produces a pronounced graining and cracking, and the smooth texture is restored with reheating to S_{LC1}. The well-defined and smooth nature of the focal conic texture of the S_{LC1} phase is unusual for a polymeric material and necessitates facile splay deformations. These features and the high fluidity suggest that there is a low degree of position order between the linear chains and that the chains are quite flexible in this phase. However, X-ray studies on the S_{LC2} mesophase of 8(Me$_2$salpn)VO indicate that positional order exists between the linear chains with major wide-angle diffraction peaks at 10.3, 9.1, 3.8, and 3.7 Å in addition to the lamellar peak at 20.2 Å.

In summary, we have developed a new type of unidirectional liquid crystalline polymer with a low-viscosity phase possessing supermolecular domains of polarization. These properties make these materials attractive candidates for poling into acentric states, and our initial experiments have indicated that the n(Me$_2$salpn)VO complexes are readily oriented to give a homogeneously ordered phase in fields of 10^3 V/cm.

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Registry No. 4(salen)VO, 138695-04-2; 5(salen)VO, 138695-05-3; 6(salen)VO, 138695-06-4; 7(salen)VO, 138695-07-5; 8(salen)VO, 138695-08-6; 10(salen)VO, 138695-09-7; 12(salen)VO, 138695-10-0; 5(Me$_2$salpn)VO, 138695-11-1; 6(Me$_2$salpn)VO, 138695-12-2; 7-(Me$_2$salpn)VO, 138695-13-3; 8(Me$_2$salpn)VO, 138695-14-4; 10-(Me$_2$salpn)VO, 138695-15-5; 12(Me$_2$salpn)VO, 138695-16-6; 14-(Me$_2$salpn)VO, 138695-17-7; 6(salpn)VO, 138695-18-8; 7(salpn)VO, 138695-19-9; 8(salpn)VO, 138695-20-2; 10(salpn)VO, 138695-21-3.

Supplementary Material Available: Tables of crystal coordinates, thermal parameters, bond distances, and bond angles of 7(Me$_2$salpn)VO, graphs of phase transitions of all of the compounds reported, DSC data for 8(Me$_2$salpn)VO, VT-IR data, and X-ray powder diffraction data on the low-temperature phases of 8(salen)VO and 8(Me$_2$salpn)VO (15 pages). Ordering information is given on any current masthead page.

Deformation Density of a Diazirine Ring in the X-ray Structure of 3-[(*p*-Nitrophenoxy)methyl]-3-chlorodiazirine

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The chemistry of the diazirines has a relatively short history, dating from the discovery of these compounds in 1960. The past 30 years have seen a high level of activity in the study of their chemistry, with advances in the field being regularly reviewed.[1-5]

Table I. Comparison of Bond Lengths and Angles in Diazirines[7]

compound	bond lengths (Å) N═N	bond lengths (Å) C—N	bond angle (deg) N—C—N
$(C_{10}H_7CH_2)ClCN_2$	1.244 (10)	1.465 (10)	50.3 (5)[a]
$MeClCN_2$	1.241 (5)	1.462	50.2 (5)
$MeBrCN_2$	1.240 (5)	1.462	50.2
$(Me)_2CN_2$	1.235 (5)	1.490 (10)	48.9
$MeHCN_2$	1.235 (5)	1.481 (10)	49.3 (3)
F_2CN_2	1.293 (9)	1.426 (4)	53.9 (4)
H_2CN_2	1.228 (3)	1.482 (3)	48.9
this work	1.229 (3)	1.460 (1)	49.8 (1)[a]

[a] Dimensions derived from single-crystal X-ray diffraction. Other dimensions derived from rotational spectra.

