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U,l-4a,5,6,7,8,8a-Hexahydro-4-phenyl-8a-(trimethylsiloxy)-4H-1,2-benzoxazine 2-Oxide
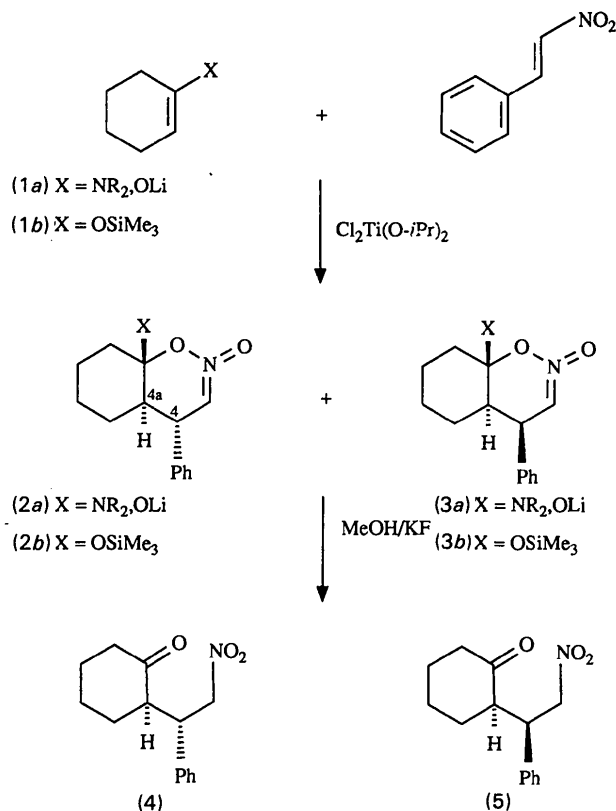
BY MICHAEL A. BROOK, R. FAGGIANI, C. J. L. LOCK* AND D. SEEBACH

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Abstract. $C_{17}H_{25}NO_3Si$, $M_r = 319.5$, monoclinic, $P2_1/c$, $a = 10.799$ (2), $b = 13.635$ (3), $c = 12.077$ (2) Å, $\beta = 98.39$ (1)°, $V = 1759.2$ (6) Å³, $Z = 4$, $D_m = 1.22$ (2), $D_x = 1.206$ g cm⁻³, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 1.488$ cm⁻¹, $F(000) = 688.3$, $T = 208$ K, $R = 0.062$ and $wR = 0.052$ for 2086 unique observed reflections and 300 parameters. The ring containing the N—O bond is a half-chair and the other ring is a chair. Both are roughly at right angles to the phenyl ring. The structural features of the N—O-containing ring are best described by C—C=N(=O)—O—C [N—O(ring), 1.434 (3); N=O, 1.258 (3) Å]. The large O—Si—C angle [132.2 (2)°] is caused by repulsive interactions. Other distances and angles are normal.

Introduction. β-Nitrostyrene undergoes a Michael addition to enamines or lithium enolates with relative topicity *lk* (1a → 4) (Colonna, Valentin, Pitacco & Risaliti, 1973). In contrast, the reaction of β-nitrostyrene with 1-(trimethylsiloxy)cyclohexene in the presence of the Lewis acid dichlorodiisopropoxytitanium leads preferentially to the other diastereomer which arises from a *ul*-addition process (1b → 5) (Brook & Seebach, 1987; Seebach & Brook, 1985). In both cases, cyclic nitronates (2a, 2b, 3a, 3b) can be isolated: the isolation of crystalline trimethylsilylated acetals (2b, 3b) is particularly unusual. The relative stereochemistry of (2b) and (3b) at the 4,4a positions was ascertained by hydrolysis to be that of the known (Risaliti, Fatutta, Forchiassin & Valentin, 1966) cyclohexanone derivatives (4) and (5), respectively. Although nuclear Overhauser-effect measurements

(1a) X = NR₂,OLi
(1b) X = OSiMe₃

Cl₂Ti(O-iPr)₂

(2a) X = NR₂,OLi
(2b) X = OSiMe₃

(3a) X = NR₂,OLi
(3b) X = OSiMe₃

MeOH/KF

(4)

(5)

suggested the relative stereochemistry at the bridgeheads (2b, 3b) is as shown, this could only be verified conclusively by X-ray structure analysis of one of the components. Only the minor component (2b) was obtained as crystals suitable for X-ray studies.

