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Deformation Density Studies of Ring Systems. 2. The Deformation Density of the Diazirine Ring in the X-ray Structure of 3-[(*p*-Nitrophenoxy)methyl]-3-chlorodiazirine

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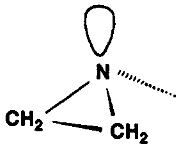
Abstract: The crystal structure and electron density of 3-[(*p*-nitrophenoxy)methyl]-3-chlorodiazirine have been analyzed using single crystal X-ray diffraction at 208 K with Mo Kα radiation to a resolution of $\sin(\theta_{max})/\lambda = 1.126$ Å^{-1}. A total of 10 440 measured reflections gave 7742 unique reflections with $R_m = 0.026$. A multipole atomic density model was fitted to these reflections to give an $R(F) = 0.0311$. The deformation density of the phenyl portion of the compound is as expected. The dynamic deformation density of the diazirine ring, however, suggests that the bonding in the three-membered ring is a combination of the classical severely-strained σ bonding system with a significant contribution of a π donation from the N=N to an sp^2 carbon. This observation is placed in the context of similar proposals for the bonding in cyclopropanes.

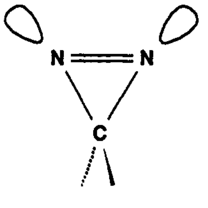
Introduction

Recently[1] the dynamic deformation density of the three-membered aziridinyl ring (**Ia**) was examined and used as an internal standard for the deformation density observations on a cyclotriphosphazene ring. While the work was in progress a crystal of a compound which contains a relatively stable diazirine ring (**Ib**) became available. This compound is 3-[(*p*-nitrophenoxy)-methyl]-3-chlorodiazirine (**II**). It was decided to examine the deformation density of **II** to compare the diazirine ring deformation density both with that of the aziridinyl ring and with that of the theoretically calculated deformation density of the diazirine ring. The results have been reported in a preliminary form.[2]

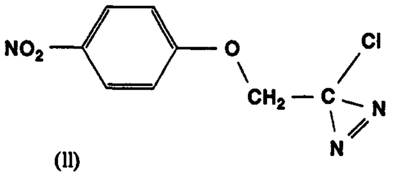
In addition to the comparison with other three-membered ring systems, the diazirine ring presents an intriguing problem for its own bonding. The dimensions of the ring have been derived from a number of simple compounds[2] and have also been determined by X-ray diffraction. However, apart from the structure of a hetero dimetal complex,[3] there is only one other light atom X-ray crystal structure containing the diazirine ring,[4] and in that case, the crystal rapidly decomposed in the X-ray beam. Although there is thus no dispute about the shape of the ring, in terms of conventional bonding, for this three-membered ring, the N=N double bond is most unusually strained. The bonding in such molecules as ethylene oxide and cyclopropane was originally derived by Walsh.[5] Dewar and Ford in 1979 further developed[6] the Walsh approach for the bonding and suggested it was possible to show a continuous transition, without any break, in a series of "three-membered" rings from ethylenic π complexes with a metal where there was back-coordination to the classical covalent three-membered ring. They concluded that, while with metal–olefin complexes the distinction between the two extremes could be drawn on the basis of geometry (or C–C stretching frequencies), with organic compounds, however, this distinction between the two systems was essentially arbitrary and could be based on the convenience of interpreting experimental data. For Dewar and Ford this concerned the ring opening reactions with nucleophiles. Cremer and Kraka[7] extended this work, reached the same conclusion, and related it to observations of the NMR of the methylene group of these three-membered rings. Thus, at the covalent limit of the series, the bonding in cyclopropane can be thought to contain some contribution from a π complex between ethylene and methylene. Since, in the present case, the diazirine



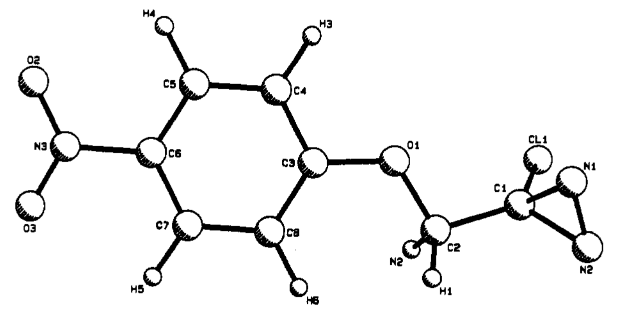
(Ia)



(Ib)



(II)



(II)

