Crystal Structure of Silyl Isocyanate at 140 K

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Summary Molecules of solid SiH_3NCO have crystallographic C_s symmetry; the Si–N–C–O chain is bent with ∠ Si–N–C = 158° and ∠ N–C–O = 176°, and hydrogen atoms adopt the staggered conformation.

THE vibrational[1] and rotational[2] spectra of silyl isocyanate, SiH_3NCO, indicate that the molecule is a symmetric top; electron diffraction[3] leads to a structure with an angle Si–N–C of 152°, the apparent distortion from linearity arising from a low-frequency bending vibration. The details of the potential function have been derived from a fuller analysis of the microwave spectrum.[4] Relatively little is yet known about the geometries of quasi-linear molecules in the solid state. We here report the crystal structure of SiH_3NCO, which becomes one of the first of such molecules to be studied by gas-phase electron diffraction, microwave spectroscopy, and *X*-ray crystallography.

The structure of SiH_3NCO (m.p. *ca.* 183 K) was determined at 140 K; *X*-ray data (Cu-K_α radiation) were collected photographically using the multi-film equi-inclination Weissenberg method for the levels *h*0—6*l*. Intensities, corrected for absorption [μ(Cu-K_α) = 39·0 cm^{-1}], were obtained from microdensitomer measurements made by the S.R.C. service at the Atlas Computing Laboratory. The molecular configuration, staggered, is shown in the Figure, and geometric parameters are given in the Table. All atoms except H(2) lie in the mirror plane; the shortest distance between neighbouring isocyanate groups is 336 pm, and there are Si···O and Si···N intermolecular contacts of 330 and 331 pm, respectively. Despite the large amplitude of the Si–N–C bending mode for the free molecule, the *X*-ray parameters are not consistent with any large amplitude bending motion in the crystal; the only notable vibration is an oscillation of oxygen in the mirror plane and perpendicular to the C–O bond, with mean square amplitude of 500 pm². Thus the linear ground state for this molecule in the vapour does not persist in the crystal, where packing forces appear to constrain the low-frequency bending vibration of the free molecule. It must be coincidence that the Si–N–C angle in the crystal is very close to that at the minima of the potential function for the free

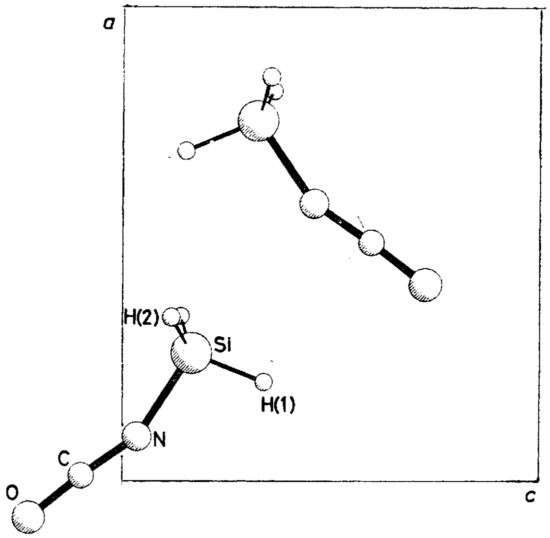

FIGURE. A PLUTO diagram showing the axial Si···N contacts between molecules lying on the same mirror plane in the molecular structure of SiH_3NCO.

TABLE. Comparison of molecular parameters. Bond lengths are in pm, and angles in degrees. E.s.d.'s (in parentheses) are in units of the last digit.

	X-Ray[b]	Microwave[c]	Electron diffraction[a]	
			Refinement (A)	Refinement (B)
Si—H(1)	136(4)	150·6	147·0(9)	147·3(10)
Si-H(2)	123(4)			
Si-N	172·3(4)	169·9	170·3(4)	170·3(4)
N-C	118·1(5)	115·0	121·6(9)	120·0(5)
C-O	116·8(5)	117·9	116·4(8)	118[d]
∠ Si-N-C	158·2(3)		151·7(12)	152·7(12)
∠ N-C-O	176·2(5)	180[d]	180[d]	180[d]
∠ H-Si-H(av)	113·5(20)	110·4	110[d]	110[d]

[a] From ref. 3. [b] E.s.d's do not include contributions from errors in the cell dimensions. [c] From ref. 2. [d] Assumed values.

molecule.[4] There is also a small distortion in the crystal at C. The Si–N bond is longer in the crystal than in the free molecule. This lengthening may be associated with the axial Si · · · N contact (331 pm), and with slight contraction of the N–Si–H angles. This may well represent what has been described as incipient 5-co-ordination; from related crystallographic situations[5] we calculate that here the intermolecular interaction, though very weak, should result in a 14 pm increase in the Si–N bond length, as against an observed increase of 20 pm, and is presumably associated with shortening of the N–C bond. It is just possible that the departure from linearity at N is also associated with the axial Si · · · N contact.

Crystal data: SiH_3NCO, $M = 73{\cdot}1$, orthorhombic, $a = 796$, $b = 652$, $c = 710$ pm (e.s.d.'s 0·3% assumed), space group *Pnma*, $Z = 4$, $D_c = 1{\cdot}32$ g cm^{-3}. The structure was solved by Fourier methods; least-squares refinement, with isotropic vibration parameters for hydrogen atoms and anisotropic parameters for other atoms, has yielded a current $R = 3{\cdot}9\%$ over 328 reflexions.

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