There are no short intermolecular contacts (Pauling, 1960), except between H(14) in the molecule whose coordinates are given in Table 1 and H(3*B*) at symmetry position $(1-x, -y, -z)$ (2·30 Å).

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X-ray Structure of Cyanamide at 108 K

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Abstract. CH_2N_2, $M_r = 42·04$, orthorhombic, *Pbca*, $a = 6·856$ (1), $b = 6·628$ (1), $c = 9·147$ (1) Å, $V = 415·7$ Å^3, $Z = 8$, $D_x = 1·343$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 1·09$ cm^{-1}, $F(000) = 176$, $T = 108$ (1) K, $R = 0·051$ for 598 unique observed reflections. The cyanamide molecule is not totally planar. It has a pyramidal structure at the amino group. The N(1)—C—N(2) angle is 178·1 (1)°. One cyanamide molecule is linked to four neighbouring molecules by two pairs of symmetry-related hydrogen bonds.

Introduction. Experimental results with microwave, infrared and Raman spectroscopy suggest that the cyanamide molecule has a non-planar structure in the ground state (Daoudi, Pouchan & Sauvaitre, 1982; Birk & Winnevisser, 1986). *Ab initio* studies on cyanamide predict a planar or a non-planar structure, depending on the basis set used (Riggs & Radom, 1985; Ichikawa, Hamada, Sugawara, Tsuboi, Kato & Morokuma, 1982). An imprecise room-temperature X-ray structure analysis on cyanamide was performed by Zvonkova & Khvatkina (1961). Dyhr-Nielsen, Hansen & Larsen (1976) reported a neutron diffraction study on cyanamide at 100 K. The low-temperature X-ray crystal structure of cyanamide was determined to establish whether the structure is planar and whether the NCN angle is linear.

Experimental. Cyanamide (m.p. 318–319 K) is a weak acid with a great affinity for water. It may polymerize to form the dimer, dicyandiamide or even the trimer, melanine. Commercially available cyanamide (99+% purity, Aldrich) was slowly vacuum sublimed at 287 K to give good quality, colourless single crystals. A crystal of approximate dimensions 0·3 × 0·3 × 0·4 mm was mounted inside a Lindemann tube. The crystal was aligned on a DEC MicroPDP computer-controlled Siemens four-circle diffractometer and was slowly cooled to 108 (1) K with the aid of a nitrogen gas stream low-temperature device designed by Dietrich & Dierks (1970). Lattice parameters from least-squares refinement of 33 reflections, $31 < 2\theta < 45°$. Ten standard reflections with a good spread in reciprocal space and of different intensities were monitored every 120 min and showed insignificant intensity fluctuations throughout the measurement. All 2200 reflections in the hemisphere *h*: −9 to 9; *k*: −9 to 9, *l*: 0 to 12, in the range $2 < \theta < 30°$ were measured with the ω–2θ scan mode (Zr-filtered Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å).

A variable scan range $\Delta\theta = (1·06 + 0·26\tan\theta)°$ was used with minimum and maximum scan speeds of 0·44 and 3·55° s^{-1}. Merging of data in the Laue class *mmm* gave 598 unique reflections, 50 unobserved ($I < 2\sigma$) ($R_{int} = 0·033$). Data corrected for Lorentz–polarization effects, but not for absorption. The structure was

solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined subsequently with *XTAL* (Hall & Stewart, 1987), H atoms from difference synthesis. Full-matrix least-squares refinement based on F of atomic positional and thermal parameters, scale factor and an isotropic extinction parameter [model by Larson (1969)] gave $R = 0.051$ and $wR = 0.050$, $w = 1/\sigma^2(F)$, extinction parameter 8·1 (3), max. $(\Delta/\sigma) = 0.04$, largest peak in final difference map$=0.26$, largest hole $= 0.23$ e Å^{-3}. Atomic scattering factors for C and N atoms from Cromer & Mann (1968), H-atom scattering factors from Stewart, Davidson & Simpson (1965).

Discussion. The structural parameters obtained for cyanamide together with the atomic numbering scheme used are depicted in Fig. 1. Final atomic coordinates and equivalent isotropic temperature factors (Hamilton, 1959) are presented in Table 1.* The structure is non-planar owing to the pyramidal nature of the amine N. This is supported by the fact that N(1) is 0·11 (1) Å from the plane through H(1), H(2) and C and that the angle between a least-squares plane through the atoms H(1), N(1), H(2) and a line through the atoms N(1) and C is 18 (1)°. The NCN bond angle deviates slightly from linearity, N(1)—C—N(2) = 178·1 (1)°. The N(1)···N(2) distance is 2·467 (1) Å. The shortest intermolecular contact between C atoms is 3·445 (1) Å.