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Table 1. Physical Properties and Parameters for Data Collection and Refinement of 3-[(*p*-Nitrophenoxy)methyl]-3-chlorodiazirine

empirical formula	$C_8H_6N_3O_3Cl$
formula weight	227.61
crystal color, habit	colorless, needle plate
crystal system	triclinic
lattice parameters	
a (Å)	6.034(1)
b (Å)	8.429(3)
c (Å)	9.805(2)
α (deg)	107.51(2)
β (deg)	96.58(2)
γ (deg)	91.21(1)
V (Å³)	471.6(4)
space group	$P\bar{1}$ (#2)
Z	2
D_{calcd} (g/cm³)	1.60
F_{000}	232.00
$\mu_{(Mo\ K\alpha)}$ (cm⁻¹)	3.91
radiation	Mo Kα (λ = 0.709 26 Å)
temp (K)	208
scan type	ω–2θ
scan width (deg)	(1.00 + 0.35 tan θ)
$2\theta_{max}$ (deg)	106
hkl range	*h*, –12 to 12; *k*, –16 to 16; *l*, 0 to 19
no. of measd reflns	10 414
no. of unique reflns	7 742 (R_m = 0.0263)
decay over the data colln	5.7%
no. of variables	141
least-squares weights	$k/[\sigma(F) + g(F)^2]$ $k = 2.0220$ $g = 0.000369$
Conventional Refinement of All Data, Weighting Scheme $1/\sigma^2(F_o)$	
agreement factor	
$R = (\Sigma\|\|F_o\| - \|F_c\|\|)/(\Sigma\|F_o\|)$	0.0473
$R_w = [(\Sigma w\|\|F_o\| - \|F_c\|\|)^2/(\Sigma w\|F_o\|)]^{1/2}$	0.0484
GOF = $(\Sigma\|\|F_o\| - \|F_c\|\|)^2/(N_{ob} - N_v))^{1/2}$	2.5461
min/max peak in final diff. map (3 269 reflns with $I > 2\sigma(I)$) (e⁻/Å³)	–0.389, 0.398
Conventional Refinement ($\theta < 25°$)	
$R = 0.038$	
$R_w = 0.0403$	
GOF = 3.505	
min/max peak in final diff. map (2 140 reflns with $I > 3\sigma(I)$) (e⁻/Å³)	–0.217, 0.283
MOLLY Refinement of All Data	
$R = 0.0311$	
$R_w = 0.0330$	
GOF = 2.84	
min/max peak in final diff. map (e⁻/Å³)	–0.22, 0.23

ring already contains a N=N double bond and a CH_2 group, it was decided to examine the dynamic deformation density of the ring to see what this might reveal about the bonding in the ring.

Experimental Section

(i) X-ray. Small colorless columnlike crystals, with well-developed faces, can be grown from a pentane solution. The crystals diffract sharply, and the diffraction pattern extends to $\sin(\theta)/\lambda = 1.126$ Å⁻¹. The crystals are relatively stable in the X-ray beam at –65 °C although they slowly crumble at lower temperatures. A total of 10 440 reflections was collected in three separate shells over the range $3 < \theta < 53°$. Each shell had a 5° overlap with the next. Within the shells, as well as the regular measurement of the intensity of standard reflections, there were also frequent remeasurements of sections of the data. The data were thus well overdetermined. These data were thoroughly examined; several small sections between standard reflections, where these standard reflections suggested that the equipment was not in good thermal equilibrium, were removed (about 400 reflections).

The data were brought to an approximate common scale by the use of the common reflections between the shells, and the scale factors of the shells were later included in the refinement to produce an overall merging *R* of 2.6% for 7742 unique reflections.

(ii) Theoretical Calculations. The theoretical electron density for just the diazirine ring (CH_2N_2) was determined from *ab initio* calculations using GAMESS[8] with a 6-31G* basis set. The deformation densities

Table 2. Non-hydrogen Fractional Atomic Coordinates (×10⁵) and Isotropic/Equivalent Temperature Factors (Å²) (×10⁴) with esd's in Parentheses[a]

atom	*x/a*	*y/b*	*z/c*	U_{eq}
Cl1	2 972(17)	28 577(14)	44 315(13)	479(3)
O1	29 167(34)	15 117(31)	15 794(19)	451(3)
O2	55 850(15)	36 611(14)	–35 597(7)	680(2)
O3	86 059(14)	44 932(13)	–20 829(8)	667(1)
N1	14 493(53)	–3 364(40)	34 996(38)	402(8)
N2	26 646(50)	2 377(40)	46 546(37)	380(8)
N3	67 340(52)	38 198(37)	–24 097(34)	352(7)
C1	22 409(55)	14 033(43)	38 417(40)	291(8)
C2	39 620(57)	18 607(49)	30 221(41)	335(9)
C3	40 029(56)	20 520(44)	6 673(40)	300(9)
C4	27 410(58)	18 757(47)	–6 663(41)	345(9)
C5	36 335(61)	24 451(47)	–16 833(41)	359(10)
C6	57 873(58)	31 664(43)	–13 775(42)	291(8)
C7	70 786(56)	33 217(45)	–666(41)	321(9)
C8	61 752(59)	27 718(46)	9 671(41)	339(9)

[a] U_{eq} is calculated as $\{U11(a^*a)^2 + U22(b^*b)^2 + U33(c^*c)^2 + 2(U12a^*b^*ab\cos(\gamma) + U13a^*c^*ac\cos(\beta) + U23b^*c^*bc\cos(\alpha))\}/3$. Thermal parameters for anisotropic vibrations are defined as $T = \exp(-2\pi^2(U11(ha^*)^2 + ... + 2U12hka^*b^* + ...))$.