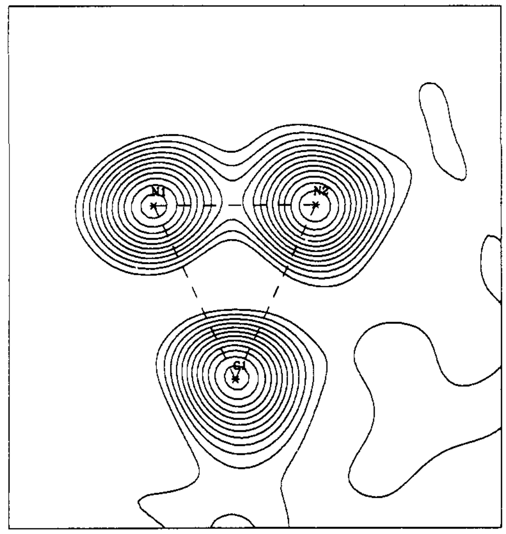
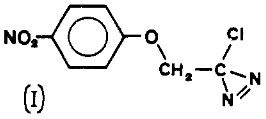
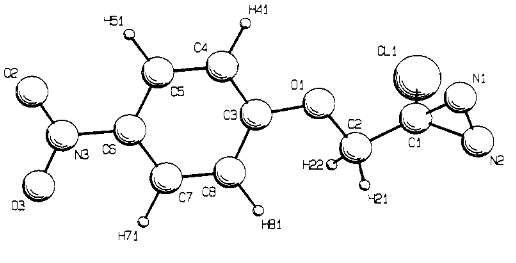


Figure 1. F_o map through the plane of the diazirine ring. Contours are at 0.5 e/Å^3.

Curiously, apart from the structure of a hetero dimetal complex,[6] only one X-ray structure of a free diazirine ring has been reported,[7] and this compound decomposed in the X-ray beam, even at low temperatures. We report here the structure of 3-[(*p*-nitrophenoxy)methyl]-3-chlorodiazirine (I), a remarkably stable compound with such a good crystalline form that it has been possible to collect low-temperature X-ray data of a quality suitable for deformation electron density studies.



(I)



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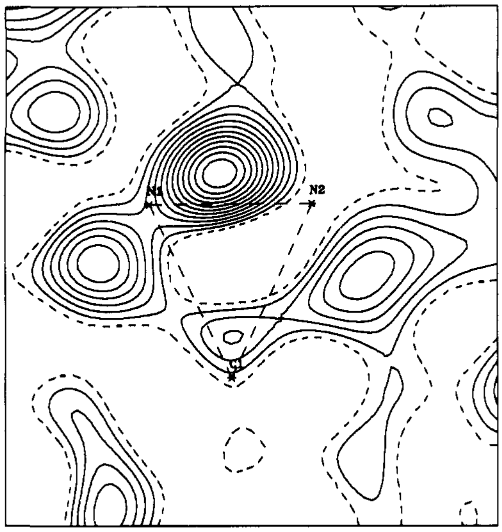

Figure 2. X–X_{HO} map on a plane through the diazirine group. Contours are at 0.04 e/Å^3. Zero and negative contour lines are broken.

Colorless crystals[8] of (I) can be grown from a pentane solution. The crystals diffract to sin $(\theta)/\lambda$ = 1.0 Å^{-1}. They are reasonably stable in the X-ray beam at −65 °C (a deterioration of 7.2% over a data collection of 10 414 reflections), though they slowly crumble at lower temperatures. At −65 °C, the diazirine ring is well defined, with an N=N bond length of 1.229 (3) Å, C—N distances of 1.459 (2) and 1.460 (2) Å, and an N—C—N bond angle of 49.8 (1)°. These compare with the dimensions of 1.228 (3), 1.482 (3) Å (mean), and 48.9° derived[9] from the rotational spectrum of H_2CN_2 and are not significantly different from all the known values for this system with the exception of F_2CN_2, where the dimensions are 1.293 (9), 1.426 (4) Å, and 53.9 (4)°, respectively (see Table I).