Experimental. Density determined by suspension in an aqueous zinc chloride solution to which a small amount of liquid detergent had been added. Crystal, rough cube, $0.30 \times 0.30 \times 0.30$ mm. Precession photographs showed space group was $P2_1/c$. Unit-cell parameters refined by least-squares fit of positional angles on 15 strong independent reflections measured on Syntex $P2_1$ diffractometer for $16 < 2\theta < 26°$, with use of graphite-monochromated Mo $K\alpha$ radiation. Intensities of $0 \le h \le 11$, $0 \le k \le 11$, $-12 \le l \le 12$, max. $45°$, measured by the θ(crystal)–2θ(counter) scan technique. Scan rate 4.88 to $29.30°$ min^{-1} in 2θ. The ratio of total background time to scan time is 1:1. Two standard reflections (e.s.d.), $25\bar{3}$ (0.011) $3\bar{3}1$ (0.011), monitored every 48 scans showed that no correction for instrument instability or crystal decay was required. 2567 reflections measured, 2298 unique reflections. $R_{int} = 0.0195$, 2086 reflections with $I > 0$ used. Lp corrections were made but not absorption. Absorption correction factor, A^*, 1.040–1.061 for max. error in F_o of $< 1.0\%$. Structure solved by heavy-atom method. Full-matrix least squares minimized $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma_F^2 + 0.000503F_o^2)^{-1}$. All H atoms were located and refined with isotropic temperature factors, other atoms anisotropic. With scale and secondary extinction ($x = 0.006$) also varied (Sheldrick, 1976). 300 parameters. Final $R = 0.062$, $wR = 0.052$. In the final refinement cycle $(\Delta/\sigma)_{max} = 0.186$, $(\Delta/\sigma)_{av} = 0.036$, $S = 1.325$. Final difference maps revealed no significant regions of electron density, with max. 0.33, min. -0.26 e Å^{-3}. Scattering factors those of Cromer & Waber (1974). Correction for anomalous dispersion for Si (Cromer & Ibers, 1974). Calculations employed *SHELX*76 (Sheldrick, 1976), *SNOOPI* (Davies, 1983) and *XTAL* (Stewart & Hall, 1983).† Atomic parameters are given in Table 1.

Table 1. *Atomic positional parameters* $(\times 10^4)$ *and equivalent isotropic temperature factors* $(\text{Å}^2 \times 10^3)$

	x	y	z	U_{eq}*
O1	1250 (2)	5695 (1)	4737 (2)	34
N2	307 (2)	6405 (2)	4881 (2)	33
C3	−489 (3)	6692 (2)	4035 (3)	33
C4	−513 (3)	6363 (2)	2853 (2)	29
C4a	280 (3)	5443 (2)	2817 (2)	28
C5	531 (4)	5181 (3)	1641 (3)	37
C6	1349 (4)	4270 (3)	1668 (3)	47
C7	2559 (4)	4387 (3)	2476 (3)	47
C8	2293 (4)	4651 (2)	3635 (3)	37
C8a	1501 (3)	5572 (2)	3592 (3)	31
O2	372 (2)	6665 (2)	5887 (2)	43
C41	−1844 (3)	6204 (2)	2293 (3)	35
C42	−2662 (3)	5615 (3)	2777 (3)	45
C43	−3851 (4)	5426 (3)	2253 (4)	59
C44	−4240 (4)	5798 (3)	1207 (4)	69
C45	−3449 (4)	6383 (4)	702 (4)	69
C46	−2251 (4)	6603 (3)	1251 (3)	50
O8	2119 (2)	6393 (1)	3258 (2)	33
Si	3175 (1)	7141 (1)	3946 (1)	34·2
C81	4316 (4)	6469 (3)	4956 (4)	53
C82	3956 (5)	7680 (3)	2836 (4)	53
C83	2382 (4)	8108 (3)	4643 (4)	53