Table 3. Bond Lengths (Å) and Angles (deg) with esd's in Parentheses

atom	atom	distance	atom	atom	distance
Cl1	C1	1.732(4)	N3	C6	1.452(6)
O1	C2	1.422(4)	C1	C2	1.494(6)
O1	C3	1.343(5)	C3	C4	1.401(5)
O2	N3	1.223(3)	C3	C8	1.394(5)
O3	N3	1.217(3)	C4	C5	1.384(6)
N1	N2	1.233(4)	C5	C6	1.385(5)
N1	C1	1.459(5)	C6	C7	1.393(5)
N2	C1	1.450(6)	C7	C8	1.392(6)

atom	atom	atom	angle	atom	atom	atom	angle
C2	O1	C3	117.6(3)	O1	C2	C1	105.9(3)
N2	N1	C1	64.5(3)	O1	C3	C4	114.2(3)
N1	N2	C1	65.3(3)	O1	C3	C8	125.5(3)
O2	N3	O3	124.0(3)	C4	C3	C8	120.3(3)
O2	N3	C6	117.5(3)	C3	C4	C5	120.0(4)
O3	N3	C6	118.5(3)	C4	C5	C6	119.5(4)
Cl1	C1	N1	115.5(3)	N3	C6	C5	120.4(3)
Cl1	Cl	N2	116.2(3)	N3	C6	C7	118.4(3)
Cl1	C1	C2	117.0(3)	C5	C6	C7	121.2(4)
N1	C1	N2	50.2(2)	C6	C7	C8	119.5(3)
N1	C1	C2	119.6(3)	C3	C8	C7	119.5(3)
N2	C1	C2	121.6(3)				

Table 4. κ Values with a Scale Factor of 1.7614(33) and an Extinction of 0.000

κ'	κ''	
1.011(5)	0.718(18)	Cl(1)
0.960(4)	0.472(17)	O(1)
0.945(3)	0.400(9)	O(2), O(3)
0.976(4)	0.544(11)	N(1), N(2)
0.946(5)	0.515(10)	N(3)
0.959(4)	0.880(15)	C(1), C(2)
0.990(4)	0.813(12)	C(3)–C(8)
1.000	1.000	H

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Table 5. Multipole Parameters from MONOPOLE to 16-POL *X*3*Y*

