The Disordered Structure of Trimethylsilyl Cyanide at 140 K which gives Sharp and Diffuse X-ray Reflexions

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Abstract

At 140 K crystals of $(CH_3)_3SiCN$, m.p. 285 K, $M_r = 99\cdot2$, are orthorhombic, $a = 6\cdot62$, $b = 7\cdot45$, $c = 6\cdot69$ Å (e.s.d.'s $0\cdot3\%$ assumed), space group $Pnm2_1$ with $Z = 2$, $U = 329\cdot9$ Å^3, $D_c = 1\cdot00$ Mg m^{-3}, Cu $K\alpha$ radiation (Ni filter), $\lambda = 1\cdot5418$ Å, $\mu = 2\cdot16$ mm^{-1}. The crystals give both sharp and diffuse X-ray reflexions; the intensities of the sharp reflexions were obtained from microdensitometer measurement of Weissenberg films taken with Cu $K\alpha$ radiation. The structure consists of chains of molecules aligned head-to-tail with an intermolecular $N\cdots Si$ distance of $3\cdot66$ (3) Å. The disorder seems to indicate that the chains may be aligned either parallel or antiparallel to **c**. A composite structure, which attempts to model the disorder, gives $R = 8\cdot2\%$ over 224 sharp reflexions.

Introduction

In solid trimethyltin(IV) cyanide the coordination around the Sn atoms is trigonal bipyramidal with disordered cyanide groups occupying the axial positions so linking (in a symmetrical manner) trigonal planar Me$_3$Sn fragments into infinite chains (Schlemper & Britton, 1966*a*). In solid trimethylgermanium(IV) cyanide (Schlemper & Britton, 1966*b*) the molecules are also aligned head-to-tail but here the coordination about the Ge atom is close to tetrahedral and the intermolecular $N\cdots Ge$ contacts are very long at $3\cdot57$ (6) Å. The difference in structure can be said to reflect the more pronounced acceptor character of Sn^{IV} relative to Ge^{IV}.

Previous studies of the crystal structures of simple silyl compounds show that even those species with very low melting points may crystallize with the formation of well-defined intermolecular interactions. In crystalline silyl isocyanate (Barrow, Ebsworth & Harding, 1980) there are Si$\cdots$O and Si$\cdots$N interactions. In crystalline disiloxane there are intermolecular Si$\cdots$O interactions which are absent in hexamethyldisiloxane. Thus methylation at the Si atom seems to reduce its ability to participate in donor–acceptor interactions (Barrow, Ebsworth & Harding, 1979).

The melting point of trimethylsilyl cyanide is 285 K, that for *tert*-butyl cyanide is 289 K, trimethylgermyl cyanide is 311 K while trimethyltin(IV) cyanide melts at 462 K. These melting points appear to reflect the extent of intermolecular interaction in the solid, at least insofar as the Ge and Sn species are concerned. While there are good grounds for presuming that *tert*-butyl cyanide will exist in the crystal as discrete molecules, the situation for trimethylsilyl cyanide is more equivocal. The structure of trimethylsilyl cyanide in the gas is already known from an electron diffraction study (Dakkouri & Oberhammer, 1974). This X-ray analysis was undertaken to determine the extent of molecular association in the crystal.

Experimental

Procedure

Pure samples were sealed in thin-walled Pyrex capillaries (external diameter 0·4 mm) and mounted on goniometer heads using heat-insulating Tufnol inserts. Single crystals were grown *in situ* on a Nonius Weissenberg goniometer. The goniometer was fitted with Nonius low-temperature nitrogen-gas-stream equipment with some locally devised modifications.

The crystals always grew with the *c* axis approximately aligned along the camera axis. All crystals examined showed sharp and diffuse X-ray reflexions on the upper Weissenberg levels (hkn) where the diffuse reflexions are centred midway between the sharp reflexions on festoons of constant *k* index (*i.e.* midway between hkl and $h + 1, k, l$). Diffuse reflexions never occurred on the $hk0$ level nor in between layer lines on oscillation photographs. This type of diffraction indicates the presence of supercells with $a' = na$ but where in projection on the ab plane there is always exact equivalence between cells separated by a unit translation along **a**.

Some diffuse reflexions had significant intensity and some extended almost up to their sharp neighbours. The reciprocal lattice for upper levels resembles Plate 18-11 in Harburn, Taylor & Welberg (1975). This plate

illustrates the optical transform from a lattice where only about 50% of the lattice points are occupied and where the distribution is partly alternating and partly random. All in all a qualitative appraisal of the X-ray diffraction from trimethylsilyl cyanide crystals strongly suggests that neighbouring unit cells are always exactly equivalent if related by unit translations along y and z but that cells separated along x are not necessarily equivalent except in projection down z.