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$.
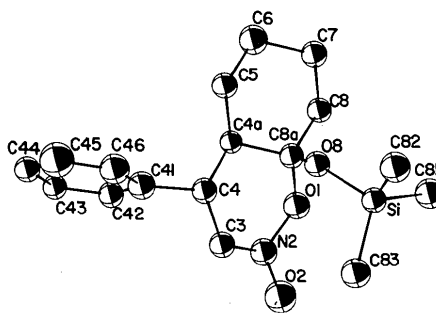

Fig. 1. The molecule, showing the atom numbering, H atoms excluded.

Discussion. One of the enantiomers is shown in Fig. 1 and interatomic distances and angles are given in Table 2. As can be seen, the molecule has the chiral centres arranged in the manner specified by the name. This is one of the first structures determined in which an NO_2 group has been incorporated into a ring. The C4a, 5, 6, 7, 8, 8a ring adopts a chair conformation, and the O1, N2, C3, 4, 4a, 8a ring a half-chair. The phenyl ring is planar and roughly at right angles to the fused-ring part of the molecule. Most of the bond lengths and angles are normal. The bond lengths within the phenyl ring (1.380 Å average) agree with previous figures as do the C—C single bonds (1.518 Å average) (Bowen, Don-

ohue, Jenkin, Kennard, Wheatley & Whiffen, 1958; Andrews, Bishop, Cleaver, Dennard, Henn, Loader, MacKay, Mendel, Morgan Owston & Phillips, 1965). The structural features of the NO_2 group are best represented by C4—C3=N2(=O2)—O1—C8a. The C8a—O1 and N2—O1 distances are consistent with single bonds; indeed the N2—O1 distance is at the upper limit of known N—O distances (Bowen *et al.*, 1958; Andrews *et al.*, 1965; Brown, Brown & Hawthorne, 1977, 1981). The N2—O2 distance is slightly longer than distances observed in the nitrate ion (1.218–1.268 Å) (Grison, Eriks & deVries, 1950; Sass, Vidale & Donohue, 1957; Hamilton, 1957) or in XNO$_2$ species (1.202–1.23 Å), X=F, Cl (Clayton, Williams & Weatherly, 1959; Smith & Magnusson, 1952) which suggests slightly less than an N=O double bond. The C3—N2 distance is marginally less than double-bond distances in formamidoxime (Hall & Llewellyn, 1956) and just larger than the Pauling value of 1.287 Å (Pauling, 1960). There is some conjugation to C3—C4

Table 2. *Selected interatomic distances* (Å) *and angles*
(°)

O1–N2	1.434 (3)	N2–C3	1.296 (4)
C3–C4	1.493 (4)	C4–C4a	1.523 (4)
C4a–C5	1.526 (5)	C5–C6	1.522 (5)
C6–C7	1.521 (5)	C7–C8	1.513 (6)
C8–C8a	1.516 (5)	C8a–O1	1.457 (4)
C4a–C8a	1.512 (4)	N2–O2	1.258 (3)
C4–C41	1.512 (4)	C41–C42	1.385 (5)
C42–C43	1.371 (5)	C43–C44	1.369 (7)
C44–C45	1.375 (7)	C45–C46	1.397 (6)
C46–C41	1.383 (5)	C8a–O8	1.393 (4)
O8–Si	1.660 (2)	Si–C81	1.846 (4)
Si–C82	1.838 (5)	Si–C83	1.841 (5)

