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The geometry of SiOCN and SiNCO linkages. The crystal structures of $(Me_3Si)_2(Ph_2MeSi)CSiMe_2OCN$ and $(PhMe_2Si)_3CSiMe_2NCO$ ☆

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Abstract

Single crystal X-ray diffraction studies have been carried out on the title compounds (in the case of the cyanate as its methylcyclohexane solvate). The geometry of the SiNCO fragment in the isocyanate $(PhMe_2Si)_2CSiMe_2NCO$ ($\angle SiNC = 155.7(5)$, $\angle NCO = 175.9(7)^\circ$, d(Si–N) = 1.739(5), d(N–C) = 1.135(8), d(C–O) 1.174(8) Å) is very similar to that in the much less crowded compounds H_3SiNCO and $ClCH_2Me_2SiNCO$, but in all three compounds the Si–N–C angle is a little smaller than in Me_3SiNCO. In the light of the results the validity of recent calculations indicating an Si–N–C angle of 180° in H_3SiNCO is questioned. In the case of the cyanate $(Me_3Si)_2(Ph_2MeSi)CSiMe_2OCN$, disorder results in considerable uncertainty in the geometry of the SiOCN linkage, but the values for the O–C–N and Si–O–C angles, 175(1)° and ca. 124 ± 6°, respectively, are consistent with those predicted by the corresponding calculations on H_3SiOCN.

Keywords: Silicon; Cyanate; Isocyanate; Crystal structure

1. Introduction

Crystal structure data for silicon isocyanates have previously been available for H_3SiNCO, **1**, (determined at −133°C [1], Me_3SiNCO, **2** (at −90°C) [2], and $ClCH_2Me_2SiNCO$, **3**, at (−90°C) [3]. In all three cases the NCO linkage was found to be close to linear. A significant difference between the value of the Si–N–O angle in **2** (163.6(6)°) and that in **3** (158.3(2)°) was attributed to crystal packing effects arising from the bulk of the chlorine atom in **3** [3]. We thought it of interest to determine the structure of the compound $(PhMe_2Si)_3CSiMe_2NCO$, **4**, in order to see whether the very bulky $(PhMe_2Si)_3C$ group would have any significant effect on the geometry of the SiNCO linkage. Added interest was provided by the results of recent calculations by Fehér and his colleagues [4] that pointed to an Si–N–C angle of 179.88° in **1** and led the authors to question the accuracy of a value of 159.84° derived earlier from microwave data [5].

H_3SiNCO	Me_3SiNCO	$ClCH_2Me_2SiNCO$
1	**2**	**3**

$(PhMe_2Si)_3CSiMe_2NCO$

4

In contrast, no structural data have previously been available for any silicon cyanate, the first example of which, viz. $(Me_3Si)_3CSiMe_2OCN$, was reported in 1982 [6], but the calculations by Fehér et al. on H_3SiOCN predicted an Si–O–C angle of 120.43° and an O–C–N angle of 178.43° [4]. We found that significant diffraction data could not be obtained for $(Me_3Si)_3CSiMe_2$-OCN, probably because the spherical nature of the molecule gives rise to plastic crystal behaviour, as is the case for $(Me_3Si)_4C$ at room temperature. We were, however, able to obtain data for $(Me_3Si)_2(Ph_2MeSi)$-$CSiMe_2OCN$, **5**, (as its methylcyclohexane solvate) though they are badly affected by disorder in the crystal.

☆ Dedicated to Professor Fausto Calderazzo on the occasion of his 65th birthday in recognition of his important contributions to organometallic and inorganic chemistry.

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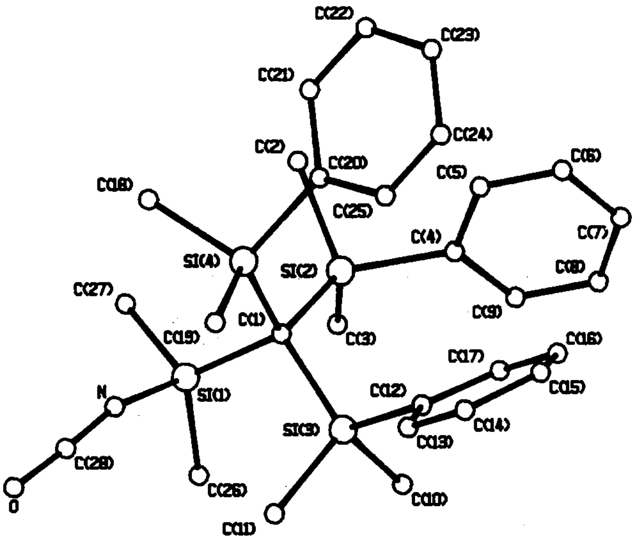

Fig. 1. Molecular structure of 4, with atom numbering scheme.