Indexing according to the sharp reflexions only gives cell dimensions of 6·62, 7·45 and 6·69 Å and the systematic absences ($0kl$ with $k + l = 2n + 1$; $0k0$ with $k = 2n + 1$; $00l$ not recorded) imply space groups $Pnm2_1$ (No. 31, C_{2v}^7) (or $Pn2_1m$) or $Pnmm$ (No. 59, D_{2h}^{13}). If the diffuse reflexions are regarded as normal reflexions occurring halfway between the sharp reflexions then the a dimension is doubled and the systematic absences would indicate space groups $Pnma$ or $Pn2_1a$.

Intensity films were exposed for the Weissenberg levels $hk0$–5 (all from one crystal) using Cu $K\alpha$ radiation and the multiple-film-pack method. A thin sheet of Ni foil was used as a diffracted-beam filter (in addition to the incident-beam Ni filter) to reduce the effects of X-ray fluorescence.

Integrated intensities for the sharp reflexions were derived from microdensitometer measurements performed by the SRC Microdensitometer Service at Daresbury Laboratory, Warrington. The data were corrected for absorption effects using the *SHELX* 76 program (Sheldrick, 1976): a sufficient number of faces were specified to define the cylindrical shape and orientation of the crystal. The intensities were further corrected for Lorentz and polarization effects. In all 491 intensities were obtained from measurements of reflexions in the hkl, $\bar{h}kl$ and $\bar{h}\bar{k}l$ octants; after merging equivalent reflexions (ignoring anomalous dispersion) there remained 224 unique sharp reflexions.

Structure solution

The Patterson function (calculated using the sharp reflexions) could be interpreted in terms of two molecules aligned with their Si—C—N axes both parallel (or anti-parallel) to **c** in a unit cell of symmetry $Pnm2_1$. The Si—C—N atoms lie in the planes of mirror symmetry at $y = \pm\frac{1}{4}$. The x/a coordinates could be inferred; one z/c coordinate is arbitrary.

An F_o Fourier synthesis calculated using phases for the Si—C—N fragments clearly revealed the methyl C atoms; but not unexpectedly this structure would not refine by least squares nor did Fourier syntheses clarify the situation. Various different composite structures were now investigated to see which would best reproduce the effect of the disorder on the sharp reflexions. It was decided to limit each composite structure to two components only, and two different scenarios were explored: composites of type (a)

simulating the effect of supercells where the subcell *shift is* $z \to z + \Delta z$, and type (b) where there is mirror reflection $z \to -\Delta z$, see Fig. 1. For each composite type, Δz was varied to investigate likely possibilities. The best model discovered was of type (b) with $2\Delta z = -0·46$ Å, see Fig. 2. A difference Fourier synthesis using phases calculated from this model showed diffuse peaks of residual electron density at positions appropriate for the H atoms.

A feature of this model, which lends the model considerable plausibility, is that the H atoms H(22*), H(31*) and H(32*) are almost superimposed on H atoms H(22), H(31) and H(32) respectively. The result is that intermolecular contacts between cells separated by a translation along x are not too different irrespective of whether the Si—C—N chain direction is the same in neighbouring cells along x or is up in one and down in the other (see Table 3). The additional short intermolecular contacts that are introduced by the disorder all involve H(33). [The H-atom positions were not well defined by the difference map. H(22), H(31) and H(32) were positioned from the difference map but H(33) and H(21) had to be placed from geometrical considerations.] The packing between cells separated
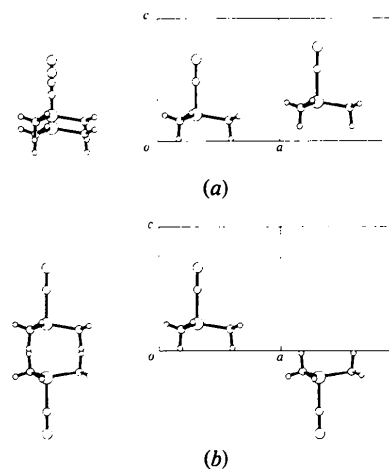

Fig. 1.(*a*) Composite of type (*a*) simulating a disorder that involves a shift of Δz between cells. (*b*) Composite of type (*b*) simulating a disorder that involves a mirror reflexion between cells.
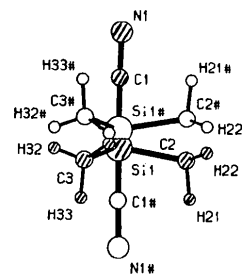

Fig. 2. Type (*b*) two-component model used for least-squares refinement.

along y is rather tighter than that between cells separated along x. So the model is consistent with disordering along x but not along y; any disorder between cells separated along z would involve head-to-head clashes between molecules.