atom	monopole	dipole *X*	dipole *Y*	dipole *Z*	4-POL *ZZ*	4-POL *ZX*	4-POL *ZY*	4-POL *YY*	4-POL *XY*	8-POL *ZZZ*	8-POL *XZZ*	8-POL *YZZ*	8-POL *XX*–*YY*
Cl1	7.51(9)	–0.07(4)	0.26(5)	0.11(6)	0.07(7)	0.44(5)	–0.16(6)	0.44(5)	–0.18(5)	0.10(8)	0.06(6)	–0.09(7)	0.10(7)
O1	6.30(8)	0.02(8)	0.30(12)	–0.14(14)	–0.26(12)	–0.27(9)	–0.23(12)	–0.25(9)	0.35(8)	0.20(12)	–0.14(11)	–0.08(14)	0.00(11)
O2	6.53(11)	0.34(28)	–0.11(35)	0.10(10)	0.35(12)	0.59(23)	–0.45(26)	–0.05(14)	–0.03(14)	0.45(16)	0.38(18)	–0.60(19)	–0.05(16)
O3	6.25(11)	0.28(28)	–0.12(35)	0.37(10)	–0.10(11)	0.51(22)	–0.29(26)	0.12(14)	0.02(14)	–0.36(14)	0.31(17)	0.11(18)	0.06(14)
N1	5.11(7)	0.26(17)	0.10(6)	0.33(5)	0.40(6)	0.12(15)	0.34(5)	–0.07(4)	–0.05(7)	0.13(6)	0.15(11)	0.11(8)	–0.14(6)
N2	from N1												
N3	4.98(18)	–0.13(26)	–0.25(22)	0.67(29)	–0.15(21)	–0.45(13)	–0.10(19)	–0.39(14)	–0.68(23)	1.11(21)	0.26(17)	0.41(32)	0.44(15)
C1	3.98(20)	0.16(6)	–0.21(7)	0.00	0.23(6)	0.00	0.00	0.11(6)	0.17(6)	0.00	–0.14(7)	0.18(7)	0.00
C2	3.97(21)	–0.09(5)	–0.29(8)	–0.02(7)	–0.18(7)	0.10(6)	0.11(6)	0.00(6)	–0.17(6)	0.46(8)	0.00(8)	–0.04(6)	–0.02(7)
C3	3.95(24)	0.08(6)	0.01(8)	0.34(9)	0.27(8)	–0.16(6)	0.15(8)	0.11(6)	–0.16(7)	0.22(9)	–0.05(8)	0.21(15)	0.40(8)
C4	4.00(18)	0.13(7)	0.16(9)	–0.27(10)	–0.11(9)	–0.30(7)	–0.02(9)	–0.13(7)	0.05(6)	0.47(10)	–0.06(9)	–0.26(15)	0.35(9)
C5	4.12(18)	–0.11(7)	0.07(8)	–0.33(10)	–0.13(9)	–0.21(7)	–0.21(9)	–0.27(7)	–0.16(6)	0.50(10)	–0.14(9)	–0.16(14)	0.28(9)
C6	3.76(24)	–0.33(8)	0.35(9)	0.22(7)	–0.10(6)	–0.10(7)	0.22(6)	–0.26(7)	–0.32(8)	–0.08(8)	–0.10(8)	–0.12(8)	0.09(11)
C7	3.87(15)	0.05(7)	0.22(8)	–0.38(9)	–0.24(9)	0.20(7)	–0.18(8)	–0.26(6)	0.07(6)	0.23(9)	–0.02(9)	–0.08(14)	0.44(8)
C8	4.03(12)	–0.10(6)	–0.16(8)	0.46(9)	0.33(8)	–0.02(7)	0.31(8)	0.06(6)	–0.03(6)	0.67(8)	0.06(8)	0.02(14)	0.19(8)
H21	0.83(7)	–0.04(5)	–0.06(4)	0.08(6)									
H22	from H21												
H41	from H21												
H51	from H21												
H71	0.72(4)	–0.01(3)	–0.06(5)	0.31(3)									
H81	from H71												

atom	8-POL *XYZ*	8-POL *XXX*	8-POL *YYY*	16-POL *Z*4	16-POL *XZ*3	16-POL *YZ*3	16-POL *X*2*Y*2	16-POL *XYZ*2	16-POL *X*3*Z*	16-POL *Y*3*Z*	16-POL *X*4+*Y*4	16-POL *X*3*Y*
Cl1	0.03(6)	–0.17(6)	–0.10(7)	–0.22(9)	–0.05(5)	–0.03(6)	0.42(8)	0.13(7)	0.10(7)	–0.09(8)	–0.09(7)	–0.78(7)
O1	–0.13(11)	–0.23(9)	0.14(9)									
O2	–0.08(15)	–0.21(10)	–0.03(10)									
O3	0.49(15)	–0.21(10)	–0.35(10)									
N1	0.07(10)	–0.06(6)	0.11(5)									
N3	–0.25(22)	0.20(13)	0.55(17)									
C1	0.00(6)	0.23(8)	–0.16(7)									
C2	0.03(7)	–0.04(7)	0.25(7)									
C3	0.03(9)	0.04(7)	–0.24(8)									
C4	–0.07(9)	–0.05(7)	0.07(8)									
C5	0.01(9)	0.08(7)	0.19(8)									
C6	–0.18(8)	0.41(9)	–0.06(13)									
C7	–0.12(9)	–0.09(7)	0.11(7)									
C8	0.07(9)	0.06(7)	0.09(7)									