2. Results and discussion

The molecular structure of 4 is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. There were no significant intermolecular contacts. (In contrast, in the case of 3 there are short C···O contacts.)

Table 1
Selected intramolecular distances (Å) and angles (°) in 4 with estimated standard deviations in parentheses

(a) Bonds			
Si(1)-N	1.739(5)	Si(1)-C(1)	1.902(5)
Si(1)-C(26)	1.871(6)	Si(1)-C(27)	1.864(7)
Si(2)-C(1)	1.938(5)	Si(2)-C(2)	1.876(5)
Si(2)-C(3)	1.886(6)	Si(2)-C(4)	1.895(5)
Si(3)-C(1)	1.942(5)	Si(3)-C(10)	1.879(6)
Si(3)-C(11)	1.878(6)	Si(3)-C(12)	1.900(6)
Si(4)-C(1)	1.937(5)	Si(4)-C(18)	1.877(6)
Si(4)-C(19)	1.876(6)	Si(4)-C(20)	1.880(5)
O-C(28)	1.174(8)	N-C(28)	1.135(8)
(b) Angles			
N-Si(1)-C(1)	108.3(2)	N-Si(1)-C(26)	104.4(3)
N-Si(1)-C(27)	103.0(3)	C(1)-Si(1)-C(26)	116.9(3)
C(1)-Si(1)-C(27)	117.5(2)	C(26)-Si(1)-C(27)	105.2(3)
C(1)-Si(2)-C(2)	112.8(2)	C(1)-Si(2)-C(3)	112.8(2)
C(1)-Si(2)-C(4)	116.3(2)	C(2)-Si(2)-C(3)	104.7(3)
C(2)-Si(2)-C(4)	104.6(2)	C(3)-Si(2)-C(4)	104.6(2)
C(1)-Si(3)-C(10)	112.4(2)	C(1)-Si(3)-C(11)	112.1(2)
C(1)-Si(3)-C(12)	115.6(2)	C(10)-Si(3)-C(11)	106.0(3)
C(10)-Si(3)-C(12)	105.1(3)	C(11)-Si(3)-C(12)	104.9(3)
C(1)-Si(4)-C(18)	112.9(2)	C(1)-Si(4)-C(19)	112.9(2)
C(1)-Si(4)-C(20)	115.6(2)	C(18)-Si(4)-C(19)	104.9(2)
C(18)-Si(4)-C(20)	104.7(2)	C(19)-Si(4)-C(20)	104.8(2)
Si(1)-N-C(28)	155.7(5)	Si(1)-C(1)-Si(2)	105.8(2)
Si(1)-C(1)-Si(3)	107.1(2)	Si(1)-C(1)-Si(4)	106.9(2)
Si(2)-C(1)-Si(3)	112.3(2)	Si(2)-C(1)-Si(4)	112.3(2)
Si(3)-C(1)-Si(4)	112.0(2)	Si(2)-C(4)-C(5)	120.5(4)
Si(2)-C(4)-C(9)	122.4(4)	O-C(28)-N	175.9(7)

Table 2
Bond lengths (Å) and angles (°) found for the SiNCO linkage in compounds 1, 3 and 4, and (1 calc.) calculated [5] for that in 1

	4	3	1	1 calc.
Si-N	1.739(5)	1.731(2)	1.723(4)	1.719
N-C	1.135(8)	1.176(2)	1.181(5)	1.205
C-O	1.174(8)	1.173(2)	1.168(5)	1.187
SiNC	155.7(5)	158.3(5)	158.2(3)	179.88
NCO	175.9(7)	177.6(3)	176.2(5)	179.99