|			
C8a–O1–N2	115.3 (2)	O1–N2–C3	120.6 (3)
N2–C3–C4	125.5 (3)	C3–C4–C4a	110.1 (2)
C4–C4a–C5	113.3 (3)	C4a–C5–C6	110.6 (3)
C5–C6–C7	111.7 (3)	C6–C7–C8	111.0 (3)
C7–C8–C8a	110.4 (3)	C8–C8a–O1	104.2 (2)
O1–N2–O2	111.5 (2)	O2–N2–C3	127.8 (3)
C3–C4–C41	110.7 (3)	C4–C41–C42	121.2 (3)
C41–C42–C43	121.8 (4)	C42–C43–C44	119.8 (4)
C43–C44–C45	119.8 (4)	C44–C45–C46	120.4 (4)
C45–C46–C41	119.8 (4)	C46–C41–C42	118.3 (3)
C46–C41–C4	120.4 (3)	C41–C4–C4a	111.8 (2)
C4–C4a–C8a	109.3 (2)	C8a–C4a–C5	110.2 (3)
C8–C8a–C4a	111.2 (3)	C4a–C8a–O1	109.6 (3)
O1–C8a–O8	110.2 (2)	C4a–C8a–O8	109.0 (2)
C8–C8a–O8	112.6 (3)	C8a–O8–Si	132.2 (2)
O8–Si–C81	111.7 (2)	O8–Si–C82	103.6 (2)
O8–Si–C83	109.7 (2)	C81–Si–C82	110.3 (2)
C81–Si–C83	111.3 (2)	C82–Si–C83	109.9 (2)
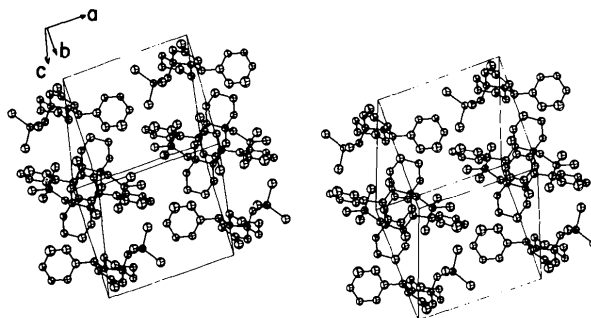
Fig. 2. The packing of the molecule within the unit cell.

reflected in the slightly shortened C3–C4 distance of 1.492 (4) Å compared to the single-bond value above. The O1N2O2C3 unit is planar, consistent with an sp^2 N atom, but the angles at N2 are markedly distorted from the ideal 120°. While the internal ring angle is close to the expected value, the angle between the N2–O2 group and the N2–O1 single bond is closed up, with consequent increase in the angle between the two double bonds, features which we and others have observed in carboxylic acids (Howard-Lock, Lock & Smalley, 1985; Howard-Lock, Lock, Martins, Smalley & Bell, 1986; Howard-Lock, Lock, Martins, Faggiani & Duarte, 1987). The N2–C3–C4 angle is also greater than 120° [125.5 (3)°] consistent with some conjugation between N2–C3 and C3–C4. C8a–O8 is slightly shorter than a single bond, but the Si–O bond

length lies in the middle of the normal range [1.606 (3)–1.703 (2) Å] (Voran, Blau, Malisch & Schubert, 1982; Appel, Barth & Knoch, 1983; Brisse, Thoraval & Chan, 1986; Appel, Porz & Knoch, 1986; Becker & Mundt, 1978, 1979; Thewalt & Rinne, 1976; Crossland, Bock & Norrestam, 1985; Weber, Reizig, Boese & Polk, 1986; Bianconi, Williams, Engeler & Lippard, 1986).