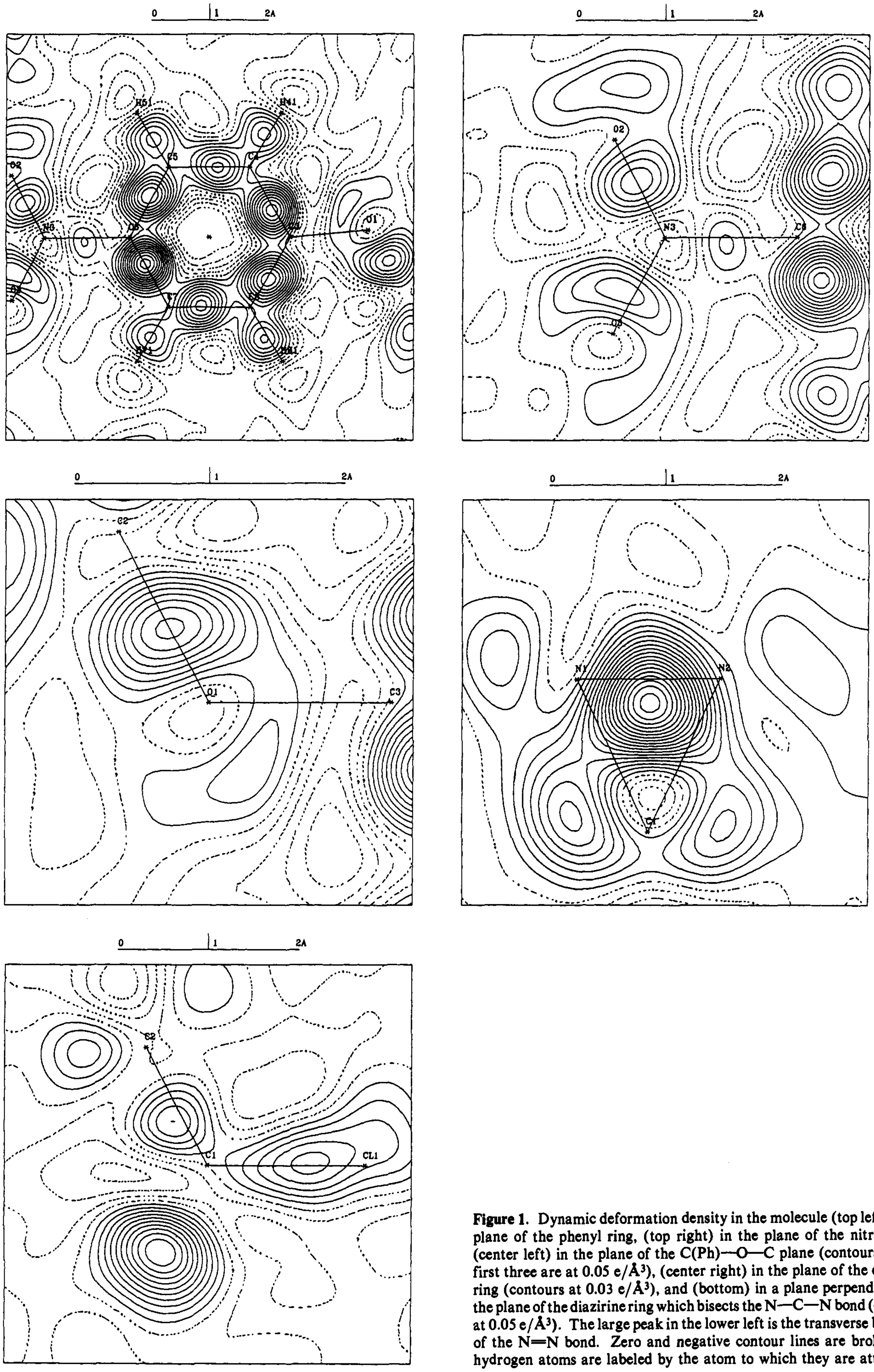

Figure 1. Dynamic deformation density in the molecule (top left) in the plane of the phenyl ring, (top right) in the plane of the nitro group, (center left) in the plane of the C(Ph)—O—C plane (contours for the first three are at 0.05 e/Å^3), (center right) in the plane of the diazirine ring (contours at 0.03 e/Å^3), and (bottom) in a plane perpendicular to the plane of the diazirine ring which bisects the N—C—N bond (contours at 0.05 e/Å^3). The large peak in the lower left is the transverse bisection of the N═N bond. Zero and negative contour lines are broken, and hydrogen atoms are labeled by the atom to which they are attached.

($\Delta\rho_m$) were derived from this according to the following expression:[9]

$$\Delta\rho_m = \rho_{\text{molecule}} - \rho_{\text{SFA}}$$

where ρ_{SFA} is the density of the spherically-averaged free atoms superimposed on the molecular geometry. In this procedure, the electron density is calculated for the whole molecule with a 6-31G* basis set and then the electron density is separately calculated for each atom in the exact position in the molecule again with a 6-31G* basis set. Great care is taken in these separate calculations to ensure that the resulting density is spherically symmetric. The atomic densities are then subtracted from the molecular densities. The results of these calculations have been deposited. A similar calculation was done for $CHClN_2$. The electron density maps for this molecule were very similar to those for CH_2N_2 except for a slight increase in the flow of electron density toward the chlorine end of the molecule. These maps have been deposited as supplementary material.

Conventional Refinement. Details of the conventional refinement have been reported previously, and they are summarized in Table 1. The final atomic parameters are given in Table 2; the interatomic distances and interbond angles are given in Table 3.

Multipole Refinement. The aspherical atomic density ρ_r can be described in terms of spherical harmonics:[10,11]

$$\rho_{\text{atom}}(r) = \rho_{\text{core}}(r) + \rho_{\text{valence}}(r) + \rho_{\text{def}}(r)$$

Thus for each atom

$$\rho_r = P_c\rho_c(r) + P_v(\kappa')^3\rho_v(\kappa' r) + \sum_{\ell}(\kappa'')^3 R_\ell(\kappa'' r)\sum_{m=0}^{\ell} P_{\ell mp} Y_{\ell mp}(\theta,\phi)$$
$$(p = +1 \text{ or } -1)$$

where the deformation term is in polar coordinates with the origin at the atomic nucleus.