In Table 2 the more significant bonding parameters for the SiNCO system in 4 are shown alongside those in 1 and 3; data for 2 are not included because, except in respect of the Si-N-C angle (see above), they are not significantly different from those for 3. Also shown are parameters determined for 1 from the microwave spectrum. There is remarkably little difference between the parameters derived for crystals of all three compounds; the N-C bond in 4 may perhaps be a little shorter than those in the other two, but the observed difference cannot be regarded as significant when account is taken of the estimated standard deviations, and seems unlikely to be real because the Si-N and C-O distances and the associated angles are so similar in all three compounds. Since there is so little difference overall between the data for the small molecule 1, the somewhat more crowded 3, and the much more crowded 4, the slightly larger Si-N-C angle in 2 appears to be somewhat anomalous, but it could be simply the result of a chance packing effect [3]. Since an Si-N-C angle in the region of 158° is found in all four crystal structures and one of 159.84° was derived for 1 from microwave data [5] it seems to us unlikely that the value of 180° recently calculated by Fehér and his colleagues for 1 [4] is valid, especially since an electron diffraction study indicated a value of 151.7° for this molecule [8].

The slight departure of the NCO linkage from linearity in the crystals of all four compounds 1–4 suggests that this is an intrinsic property of the linkage, but the value of 179.99° calculated for 1 [4] could be correct for the gas phase. The Me-Si-Me angle in the $SiMe_2NCO$ system is much smaller for 4, viz. 105.2(3)°, than for 3, 113.5(1)°, presumably because the Me groups in 4 move together, away from the $(PhMe_2Si)_3C$ group, to relieve the strain. Correspondingly the mean Me-Si-N angle in 4, 103.7(3)°, is much smaller than that in 3 (110.7(1)°).

There is some interest in the conformation adopted by the $(PhMe_2Si)_3C$ group [9,10], which in 4 is similar to that in, e.g. $(PhMe_2Si)_3CSiCl_3$ [9], $[\{(PhMe_2Si)_3CHgCl\}_2]$ [10], and $(PhMe_2Si)_3CSnMe_2F$ [11]]; i.e. the three Ph groups are arranged in a propeller fashion (the dihedral angles between the plane of the Si(2), Si(3), and Si(4) atoms and the planes of the C(4)–C(9),

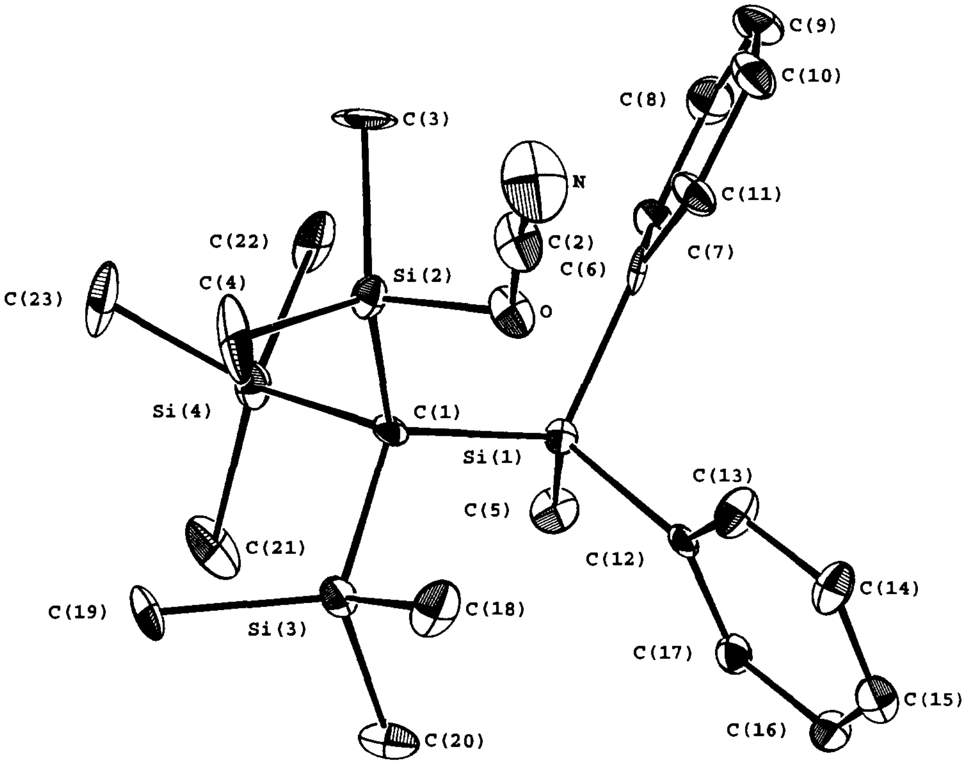

Fig. 2. Structure of the major component in the disordered crystal of 5. (MeC_6H_{11}), with atom numbering scheme. The atoms are shown as 20% thermal vibration ellipsoids.

