, 2H); 5.52 (dt, J_d = 7 Hz, J_t = 7 Hz, 1H); 5.75 (dt, J_d = 7 Hz, J_t = 1 Hz, 1H).
(E)-1-Chloro-3-(4'-biphenyl)propene ((*E*)-**6c**) (25 %): δ 2.89 (dd, J_d = 7 Hz, J_d = 1 Hz, 2H); 5.64 (dt, J_d = 13 Hz, J_t = 1 Hz, 1H); 5.83 (dt, J_d = 13 Hz, J_t = 7 Hz, 1H).

Solid state photolysis of **4c**. The solid photolysis product mixture was dissolved in $CDCl_3$ and analyzed by ^1H NMR (400 MHz). Products were identified and ratios assigned based on the following major signals.
(Z)-1-Chloro-3-(4'-biphenyl)propene ((*Z*)-**6c**): δ 3.63 (dd, J_d = 7 Hz, J_d = 1.5 Hz, 2H); 5.99 (dt, J_d = 7 Hz, J_t = 7 Hz, 1H); 6.18 (dt, J_d = 7 Hz, J_t = 1.5 Hz, 1H).
(E)-1-Chloro-3-(4'-biphenyl)propene ((*E*)-**6c**): δ 3.43 (d, *J* = 6 Hz, 2H).
1,8-Bis(4'-biphenyl)-3,6-dichloro-4,5-diaza-3,5-octadiene (**9c**): δ 3.02 (t, *J* = 7 Hz, 4H); 3.11 (t, *J* = 7 Hz, 4H).
Minor impurities in the sample were removed by passing the product mixture through a short column of silica gel and eluting with 1:1 CH_2Cl_2-pentane. Thus was obtained a pure mixture whose ^1H NMR spectrum showed signals for (*Z* + *E*)-**6c** and **9c**; MS analysis on this sample produced corresponding M^+ peaks:
6c HRMS (EI): Calculated for $C_{15}H_{13}Cl$, 228.0706; found, 228.0711.
9c HRMS (EI): Calculated for $C_{30}H_{26}Cl_2N_2$, 484.1473; found, 484.1481.

Solution photolysis of **4d**. Prior to photolysis, the following ^1H NMR spectrum was obtained for chlorodiazirine **4d** (400 MHz, C_6D_6): δ 0.99 (s, 6H); 7.1-7.6 (m, 9H). After 120 min photolysis, the product **6d** was assigned on the basis of the following signals (residual **4d** = 4 %).
1-(4'-Biphenyl)-1-chloro-2-methylpropene (**6d**) (96 %): δ 1.53 (s, 3H); 1.88 (s, 3H); 7.1-7.5 (m, 9H).
After photolyzing the sample for an additional 2 h, no starting material was apparent by ^1H NMR, leaving a relatively pure sample of **6d**. This sample was then used for additional characterization: ^{13}C NMR (100 MHz, C_6D_6) δ 21.8, 22.1, 127.1, 127.3, 127.4, 129.0, 129.1, 130.1, 130.7, 138.6, 141.1. HRMS (EI): Calculated for $C_{16}H_{15}Cl$, 242.0862; found, 242.0866.

Solid state photolysis of **4d**. The solid photolysis product mixture was dissolved in $CDCl_3$ and analyzed by ^1H NMR (400 MHz). Integration of methyl signals indicated foprmation of **6d** as the only product. Some melting was observed at high conversion values.

Table 1. Crystal data and structure refinement for 3-(4'-Biphenylmethyl)-3-chlorodiazirine (**4b**).