Refinement

The two-component model was refined by least squares within the symmetry of space group $Pnm2_1$. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. The two components were placed symmetrically above and below $z = \frac{1}{4}$ so that corresponding atoms were related by the transformation $x, y, \frac{1}{2} - z$. Thus, pseudo planes of mirror symmetry occur at $z = \pm\frac{1}{4}$ and pseudo centres of symmetry at the origin and related positions. Of course if the two components are present in the ratio 50:50 then the effective space group is $Pnmm$. However, a series of trial least-squares calculations gave a minimum R factor for a population ratio of approximately 75:25. During refinement the atomic parameters were treated as follows: e.g. for Si and Si^u, $x(\text{Si}^u) = -x(\text{Si})$ refined as one parameter, similarly for $y(\text{Si}^u) = -y(\text{Si})$ and $z(\text{Si}^u) = -z(\text{Si})$, while $U(\text{Si}^u) = U(\text{Si})$ again refined as one parameter. This procedure also fixes the origin in the z direction. The H atoms did not refine sensibly and were eventually held at fixed positions with $U = 0.05\ \text{Å}^2$ (fixed). The refinement converged at $R = 8.2\%$ (over the 224 sharp reflexions) using a unit weighting scheme and individual isotropic vibration parameters for the Si, C and N atoms.

Calculation of diffuse intensities

A model of a supercell, with $a' = 4a, b' = b, c' = c$, was constructed from three subcells of *up* chains and one of *down* chains. Structure factors were calculated for reflexions $h'kl$ where $h' = 4n + 1, 4n + 2, 4n + 3$, i.e. for those regions of reciprocal space between the

sharp reflexions. The agreement between the calculated diffuse intensities and observed intensities (as estimated by eye) was only moderate. So clearly the model does not fully reproduce the arrangement in the crystal. Furthermore, anisotropic refinement of the composite structure reduced R to 5.1% through extension of the

Table 2. *Bond distances* (Å) *and angles* (°)

The e.s.d.'s given here are twice the least-squares values so as to reflect the extra uncertainty arising from the disorder.

Si–C(1)	1.82 (3)	C(2)–H(21)	1.00*
C(1)–N	1.21 (4)	C(2)–H(22)	1.00†
Si–C(2)	1.81 (3)	C(3)–H(31)	1.05†
Si–C(3)	1.81 (2)	C(3)–H(32)	0.86†
		C(3)–H(33)	1.00*
Si–C(1)–N	179 (3)	Si–C(2)–H(21)	106*
C(1)–Si–C(2)	100 (2)	Si–C(2)–H(22)	119†
C(1)–Si–C(3)	101 (1)	Si–C(3)–H(31)	103†
C(2)–Si–C(3)	117 (1)	Si–C(3)–H(32)	110†
C(3)–Si–C(3')	117 (1)	Si–C(3)–H(33)	111*

* H atom at calculated position.
† H atom positioned from difference map.

Table 3. *Intermolecular contacts and geometry of the* Si $\cdots$ N *contact*

(a) Intermolecular contacts (Å) at less than (the sum of van der Waals radii + 0.4 Å), where the van der Waals radii are Si, 2.10 Å; N, 1.55 Å; C, 1.70 Å; H, 1.20 Å. The left-hand column gives contacts for a molecule in an 'up' chain that is completely surrounded by other 'up' chains (these would be appropriate for a fully ordered portion of the crystal). The right-hand column gives contacts for a molecule in a row of 'down' chains (e.g. the third row of cells in Fig. 3) that is trapped between cells of 'up' chains at $x = -1$ and at $x = +1$. This would be the worst possible case arising from the disorder.