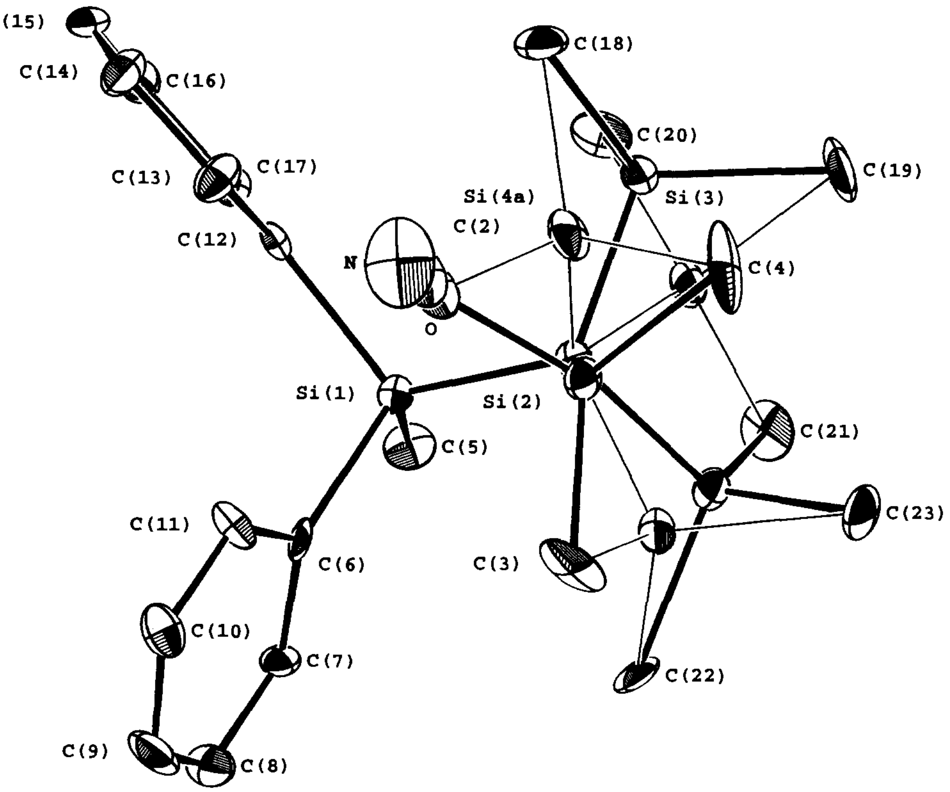

Fig. 3. Diagram showing the nature of the disorder in the crystal of 5. (MeC_6H_{11}). The thick and thin lines indicate bonds in the major and minor component, respectively.

C(12)-C(17), and C(20)-C(25) rings are 85, 94, and 92°, respectively), with all three of the Ph groups pointing away from the fourth ligand on the central carbon, and an ortho-proton of one of the groups lying above the plane of the ring of another, a disposition that would be expected to show up in the ^{1}H NMR spectrum in solution at low temperature [9]. In contrast, in, e.g. $(PhMe_2Si)_3CH$ [12] and $(PhMe_2Si)_3CHgC\{SiMe_3)_3\}$ [13], two Ph groups lie away from the fourth ligand and one towards it, and one Me group of each $SiMe_2Ph$ fragment lies above the plane of another Ph group, again with consequences for the low temperature ^{1}H NMR spectrum [9].

Other features of the geometry of the $(PhMe_2Si)_3C$ group are as usual. Thus, the C(1)-$SiMe_2Ph$ bonds, mean 1.939(2) Å, are longer than the Si-Me, mean 1.879(3) Å, and Si-Ph bonds, mean 1.892(8) Å (and are also longer than the C-$SiMe_2NCO$ bond, 1.902(5)°), and the C(1)-Si-Me angles, mean 112.6(3)°, are markedly larger than, and the Me-Si-Me angles, mean 105.2(3)°, markedly smaller than, the tetrahedral angle; the C(1)-Si-Ph angles, mean 115.8(4)°, are even larger. The Si-Me bond lengths in the $SiMe_2NCO$ group, mean 1.868(6) Å, are not significantly different from those in the $(PhMe_2Si)_3C$ group, but they are somewhat longer than those in **3**, mean 1.843(5) Å. The N atom lies only 3.274(4) Å from Si(4), a distance appreciably below the sum, 3.65 Å, of the relevant van der Waals radii, but such short intramolecular contacts are common in compounds containing $(Me_3Si)_3C$, $(PhMe_2Si)_3C$ or a related group, and are thought to be a consequence of the crowding and not to reflect weak bonding interactions [14].