The procedure for the use of this expression in refinement is now well established.[12] In this particular instance, the positional parameters and anisotropic temperature factors of the heavy atoms were refined first using the high-angle data. The hydrogen atoms were adjusted to positions determined from neutron refinement of similar structures.[13] Then the multipole parameters were refined (program MOLLY[11]) with the atomic positions and temperature factors fixed. The chlorine atom required hexadecapolar parameters ($\ell = 4$), the remaining heavy atoms had octapolar parameters ($\ell = 3$), and the hydrogen atoms had a simple dipole. In the multipole refinement a mirror plane of symmetry was imposed, by constraints, on the diazirine ring. This plane, perpendicular to the plane of the ring, contained the carbon atom and bisected the N=N bond. Thus the multipole parameters of N(1) were made equivalent, by C_s symmetry, to those of N(2). Proper constraints were applied to the multipole parameters of C(1) to maintain the C_s symmetry at this site too. When this refinement had converged, the multipole parameters were fixed and the positions and temperature factors (isotropic for hydrogen) of all atoms were refined for the full data. Finally all the parameters were refined together. Details of the refinement are given in Table 1. The final calculated structure amplitudes F_c(mult) were then used to calculate the *dynamic deformation* density maps using Fourier coefficients derived by

$$F(\text{dynamic}) = F_c(\text{mult}) - F_c(\text{sph})$$

where F_c(sph) is the structure factor calculated for spherical atoms with $\kappa' = 1$ for each atom, P_v is the number of valence electrons, and $P_{\ell m} = 0$. The final multipole parameters are given in Table 5.

Results and Discussion

Figure 1 shows details of the dynamic deformation density in the molecule. Figure 1 (top left) shows the deformation density in the plane of the phenyl ring, and since the plane of the nitro group is inclined at an angle of 2.57(1)° to this plane, Figure 1 (top right) shows the density in the plane of the nitro group. Figure 1 (center left) shows the density in the C—O—C plane of the phenoxy oxygen. Figure 1 (center right) shows the plane of the diazirine ring, and Figure 1 (bottom) shows the plane perpendicular to the diazirine ring which contains C(1) and bisects the N=N bond.

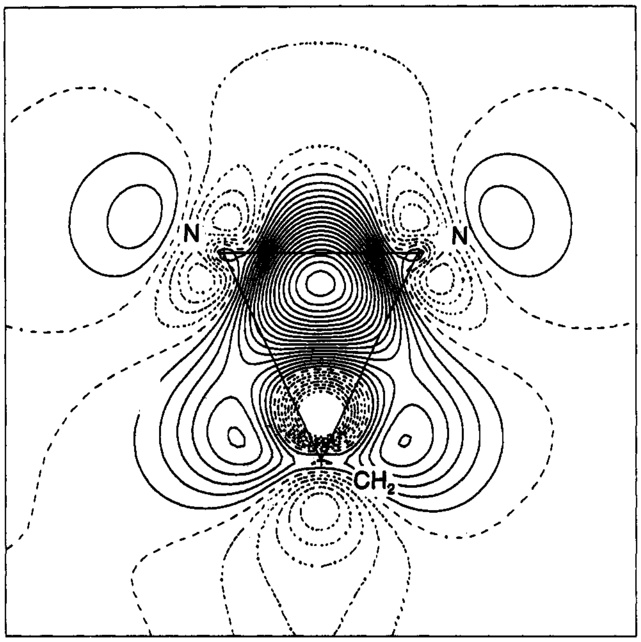

Figure 2. Static deformation density in the plane of the diazirine ring (contours at 0.05 e/Å^3). Zero and negative contour lines are broken.

The residual map in the plane of the phenyl ring and the residual map in the plane of the diazirine ring have been deposited. These are essentially featureless. Figure 2 shows the static deformation density, the electron density calculated from the values of the refined multipole parameters, for the plane of the diazirine ring.

(1) The Phenyl Ring and Its Substituents. The general appearance of the dynamic deformation density in the plane of the phenyl ring (Figure 1 (top left)) closely resembles that observed by others.[14,15] The ring is *para* substituted with electron withdrawing groups at both positions. These electron withdrawing groups would be expected[16] to increase the bonding electron density in the ring C–C bonds at C(3) and C(6), and this is observed. Correspondingly, the bonding electron density in the C(4)–C(5) and C(7)–C(8) bonds should diminish. This too is observed.