The deformation electron densities have been calculated for the molecule. Figure 1 shows the electron density for the diazirine ring, and Figure 2 shows the deformation density calculated by routine X–X_{HO} techniques. Figure 2 clearly shows the expected[10] "bent" bonds for the three-membered ring and also shows the effect of the double bond between the nitrogen atoms. The bonding density along the C-N bonds can be seen to be drawn toward the nitrogen atoms, and at the nitrogen atoms the lone-pair electrons can also be seen. It has been observed[14] before that the lone-pair electron density at a nitrogen atom is noticeably less than that observed in the nitrogen π bonds. These effects can best be seen if an exact transparent copy of Figure 2 is placed over Figure 1. The observed density in the diazirine ring does not contain a perfect 2-fold axis nor would this be expected. The torsional angle O_1–C_2–C_1–Cl is −82.4°, which brings the diazirine C_1–N_1 bond to the "inside" of the molecule, oriented toward the phenoxy oxygen atom, while C_1–N_2 is on the "outside" of the molecule. Thus C_1–N_1, but not C_1–N_2, comes close to one set of lone-pair electrons on the oxygen O_1. This will cause more compression of the bonding density toward the C–N bond axis for C_1–N_1 and allow the density associated with C_1–N_2 to spread further away from its bond axis (see Figure 2). Interestingly, the two C–N bond densities integrate planimetrically within 1% to the same total density. The lone-pair electron densities are also different on N_1 and N_2. In this context, it may be significant that the axis of the lone pair on N_2 points toward the plane of the phenyl ring (close to C_6) of a related molecule. An interaction between the lone pair on N_2 and the aromatic system would reduce the lone-pair density at N_2 (see Figure 2). The deformation density of the aromatic portion of the ring (details deposited) resembles that reported[15] for *p*-nitropyridine *N*-oxide, except that it shows a slight tendency toward a quinoidal form. Work is continuing with data refinements which include multipole parameters.[14,15]

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Supplementary Material Available: Tables of fractional coordinates and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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[8] IR 1588 cm^{-1}; ^{1}H NMR δ 4.05 (s, CH_2, 2 H), 6.3–8.00 (arom, 4 H); mp 35 °C, prepared by Graham[11] oxidation of the corresponding amidine hydrochloride. Unlike other diazirines, I does not exhibit fine structure in the 310–360-nm UV region. Crystal Data: triclinic $P\bar{1}$; a = 6.034 (1) Å, b = 8.492 (3), c = 9.805 (2), α = 107.51 (2), β = 96.58 (2), γ = 91.21 (1); V = 471.6 (2) Å^3; Z = 2, T = 208 ± 1 K, μ = 3.905 cm^{-1}; CAD4 diffractometer, λ(Mo $K_{\alpha 1}$) 0.709 26 Å, sin $(\theta_{max})/\lambda$ = 1.0 Å^{-1}, 10 414 measured reflections, 2410 unique observed ($I > 3\sigma(I)$), R = 0.0297, R_w = 0.030. Structure refined by CRYSTALS with Dunitz and Seiler weights.[12,13] X–X_{HO} maps[14,15] calculated for deformation density; multipole[14,15] refinement now in progress.

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Activation of Alkynes by Rhenium Polyhydrides in the Presence of Electrophiles: Facile Formation of Hydrido–Alkylidyne Complexes

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While rhenium forms a myriad of mononuclear hydride complexes that can contain up to nine hydrido ligands per metal center,[1] the *protonolysis* of such species in the presence of unsaturated organic substrates has not hitherto led to any extensive organometallic chemistry, although a variety of well-defined coordination compounds can be formed through protonation,[2] a process that may be followed by loss of dihydrogen and the coordination of various ligand molecules.[3] This behavior contrasts with the relative ease of activating compounds such as $ReH_7(PR_3)_2$ and $ReH_5(PR_3)_3$ toward reaction with saturated and unsaturated organic molecules under thermal[4,5] and photochemical conditions,[5,6] as well as in the presence of a hydrogen acceptor such

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[1] For example, see: (a) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1 and references contained therein. (b) Conner, K. A.; Walton, R. A. In *Comprehensive Coordination Chemistry*; Pergamon: Oxford, England, 1987; Chapter 43, pp 125–213.

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[3] The remarkable stability of some of these species is illustrated by the failure of the $[ReH_4(PMe_2Ph)_4]^+$ cation to react with the unsaturated organic molecules C_2H_4, PhC≡CPh, CO, and CH_3CN.[2b]

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