Table 4
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å $\times 10^3$) for **4**

	x	y	z	U_{eq} [a]
Si(1)	8445.9(14)	460.9(8)	1173.6(6)	54(1)
Si(2)	10685.9(13)	1196.7(8)	771.1(5)	42(1)
Si(3)	9987.3(15)	1428.9(9)	1818.2(5)	50(1)
Si(4)	8372.2(13)	2181.2(8)	1039.6(5)	41(1)
O	5350(5)	446(3)	1835(2)	148(4)
N	7062(4)	657(3)	1417(2)	69(3)
C(1)	9401(4)	1346(3)	1202(2)	38(3)
C(2)	10214(5)	1388(3)	174(2)	55(3)
C(3)	11256(5)	198(3)	763(2)	65(4)
C(4)	12076(4)	1793(3)	855(2)	43(3)
C(5)	12099(4)	2537(3)	712(2)	49(3)
C(6)	13105(5)	2978(3)	760(2)	65(4)
C(7)	14118(5)	2687(4)	949(2)	80(4)
C(8)	14141(5)	1942(4)	1088(2)	78(4)
C(9)	13126(4)	1505(3)	1035(2)	60(3)
C(10)	11276(6)	776(3)	1933(2)	69(4)
C(11)	8802(6)	1185(4)	2244(2)	76(4)
C(12)	10542(5)	2397(3)	1992(2)	53(3)
C(13)	9875(6)	2856(4)	2279(2)	80(4)
C(14)	10271(7)	3555(4)	2408(2)	105(5)
C(15)	11393(7)	3813(4)	2265(2)	103(5)
C(16)	12092(6)	3362(4)	1997(2)	78(4)
C(17)	11688(5)	2657(3)	1868(2)	59(3)
C(18)	7268(5)	1935(3)	585(2)	61(3)
C(19)	7434(5)	2524(3)	1524(2)	57(3)
C(20)	9162(4)	3044(3)	824(2)	44(3)
C(21)	9152(5)	3226(3)	355(2)	55(3)
C(22)	9745(6)	3855(3)	191(2)	70(4)
C(23)	10334(6)	4333(3)	484(2)	79(4)
C(24)	10315(5)	4188(3)	945(2)	69(4)
C(25)	9730(5)	3561(3)	1107(2)	54(3)
C(26)	9004(6)	−381(3)	1489(2)	88(5)
C(27)	8035(6)	102(3)	602(2)	76(4)
C(28)	6238(6)	537(3)	1630(2)	71(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

2.1. *Structure of $(Me_3Si)_2(Ph_2MeSi)CSiMe_2OCN$. MeC_6H_{11}*

Unfortunately, severe disorder was encountered in the crystal of the cyanate and gave rise to such uncertainty in the geometry of the SiOCN fragment that we publish the results simply because they provide the only structural data for any silicon cyanate. The disorder involved alternative sites for Si(2), Si(3) and Si(4) in a 55/45 occupancy ratio, with the two alternative sets of Si sites sharing overlapping Me and OCN sites that are unresolvable (see Figs. 2 and 3). From the parameters listed in Table 3 it can be seen that the O-C-N angle (which is not directly affected by the disorder) is 175(1)° and the Si-O-C angle can be estimated to be 124 ± 6°, both values being consistent with those (178.4 and 120.4°, respectively) calculated for H_3SiOCN [4]. Certainly there is no doubt that the Si-O-C angle in the cyanate is much smaller than the Si-N-O angle in the various isocyanates. The observed approximate lengths of the O-C and C-N bonds, 1.27(2) and 1.12(2) Å, respectively, are also consistent with those, 1.330 and 1.185 Å, calculated for H_3SiOCN.