Identification code	gg1101	
Empirical formula	C14 H11 Cl N2	
Formula weight	242.70	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.4274(12) Å	α = 90°.
	b = 5.6755(8) Å	β = 96.963(3)°.
	c = 25.158(4) Å	γ = 90°.
Volume	1194.4(3) $Å^3$	
Z	4	
Density (calculated)	1.350 Mg/m^3	
Absorption coefficient	0.296 mm^{-1}	
F(000)	504	
Crystal size	0.4 x 0.15 x 0.1 mm^3	
Theta range for data collection	1.63 to 28.25°.	
Index ranges	-10<=h<=11, -6<=k<=7, -33<=l<=24	
Reflections collected	6572	
Independent reflections	2588 [R(int) = 0.0275]	
Completeness to theta = 28.25°	87.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000000 and 0.837052	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2588 / 8 / 177	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0543, wR2 = 0.1405	
R indices (all data)	R1 = 0.0822, wR2 = 0.1588	
Extinction coefficient	0.000(2)	
Largest diff. peak and hole	0.397 and -0.383 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 3-(4'-Biphenylmethyl)-3-chlorodiazirine (**4b**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	1858(2)	4754(7)	267(1)	52(1)
N(1)	4399(5)	7677(5)	176(1)	49(1)
N(2)	3066(6)	8472(8)	409(2)	37(1)
Cl(1')	3830(9)	8700(12)	546(3)	71(2)
N(1')	3018(15)	4143(19)	-31(4)	51(3)
N(2')	2070(20)	4850(70)	271(12)	50
C(1)	3609(4)	5980(6)	520(1)	48(1)
C(2)	4623(3)	4710(5)	952(1)	33(1)
C(3)	3893(3)	4638(4)	1474(1)	25(1)
C(4)	2952(3)	2766(4)	1601(1)	35(1)
C(5)	2299(3)	2705(4)	2082(1)	31(1)
C(6)	2578(2)	4509(4)	2456(1)	20(1)
C(7)	3527(3)	6393(4)	2325(1)	25(1)
C(8)	4165(3)	6453(4)	1844(1)	26(1)
C(9)	1925(2)	4412(4)	2984(1)	20(1)
C(10)	1011(4)	2567(6)	3119(1)	55(1)
C(11)	428(5)	2465(6)	3610(1)	61(1)
C(12)	752(3)	4189(5)	3982(1)	32(1)
C(13)	1628(5)	6054(7)	3851(1)	72(1)
C(14)	2208(5)	6167(6)	3358(1)	70(1)

Table 3. Bond lengths [Å] and angles [°] for 3-(4'-Biphenylmethyl)-3-chlorodiazirine (**4b**).

Cl(1)-C(1)	1.685(4)
N(1)-N(2)	1.404(6)
N(1)-C(1)	1.503(4)
N(2)-C(1)	1.502(5)
Cl(1')-C(1)	1.556(7)
N(1')-N(2')	1.237(19)
N(1')-C(1)	1.758(9)
N(2')-C(1)	1.513(19)
C(1)-C(2)	1.486(4)
C(2)-C(3)	1.516(3)
C(3)-C(4)	1.386(3)
C(3)-C(8)	1.389(3)
C(4)-C(5)	1.389(3)
C(5)-C(6)	1.391(3)
C(6)-C(7)	1.398(3)
C(6)-C(9)	1.500(3)
C(7)-C(8)	1.384(3)
C(9)-C(10)	1.367(3)
C(9)-C(14)	1.371(4)
C(10)-C(11)	1.385(4)
C(11)-C(12)	1.358(4)
C(12)-C(13)	1.353(4)
C(13)-C(14)	1.388(4)
N(2)-N(1)-C(1)	62.1(3)
N(1)-N(2)-C(1)	62.2(2)
N(2')-N(1')-C(1)	57.6(10)
N(1')-N(2')-C(1)	78.8(11)
C(2)-C(1)-N(2)	136.7(3)
C(2)-C(1)-N(1)	118.5(3)
N(2)-C(1)-N(1)	55.7(3)
C(2)-C(1)-N(2')	119.1(17)
N(2)-C(1)-N(2')	95.4(16)
N(1)-C(1)-N(2')	116.8(15)
C(2)-C(1)-Cl(1')	113.3(3)
N(2)-C(1)-Cl(1')	26.6(2)
N(1)-C(1)-Cl(1')	47.9(3)
N(2')-C(1)-Cl(1')	122.0(16)
C(2)-C(1)-Cl(1)	118.4(3)
N(2)-C(1)-Cl(1)	94.9(3)
N(1)-C(1)-Cl(1)	118.4(3)
N(2')-C(1)-Cl(1)	2.4(10)
Cl(1')-C(1)-Cl(1)	121.4(3)
C(2)-C(1)-N(1')	111.9(4)
N(2)-C(1)-N(1')	111.2(5)
N(1)-C(1)-N(1')	91.7(4)
N(2')-C(1)-N(1')	43.6(8)
Cl(1')-C(1)-N(1')	130.0(5)
Cl(1)-C(1)-N(1')	46.0(5)
C(1)-C(2)-C(3)	112.9(2)
C(4)-C(3)-C(8)	117.8(2)
C(4)-C(3)-C(2)	121.6(2)
C(8)-C(3)-C(2)	120.6(2)
C(3)-C(4)-C(5)	121.2(2)
C(4)-C(5)-C(6)	121.2(2)
C(5)-C(6)-C(7)	117.3(2)