'Ordered' portion of crystal (both atoms part of 'up' chain)		Worst disordered situation (first atom listed is in a 'down' chain)	
H(21)$\cdots$H(31^i)	2.56	H(32)$\cdots$H(33^{ii})	2.23*
H(32)$\cdots$H(33^{ii})	2.63	H(33)$\cdots$H(33^{ii})	2.29*
H(22)$\cdots$H(33^{iii})	2.68	H(21)$\cdots$H(31^{iii})	2.56
H(22)$\cdots$H(32^{iv})	2.70	C(3)$\cdots$H(33^{ii})	2.68*
N$\cdots$H(22^{iii})	2.91	H(22)$\cdots$H(33^i)	2.68
N$\cdots$H(21^v)	2.99	H(22)$\cdots$H(32^{iv})	2.77*
N$\cdots$H(33^v)	3.07	N$\cdots$H(22^i)	2.91
N$\cdots$H(31^{iii})	3.08	N$\cdots$H(21^{vi})	2.99
C(1)$\cdots$H(22^{iii})	3.24	C(3)$\cdots$H(32^{ii})	3.06*
Si$\cdots$N^{vi}	3.66 (3)	N$\cdots$H(33^{vi})	3.07
		N$\cdots$H(31^i)	3.08
		C(1)$\cdots$H(22^i)	3.24
		C(3)$\cdots$C(3^{ii})	3.33*
		Si$\cdots$N^v	3.66 (3)

(b) The geometry of the Si$\cdots$N contact

Si$\cdots$N^{vi} 3.66 (3) Å

C(1)–Si$\cdots$N^{vi} 179 (1)°   Si$\cdots$N^{vi}–C(1^{vi})   178 (2)°

Symmetry code: (i) $1 - x, 1 - y, z - \frac{1}{2}$; (ii) $-x, 1 - y, z + \frac{1}{2}$; (iii) $1 - x, 1 - y, z + \frac{1}{2}$; (iv) $1 + x, y, z$; (v) $x, y, 1 + z$; (vi) $x, y, z - 1$.

* Indicates an interaction between 'down' chain and 'up' chain.

Table 1. *Atomic parameters* (*with e.s.d.'s from the inverted least-squares matrix*) *for the* 75% *component*

	x	y	z	U (Å^2)
Si	0.3144 (7)	0.25	0.2155 (17)	0.042 (2)
N	0.3193 (15)	0.25	0.6689 (17)	0.014 (3)
C(1)	0.3148 (20)	0.25	0.4880 (26)	0.014 (2)
C(2)	0.5842 (19)	0.25	0.1691 (26)	0.026 (3)
C(3)	0.1811 (14)	0.4566 (12)	0.1663 (21)	0.033 (3)
H(21)	0.60	0.25	0.02	
H(22)	0.665	0.36	0.20	
H(31)	0.275	0.555	0.23	
H(32)	0.06	0.45	0.21	
H(33)	0.17	0.48	0.02	

H atoms were held fixed with $U = 0.05\ \text{Å}^2$.

Atomic parameters are referred to an origin on $n2_1$ (non-standard setting); the equivalent positions are: x,y,z; $x, \frac{1}{2} - y, z$; $-x, -y, \frac{1}{2} + z$; $-x, \frac{1}{2} + y, \frac{1}{2} + z$.

The coordinates for the 25% component are obtained from the transformation: $x, y, \frac{1}{2} - z$.

thermal ellipsoid for Si along z ($U_{33} \rightarrow 0.17$ Å^2) while U_{33} for C(1) and N(1) became negative. It is very likely that, in addition to the mirror-reflexion type (b) situation, there are further contributions to the actual disorder from type (a) involving additional Δz shifts between cells separated along x.

Results

Table 1 lists the atomic parameters appropriate for the 75% component of the composite structure (isotropic atomic vibrations, $R = 8.2\%$). Tables 2 and 3 give details of the intra- and intermolecular geometry. The e.s.d.'s in these tables exclude contributions from errors in the unit-cell dimensions.

Calculations were performed using computers of the Edinburgh Regional Computing Centre and using programs written here together with the program systems XRAY 76 (1976), SHELX 76 (Sheldrick, 1976) and PLUTO (Motherwell, 1976). Structure-factor calculations utilized atomic scattering factors listed in International Tables for X-ray Crystallography (1974) and included allowance for f' but not f''.*