Table 3
Selected bond lengths (Å) and angles (°) in $(Me_3Si)_2(Ph_2MeSi)CSiMe_2OCN$, **5**

(a) *Bonds*			
Si(1)-C(1)	1.921(10)	Si(1)-C(5)	1.842(12)
Si(1)-C(6)	1.882(11)	Si(1)-C(12)	1.899(11)
Si(2)-O	1.756(10)	O-C(2)	1.27(2)
N-C(2)	1.12(2)	O-Si(4a)	1.774(11)
(b) *Angles*			
C(1)-Si(1)-C(5)	111.5(5)	C(1)-Si(1)-C(6)	114.2(5)
C(1)-Si(1)-C(12)	114.0(4)	C(5)-Si(1)-C(6)	104.0(50)
C(5)-Si(1)-C(12)	105.2(5)	C(6)-Si(1)-C(12)	107.1(5)
Si(2)-O-C(2)	118.1(8)	O-C(2)-N	175(1)
Si(4a)-O-C(2)	130.2(8)		

The geometry of the OCN group in **5** is remarkably similar to that in a representative aryl cyanate, 4-chloro-3,5-dimethylphenyl cyanate, for which the relevant bond lengths and angles are as follows: *d*(O–C) 1.27 Å, *d*(C–N) 1.14 Å, C–O–C 118.3°, O–C–N 173.5° [15].

Table 5
Crystal structure determination details for $5 \cdot MeC_6H_{11}$

Crystal data	
Formula	C27 H36N OSi4
Formula weight	508.9
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (No. 19)
a (Å)	9.726(4)
b (Å)	16.010(6)
c (Å)	20.913(7)
Alpha (°)	90
Beta (°)	90
Gamma (°)	90
Cell volume (Å^3)	3256(2)
Z	4
D_{calc} (g cm^{-3})	1.04
$F(000)$	1100
Monochromated Mo Kα radiation	
λ (Å)	0.71073
μ (cm^{-1})	1.9
Temperature	173 K
Data collection	
Crystal size (mm^3)	Cut to 0.3 × 0.3 × 0.2
Diffractometer	Enraf-Nonius CAD4
Reflections for calculating cell	
Number, θ min, θ max	25, 7, 10
Scan mode for data collection	$\theta - 2\theta$
Data reflection ranges, θ min and max (°)	h 0 → 12, k 0 → 21, l 0 → 27; 2 → 28
Total unique reflections measured	4402
Significant reflections, $\lvert F^2 \rvert > 2\sigma(F^2)$	2332
Max change in standard reflections	+7.4%
Decay correction	Yes
Empirical absorption correction, T_{max}, T_{min}	No
Structure solution and refinement	
Non-H atoms located by	direct methods SHELXS-86
Refinement by	Full matrix least squares non-H atoms anisotropic Enraf-Nonius MolEN programs
Hydrogen atoms	for H's on Si(1) only fixed calculated positions $U_{iso} = 1.3U_{eq}$ for parent atom
R	0.104
R'	0.111
S	1.3
No. variables	352
No. observed reflections	2332
(Δ/σ) max	0.6
$(\Delta\rho)$ max, min (e Å^{-3})	+0.52, −0.22

$\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/L_p$, $w = \sigma^{-2}(F)$, $\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$ minimised.

Table 6
Fractional atomic coordinates and equivalent isotropic thermal parameters for **5**