The plane of the nitro group is slightly inclined to that of the phenyl ring (2.57(1)°). The dynamic deformation density in this group also has generally the expected appearance. There is a somewhat lower density along the N(3)–C(6) bond, and the two N–O bond densities are not equivalent. The chemical environments of these two oxygen atoms are rather different. Figure 3 shows the packing in the unit cell, and from this it can be seen that, while O(2) has close contacts of 3.149(2) Å to C(1), 3.231(2) Å to N(2) in the adjacent diazirine ring, and 2.793 Å to H(2) beneath it in Figure 3, the shortest contact to O(3) is 3.413(2) Å to O(1) beneath it and 3.091 Å to H(4) in an adjacent phenyl group. The close contact to O(2) probably has steric (and electronic) significance since the slight twist of the nitro group out of the plane of the phenyl group has O(2) twisting away from

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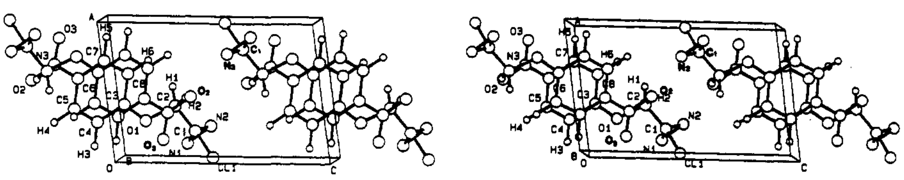


Figure 3. Packing of the molecule in the unit cell.

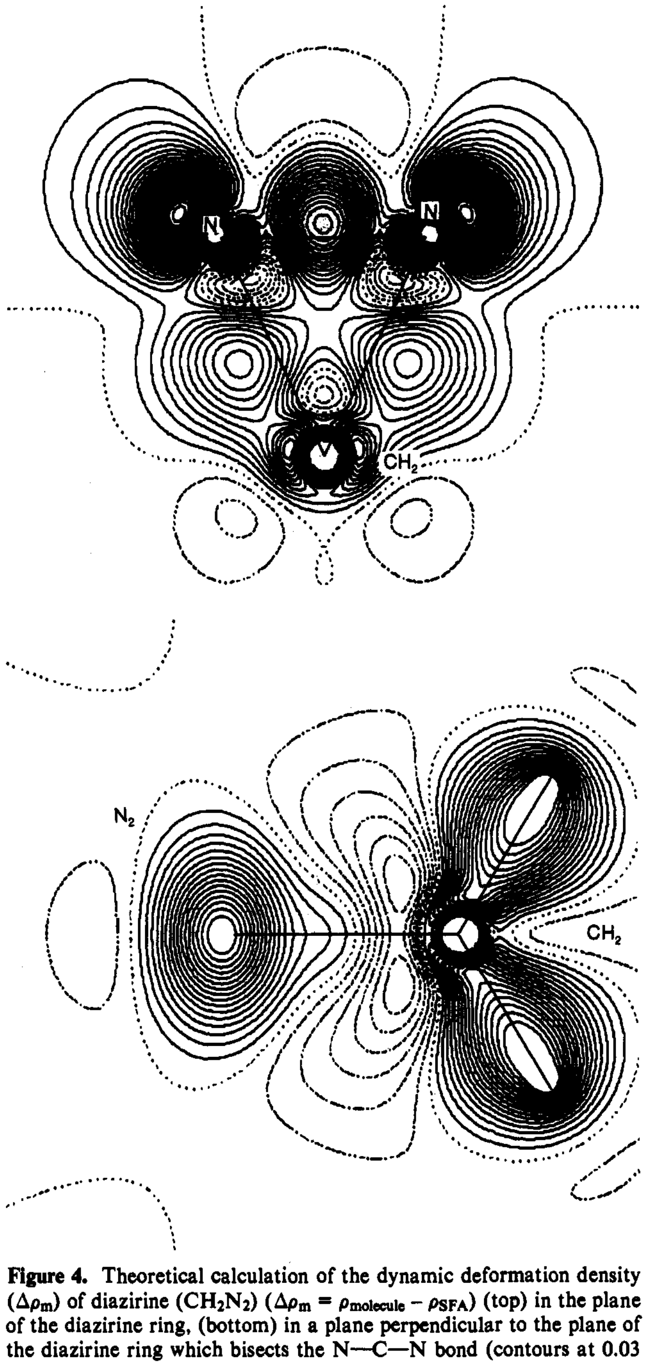


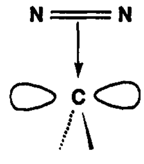
Figure 4. Theoretical calculation of the dynamic deformation density ($\Delta\rho_m$) of diazirine (CH_2N_2) ($\Delta\rho_m = \rho_{molecule} - \rho_{SFA}$) (top) in the plane of the diazirine ring, (bottom) in a plane perpendicular to the plane of the diazirine ring which bisects the N—C—N bond (contours at 0.03 e/Å^3).