A packing diagram illustrating the intermolecular hydrogen bonds is shown in Fig. 2. Their contact distances are N(1)···N(2) = 3·014 (1) and H(1)···N(2) = 2·12 (1) Å at $\frac{1}{2}-x$, $-y$, $\frac{1}{2}+z$, N(1)···N(2) = 3·037 (1) and H(2)···N(2) = 2·22 (1) Å at $-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$. Each cyanamide molecule is hydrogen bonded to four other cyanamide molecules by two pairs of symmetry-related bonds. It can be seen from Fig. 2 that six molecules are linked in a macrocyclic ring (I) formed by molecules (1)–(6), a second ring (II) being the centrosymmetric image of ring I is formed by molecules (1')–(6') (numbering code of Fig. 2). There is a connection between ring I and its translated image in the x direction through ring II by the molecules (3) and (7), where (3) belongs to ring I and (7) to the 1+x cell. Rings neighbouring in the y direction have (5) and (4) as common molecules.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51180 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters*

	x	y	z	U, U_{eq}* (Å$^2 \times 10^2$)
N(1)	0·1459 (1)	0·1699 (1)	0·10179 (9)	2·687 (3)
N(2)	0·1401 (1)	0·0125 (1)	0·34609 (9)	2·438 (2)
C	0·1412 (1)	0·0837 (1)	0·2312 (1)	1·945 (2)
H(1)	0·197 (2)	0·111 (2)	0·022 (1)	3·85 (3)
H(2)	0·059 (2)	0·266 (2)	0·087 (1)	6·03 (4)

* U_{eq} = one third of the trace of the orthogonalized matrix U_{ik}.
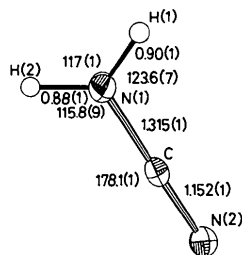

Fig. 1. An *ORTEP* (Johnson, 1970) representation of the cyanamide molecule showing the atomic numbering scheme, bond lengths (Å), and angles (°) with e.s.d.'s in parentheses.
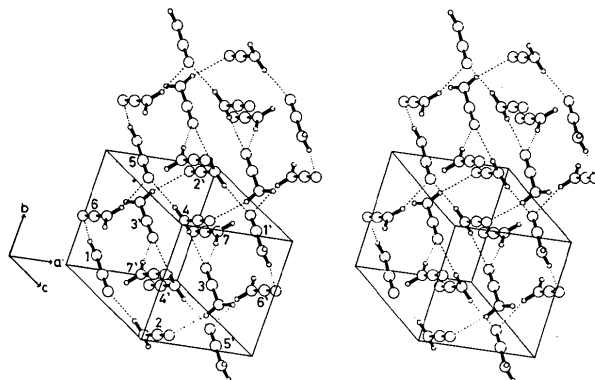

Fig. 2. Packing diagram (*SCHAKAL*86; Keller, 1986) for cyanamide. Molecules having numbers refer to the following symmetry code: (1) x, y, z; (2) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (3) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (4) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (5) $x, 1+y, z$; (6) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (7) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$. (1')–(7') are obtained from (1) to (7) by the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Dotted lines represent hydrogen bonds.

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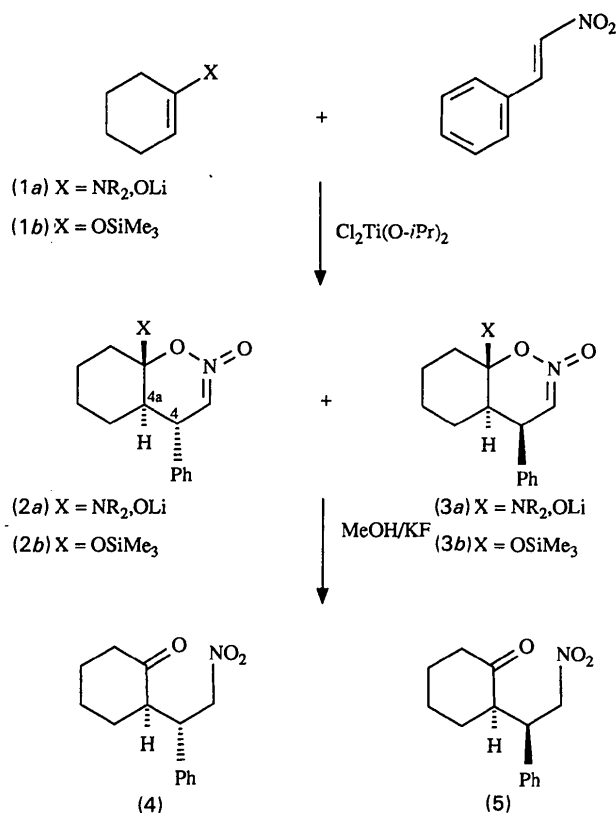# U,l-4a,5,6,7,8,8a-Hexahydro-4-phenyl-8a-(trimethylsiloxy)-4H-1,2-benzoxazine 2-Oxide

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) Å^3, $Z = 4$, $D_m = 1.22$ (2), $D_x = 1.206$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ 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* (1*a* → 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 (1*b* → 5) (Brook & Seebach, 1987; Seebach & Brook, 1985). In both cases, cyclic nitronates (2*a*, 2*b*, 3*a*, 3*b*) can be isolated: the isolation of crystalline trimethylsilylated acetals (2*b*, 3*b*) is particularly unusual. The relative stereochemistry of (2*b*) and (3*b*) 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

(1*a*) X = NR₂,OLi
(1*b*) X = OSiMe₃

(2*a*) X = NR₂,OLi
(2*b*) X = OSiMe₃

(3*a*) X = NR₂,OLi
(3*b*) X = OSiMe₃

(4)

(5)

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

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