	x	y	z	U_{eq} [a]
Si(1)	0.0606(3)	0.8186(2)	0.0869(1)	0.027(1)
Si(2)	0.0849(7)	0.9624(4)	0.1934(3)	0.038(3)
Si(3)	−0.0828(6)	0.8032(4)	0.2249(3)	0.037(3)
Si(4)	−0.1873(7)	0.9382(4)	0.1282(3)	0.041(3)
O	0.2462(8)	0.9148(5)	0.2030(3)	0.050(5)
N	0.4274(12)	0.9870(9)	0.2573(6)	0.111(9)
C(1)	−0.0247(10)	0.8775(6)	0.1563(5)	0.027(5)
C(2)	0.3392(14)	0.9549(9)	0.2330(5)	0.059(8)
C(3)	0.1116(17)	1.0593(7)	0.1406(6)	0.082(9)
C(4)	0.0402(14)	0.9843(10)	0.2819(6)	0.094(9)
C(5)	−0.0683(13)	0.7733(7)	0.0324(5)	0.046(7)
C(6)	0.1694(11)	0.8861(7)	0.0334(5)	0.033(6)
C(7)	0.1291(11)	0.9041(7)	−0.0275(5)	0.034(6)
C(8)	0.2062(13)	0.9523(8)	−0.0675(5)	0.052(8)
C(9)	0.3309(15)	0.9824(8)	−0.0478(6)	0.061(8)
C(10)	0.3817(12)	0.9618(8)	0.0122(6)	0.051(8)
C(11)	0.3034(12)	0.9149(7)	0.0521(5)	0.043(7)
C(12)	0.1710(11)	0.7276(6)	0.1128(4)	0.027(5)
C(13)	0.2936(12)	0.7323(7)	0.1461(5)	0.046(7)
C(14)	0.3734(13)	0.6641(8)	0.1595(6)	0.051(8)
C(15)	0.3296(13)	0.5871(7)	0.1420(5)	0.051(7)
C(16)	0.2115(13)	0.5788(7)	0.1083(5)	0.046(7)
C(17)	0.1332(11)	0.6478(7)	0.0950(5)	0.037(6)
C(18)	0.0871(16)	0.7746(8)	0.2750(5)	0.065(8)
C(19)	−0.2320(15)	0.8523(9)	0.2734(7)	0.087(9)
C(20)	−0.1659(14)	0.7044(8)	0.1888(6)	0.058(8)
C(21)	−0.3400(12)	0.8563(10)	0.1203(7)	0.072(9)
C(22)	−0.1520(13)	0.9942(8)	0.0465(5)	0.057(8)
C(23)	−0.2237(16)	1.0347(9)	0.1826(6)	0.086(9)
C(1s)	0.0271(20)	0.2612(16)	0.9839(8)	0.139(16)
C(2s)	0.1184(24)	0.1960(13)	0.9583(11)	0.194(19)
C(3s)	0.0771(24)	0.1692(9)	0.8912(10)	0.141(15)
C(4s)	0.0727(22)	0.2358(17)	0.8487(14)	0.280(22)
C(5s)	−0.0186(24)	0.2851(14)	0.8629(11)	0.188(20)
C(6s)	0.0006(25)	0.3252(12)	0.9342(8)	0.151(17)
C(7s)	0.0751(31)	0.2990(17)	1.0391(8)	0.207(23)
Si(2a)	−0.1928(8)	0.8214(5)	0.1774(4)	0.045(4)
Si(3a)	−0.0721(9)	0.9905(5)	0.1287(4)	0.044(4)
Si(4a)	0.0812(9)	0.8813(5)	0.2285(3)	0.048(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

For Si(2), Si(3), and Si(4) the occupancy is 0.55.

For Si(2a), Si(3a), and Si(4a) the occupancy is 0.45.

3. Experimental details

3.1. Compound 4

Crystallization of **4** [7] from hexane gave crystals suitable for the diffraction study. A crystal of dimensions 0.18 × 0.30 × 0.18 mm^3 was used for the data collection.

Crystal data. $C_{28}H_{39}ONSi_4$: $M = 518.0$, orthorhombic, space group *Pbca*, $a = 11.160(3)$, $b = 17.766(2)$,

$c = 29.602(7)$ Å, $U = 5868.8$ Å^3, $Z = 8$, $D_c = 1.2$ g cm^{-3}, $F(000) = 2224$, Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 2.2$ cm^{-1}.

Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer. Intensities of 5737 unique reflections with $+h+k+l$ and $2 < \theta < 25°$ were measured by a $\theta/2\theta$ scan with width $\theta = (0.8 + 0.35 \tan \theta)°$ and a maximum scan time of 1 min. There was no decay during the data collection. Corrections were made for Lorentz and polarization effects. A total of 2582 unique reflections with $|F^2| > 2\sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/L_p$.

Direct methods were used to find the Si atoms and a difference map to find the C, O, and N atoms, and all these were refined by full matrix least squares with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions with $U_{iso} = 1.3U_{eq}$ for the atoms to which they are attached. Refinement converged at $R = 0.063$, $R' = 0.057$ with weighting scheme $w = 1 | \sigma^2(F)$.

Atomic coordinates are listed in Table 4. A complete list of bond lengths and angles and tables of anisotropic thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

3.2. Compound 5

This compound was made as described previously [16] and recrystallized from methylcyclohexane as the monosolvate.

Details of the data collection and refinement are shown in Table 5. Two standard reflections monitored every hour showed a small increase in intensity and a correction was made for this. Refinement as the opposite absolute structure gave identical results. Atomic coordinates are listed in Table 6. A complete list of bond lengths and angles and tables of hydrogen atom coordinates and ansotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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