C(5)-C(6)-C(9)	121.5(2)
C(7)-C(6)-C(9)	121.19(19)
C(8)-C(7)-C(6)	121.2(2)
C(7)-C(8)-C(3)	121.2(2)
C(10)-C(9)-C(14)	116.2(2)
C(10)-C(9)-C(6)	121.8(2)
C(14)-C(9)-C(6)	122.0(2)
C(9)-C(10)-C(11)	121.7(3)
C(12)-C(11)-C(10)	121.3(3)
C(13)-C(12)-C(11)	117.8(2)
C(12)-C(13)-C(14)	121.0(3)
C(9)-C(14)-C(13)	121.9(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 3-(4'-Biphenylmethyl)-3-chlorodiazirine (**4b**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	42(1)	79(1)	33(1)	-3(1)	-2(1)	2(1)
N(1)	88(3)	33(2)	30(2)	0(1)	29(2)	-3(2)
N(2)	74(3)	17(2)	21(2)	2(2)	17(2)	10(2)
Cl(1')	111(5)	50(3)	52(3)	-3(2)	14(3)	0(3)
N(1')	79(8)	44(6)	28(5)	-17(4)	-2(5)	5(6)
C(1)	64(2)	54(2)	30(1)	10(1)	25(1)	22(2)
C(2)	35(1)	36(1)	30(1)	-2(1)	14(1)	1(1)
C(3)	26(1)	27(1)	24(1)	1(1)	7(1)	4(1)
C(4)	54(2)	23(1)	29(1)	-9(1)	15(1)	-6(1)
C(5)	43(2)	23(1)	30(1)	-3(1)	14(1)	-9(1)
C(6)	18(1)	20(1)	21(1)	1(1)	1(1)	3(1)
C(7)	27(1)	25(1)	21(1)	-3(1)	0(1)	-6(1)
C(8)	24(1)	29(1)	24(1)	2(1)	0(1)	-9(1)
C(9)	18(1)	21(1)	21(1)	2(1)	1(1)	2(1)
C(10)	87(2)	43(2)	42(2)	-19(1)	35(2)	-37(2)
C(11)	98(3)	45(2)	49(2)	-10(2)	43(2)	-37(2)
C(12)	32(1)	44(2)	22(1)	3(1)	7(1)	-2(1)
C(13)	103(3)	75(3)	47(2)	-38(2)	45(2)	-57(2)
C(14)	110(3)	58(2)	52(2)	-31(2)	53(2)	-58(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 3-(4'-Biphenylmethyl)-3-chlorodiazirine (**4b**).

	x	y	z	U(eq)
H(2A)	5679	5491	1015	39
H(2B)	4795	3077	833	39
H(4)	2750	1502	1354	41
H(5)	1650	1407	2156	37
H(7)	3738	7655	2572	29
H(8)	4802	7760	1765	31
H(10)	769	1324	2870	66
H(11)	-212	1161	3689	74
H(12)	376	4091	4322	39
H(13)	1850	7303	4100	86
H(14)	2819	7499	3278	84

Table 6. Torsion angles [°] for 3-(4'-Biphenylmethyl)-3-chlorodiazirine (**4b**).

N(1)-N(2)-C(1)-C(2)	96.8(4)
N(1)-N(2)-C(1)-N(2')	-118.9(11)
N(1)-N(2)-C(1)-Cl(1')	63.2(9)
N(1)-N(2)-C(1)-Cl(1)	-121.3(3)
N(1)-N(2)-C(1)-N(1')	-76.9(5)
N(2)-N(1)-C(1)-C(2)	-129.2(4)
N(2)-N(1)-C(1)-N(2')	77.5(14)
N(2)-N(1)-C(1)-Cl(1')	-32.6(3)
N(2)-N(1)-C(1)-Cl(1)	75.4(3)
N(2)-N(1)-C(1)-N(1')	114.7(5)
N(1')-N(2')-C(1)-C(2)	-92.0(19)
N(1')-N(2')-C(1)-N(2)	115.3(18)
N(1')-N(2')-C(1)-N(1)	61(2)
N(1')-N(2')-C(1)-Cl(1')	116.3(16)
N(1')-N(2')-C(1)-Cl(1)	-167(45)
N(2')-N(1')-C(1)-C(2)	110(3)
N(2')-N(1')-C(1)-N(2)	-75(3)
N(2')-N(1')-C(1)-N(1)	-129(3)
N(2')-N(1')-C(1)-Cl(1')	-97(3)
N(2')-N(1')-C(1)-Cl(1)	1(3)
N(2)-C(1)-C(2)-C(3)	67.3(5)
N(1)-C(1)-C(2)-C(3)	136.2(3)
N(2')-C(1)-C(2)-C(3)	-71.1(11)
Cl(1')-C(1)-C(2)-C(3)	82.9(4)
Cl(1)-C(1)-C(2)-C(3)	-68.4(3)
N(1')-C(1)-C(2)-C(3)	-119.1(5)
C(1)-C(2)-C(3)-C(4)	93.1(3)
C(1)-C(2)-C(3)-C(8)	-87.6(3)
C(8)-C(3)-C(4)-C(5)	0.1(4)
C(2)-C(3)-C(4)-C(5)	179.4(2)
C(3)-C(4)-C(5)-C(6)	-0.6(4)
C(4)-C(5)-C(6)-C(7)	0.6(4)
C(4)-C(5)-C(6)-C(9)	-177.8(2)
C(5)-C(6)-C(7)-C(8)	-0.2(3)
C(9)-C(6)-C(7)-C(8)	178.3(2)
C(6)-C(7)-C(8)-C(3)	-0.3(4)
C(4)-C(3)-C(8)-C(7)	0.3(4)
C(2)-C(3)-C(8)-C(7)	-179.0(2)
C(5)-C(6)-C(9)-C(10)	-0.9(4)
C(7)-C(6)-C(9)-C(10)	-179.2(3)
C(5)-C(6)-C(9)-C(14)	179.2(3)
C(7)-C(6)-C(9)-C(14)	0.9(4)
C(14)-C(9)-C(10)-C(11)	-1.0(5)
C(6)-C(9)-C(10)-C(11)	179.0(3)
C(9)-C(10)-C(11)-C(12)	-0.6(6)
C(10)-C(11)-C(12)-C(13)	1.8(6)
C(11)-C(12)-C(13)-C(14)	-1.5(6)
C(10)-C(9)-C(14)-C(13)	1.3(6)
C(6)-C(9)-C(14)-C(13)	-178.7(4)
C(12)-C(13)-C(14)-C(9)	-0.1(7)