H(2). It has been noted[15] by Dunitz, Schweizer, and Seiler in their study of tetrafluorophthalodinitrile that the C–X (X = N, O, F) single bond deformation densities are less than that for the C–C bond and decrease in the order C–N > C–O > C–F. Hirshfeld explains[17] this observation in terms of the increasing electron density on the atoms, in the direction of the bond, in the order N < O < F. In the chlorodiazirine, the observed density in C(6)–N(3) is in accordance with this sequence. The density from the oxygen nonbonded electron is also visible in this plane of the nitro group. Conventionally the maxima should be at 120° to the N–O bond. While there is some density in this region and it would be expected to be much less than that of the N–O bond, it is not thoroughly convincing.

The phenoxy C(3)–O(1) bond density (Figure 1 (top left and center left)) is even less than that observed in the nitro C(6)–N(3) bond. However such would be expected from the Dunitz/Hirshfeld work.

(ii) The Diazirine Ring. The deformation density in the phenyl portion of the molecule appears to follow closely the expected or predicted pattern. However, when the deformation density was calculated in the plane of the diazirine ring (Figure 1 (center right)), it was seen to be significantly different from that observed for the aziridinyl ring. There is a large concentration of density in the region of the N=N bond, but the maximum of this density, unlike the aziridinyl[1,18] and cyclopropane[19] systems, comes inside the framework of the ring, not outside. There are two much smaller peaks at ~0.6 Å from each nitrogen atom in the expected position for the nitrogen nonbonding electron pair. It has been noticed[20] before that the lone pair electron density is much smaller than the bonding pair density. There is some density along the C–N bonds, and this shows a slight distortion to extend it outside the ring, but there is a lot less density there than was observed[1] in the aziridinyl system.

Initially, the really unexpected features of the deformation map were the two symmetric maxima on either side of the carbon atom (Figure 1 (center right)). The static deformation map and the map derived from the theoretical calculations of the deformation density for the diazirine system $CHClN_2$ (Figure 4 (top left)) show a very similar pattern on either side of this carbon atom. However, it should be remembered that the carbon atom of the diazirine ring has two other atoms bonded to it, one above the other, below the plane of the ring. All the observations can then be reconciled by considering the ring to be formed with a contribution to an sp^2 carbon atom by π donation from the N=N in a manner analogous to a metal π complex (**III**, where the N–C covalent bonds have been omitted for clarity). This places the diazirine ring right in the sequence first proposed by Dewar and Ford.



(III)

This conclusion is supported by observations on the thermal decomposition of the diazirine ring which have been explained[21] in terms of a similar π contribution to the structure.

The theoretical calculations (Figure 4 (top left)) however show electron density maxima outside the ring along the C–N bonds.

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There is significant electron density in these locations in both the dynamic and the static deformation density maps (Figures 1 (center right) and 2), but in these cases, there is a saddle point, rather than a maximum, between the maxima from the N=N bond and those from the sp^2 carbon. Similarly, the maximum along the N=N bond is just outside the ring for the theoretical calculations while the experimental results show the maximum just inside the ring. In these instances the theoretical deformation densities suggest a larger contribution to the bonding from the classical strained σ bonds than is observed in either the dynamic or the static deformation densities. Figure 4 (top right) shows the theoretical deformation densities viewed in the plane of the diazirine ring along the N=N bond. Here the donation of the nitrogen π system toward the sp^2 carbon can be seen as can the elongation of the N=N π system in a plane perpendicular to the ring. This "T" shaped density is also indicative of a contribution of the Dewar and Ford model to the bonding of the ring. In this case the theoretical calculations suggest a slightly greater contribution of the π bonding than is observed in the experimental results (Figure 1 (bottom)). On balance the theoretical studies may suggest a smaller contribution from this π bonding than is observed. Clearly there is a discrepancy between the theoretical calculations and experimental results. Additional experimental deformation density studies on other diazirines are needed to resolve the questions both of the extent of the bonding contributions to the ring and of the discrepancy between the theoretical and experimental results. Attempts are being made to prepare these compounds.

Summary

The dynamic deformation density of the phenyl portion of 3-[(*p*-nitrophenoxy)methyl]-3-chlorodiazirine is generally exactly as would be expected. The deformation density of the diazirine ring has additional features not found in the related cyclopropane or aziridinyl systems. The bonding in the ring, therefore, does not appear to be consistent with a severely strained σ bonding system alone but can be explained with a π contribution from the N=N double bond to an sp^2 carbon. The theoretical calculations support this conclusion but suggest a larger contribution from the σ bonding system than is observed.

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Supplementary Material Available: Tables of fractional coordinates and thermal parameters, a listing summarizing of the results of *ab initio* calculations, and maps showing the residual deformation density in the plane of the phenyl ring and in the plane of the diazirine ring and the theoretical deformation density in the plane of the diazirine ring for N_2CHCl (9 pages); listings of structure factors (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.