The C–O–Si angle [132.2 (2)°] is much larger than that expected for an sp^3 O atom but C–O–Si angles vary markedly [range 117.1 (4) to 152.2 (3)°]. There appears to be little correlation of the C–O–Si angle with C–O distances which, apart from one large and one small value, show no significant variation. There is an inverse correlation with Si–O distances, however, which is probably curvilinear, but can be adequately expressed by the rectilinear relationship

$$\text{bond length (Å)} = -0.00266 \text{ (angle,°)} + 2.024.$$

The values obtained here fit this relationship reasonably well. Brisse *et al.* (1986) have argued that the large angles are associated with intramolecular repulsive interactions, and this is the case here, as is the rotation of the SiMe$_3$ group away from C8 and towards O2. This results in $X\cdots$H distances [H8'$\cdots$H81, 2.49; H8'$\cdots$H, 2.50; O2$\cdots$H89, 2.59; N2$\cdots$H89, 2.69 Å] comparable to or shorter than the H$\cdots$H, O$\cdots$H and N$\cdots$H van der Waals distances of 2.40–2.98, 2.70–2.95 and 2.75–3.00 Å respectively (Bondi, 1964).

The packing is shown in Fig. 2. All interactions are van der Waals. There is no evidence of co-stacking of the phenyl rings in order to maximize π–π interactions.

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Structures of *N*-(3-Diethylaminopropyl)dithiocarbamic Acid and *N*-(2-Diethylaminoethyl)dithiocarbamic Acid

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Abstract. $C_8H_{18}N_2S_2$, $M_r = 206 \cdot 4$, monoclinic, $P2_1/n$, $a = 13 \cdot 187$ (2), $b = 11 \cdot 558$ (1), $c = 7 \cdot 3701$ (9) Å, $\beta = 99 \cdot 62$ (1)°, $V = 1107 \cdot 55$ Å^3, $Z = 4$, $D_m = 1 \cdot 226$, $D_x = 1 \cdot 237$ Mg m^{-3}, m.p. = 417 K, λ(Mo $K\alpha$) = $0 \cdot 71069$ Å, $\mu = 0 \cdot 418$ mm^{-1}, $F(000) = 448$, $T = 295$ K, $R = 0 \cdot 051$ for 1525 unique observed reflections. $C_7H_{16}N_2S_2$, $M_r = 192 \cdot 4$, monoclinic, $P2_1/n$, $a = 11 \cdot 916$ (2), $b = 13 \cdot 351$ (2), $c = 6 \cdot 487$ (1) Å, $\beta = 96 \cdot 80$ (2)°, $V = 1024 \cdot 73$ Å^3, $Z = 4$, $D_m = 1 \cdot 233$, $D_x = 1 \cdot 246$ Mg m^{-3}, m.p. = 422 K, λ(Mo $K\alpha$) = $0 \cdot 71069$ Å, $\mu = 0 \cdot 447$ mm^{-1}, $F(000) = 416$, $T = 295$ K, $R = 0 \cdot 056$ for 1274 unique observed reflections. Both molecules exist as zwitterions, $(C_2H_5)_2$-$N^+H(CH_2)_3NHCS_2^-$ and $(C_2H_5)_2N^+H(CH_2)_2NHCS_2^-$,

the bonding at the ammonium nitrogen being approximately tetrahedral. In the planar dithiocarbamate groups the C–S bond lengths in the first compound, $1 \cdot 706$ (5) and $1 \cdot 712$ (5) Å, are nearly equal while those in the second one, $1 \cdot 685$ (5) and $1 \cdot 717$ (5) Å with a difference of $4 \cdot 5\sigma$, are not equivalent. In both structures intermolecular N–H$\cdots$S hydrogen bonds result in interconnected infinite zigzag chains of molecules extending along the *b* axis.

Introduction. The structure of *N*-(3-dimethylaminopropyl)dithiocarbamic acid (DMAP hereafter) was recently studied (Schramm, Kokkou & Karagiannidis, 1984) in an attempt to delineate the substituent effects on the structure of dithiocarbamates without the attendant effects of a complexing metal ion. The availability of a series of substances prompted us to extend our study to two more compounds, *N*-(3-

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