Symmetry transformations used to generate equivalent atoms:

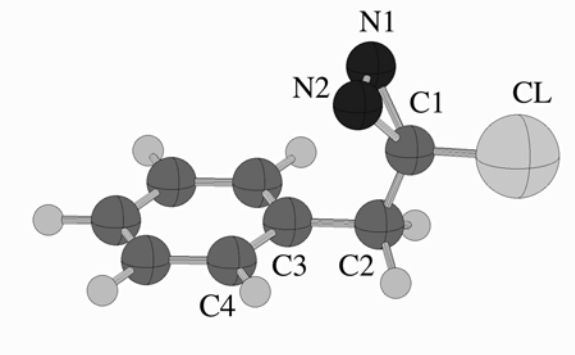

Figure 1. Lowest energy conformer of benzylchlorodiazirine calculated with the AM1 method: N=N=1.228 Å, Cl-C=1.745 Å, N-C=1.473 Å, N-C-N=65.4^{o} and Cl-C-N= –104.5^{o}

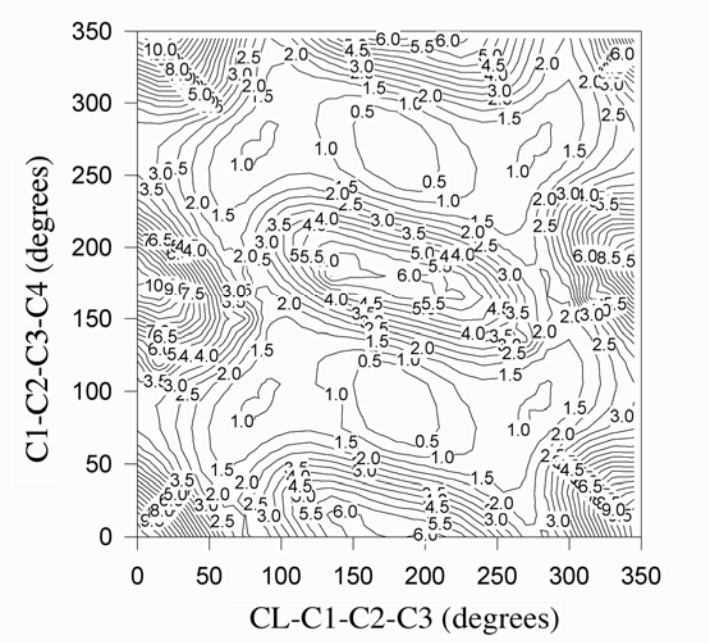

Figure 2. Contour surface of benzylchlorodiazirine calculated with the AM1 method ilustrating a lowest energy minimum with the diazirine group directed orthogonal to the aromatic plane (C1-C2-C3-C4=90 °) and the chlorine atom anti-to the aromatic ring (CL-C1-C2-C3=180 °). Two local minima with CL-C1-C2-C3 dihedrals of *ca*. +75° and –75° are the ones represented in the crystal structure.