Discussion

The structure model proposed for crystalline trimethyl-silyl cyanide has two molecules in a unit cell of symmetry $Pnm2_1$. The molecules lie in the mirror planes at $y = \frac{1}{4}$ or $\frac{3}{4}$ with the Si—C—N molecular axes more or less parallel to z, so the space-group symmetry requires both molecules to point the same way. The unit cell down z is only one molecule thick so the molecules are aligned head-to-tail as in a chain (Fig. 3). The disorder arises from the possibility that in neighbouring unit cells, but only those separated along x, the chain direction may be reversed, see Fig. 4. This model provides a satisfactory explanation for the presence of the diffuse reflexions and their systematic absence on $hk0$ and is consistent with packing requirements. There are indications (from the aniso-tropic refinement and from the calculated intensities of diffuse reflexions) that the two-component model described in the Experimental section does not fully reproduce the disorder. Nevertheless the model does seem to simulate at least the major components of the disorder; also the head-to-tail arrangement of mol-ecules appears to be beyond doubt.
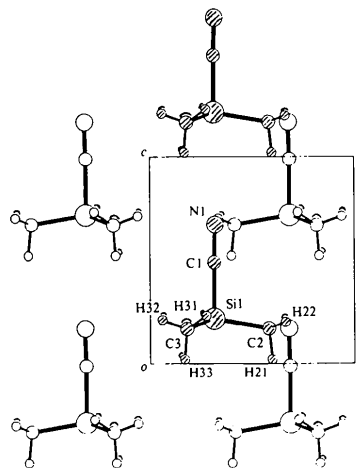
Fig. 3. View of an ordered portion of the crystal projected along y showing the head-to-tail alignment of molecules along z. Shaded atoms refer to molecules lying on the mirror plane at $y = \frac{1}{4}$, open atoms refer to molecules lying on the mirror plane at $y = \frac{3}{4}$.
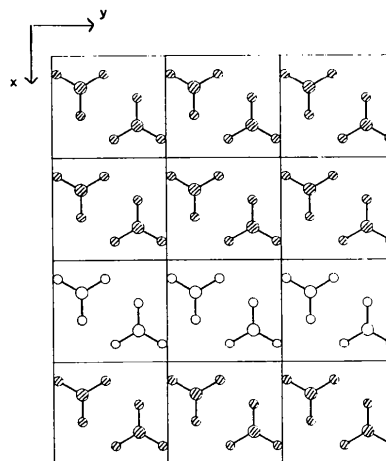

Fig. 4. Cross section (through ab plane) of a disordered portion of the crystal. Shaded atoms denote molecules where the Si $\rightarrow$ C $\rightarrow$ N chain direction is up, open atoms for where the chain direction is down. The H atoms have been omitted.

The structural feature of overriding chemical signifi-cance is the length of the intermolecular N$\cdots$Si contact. Fortunately this distance is probably the best determined parameter of this analysis. (The intra-molecular geometry should be regarded with some caution: the internal bond lengths and angles will be particularly sensitive to shortcomings in the model and will not be discussed further.) The intermolecular N$\cdots$Si distance is 3.66 (3) Å, equal to the sum of van der Waals radii for Si (2.10 Å) and N (1.55 Å). Although this intermolecular contact is directionally specific, C(1)—Si$\cdots$N = 179 (1)° and C(1)—N$\cdots$Si = 178 (2)°, the length implies a null interaction. The importance of this observation can be seen as follows. First, contrary to the trend in atomic radii the N$\cdots M$

contact in trimethylsilyl cyanide is longer than in the germyl analogue, where $N \cdots Ge = 3 \cdot 57$ (6) Å, while in the Sn^{IV} species the separation is only $2 \cdot 49$ (2) Å. Thus, there is a progression down Group IV from discrete tetrahedral molecules (Me_3SiCN) through to trigonal-bipyramidal coordination (Me_3SnCN). Variations in coordination geometry from tetrahedral to trigonal bipyramidal are also found in crystal structures involving the same metal but in different chemical and/or crystal environments. This behaviour has been examined using structural correlation methods and invoking analogy to an S_N2 reaction mechanism. Sn^{IV}, Pb^{IV} and Ge^{IV} species have been studied by Britton & Dunitz (1981) while Si species have been studied by Barrow et al. (1980) and Pestunovich, Sidorkin, Dogaev & Voronkov (1980). Continuing with the S_N2 reaction-scheme analogy suggests that, all other things being equal, there is an increasing tendency on proceeding down Group IV for the trigonal-bipyramidal 'intermediate' or 'transition state' to be stabilized relative to the tetrahedral 'reactant'.

The second point arising from this analysis again concerns the observation that by comparison with the Ge and Sn analogues the $N \cdots Si$ contact in Me_3SiCN could be much shorter than the van der Waals distance. That it is not, reinforces a previous argument (Barrow et al., 1979) that the $-SiMe_3$ group is too poor an acceptor to noticeably participate in intermolecular interactions, even though here the conditions appear favourable. Furthermore the corollary of this argument is that the much shorter $Si \cdots O$ and $Si \cdots N$ intermolecular contacts found in crystal structures involving $-SiH_3$ groups are indeed likely to indicate some kind of electronic interaction (Barrow et al., 1979, 1980 and references therein).

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