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THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(TRIPHENYLSILICON) CARBODIIMIDE

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Summary

The structure of $(Ph_3SiN)_2C$ has been determined by single crystal X-ray diffraction. The structure was solved by direct methods and refined to R = 0.071 for 593 independent diffractometer data. The crystals are rhombohedral, $R\bar{3}$, with $a = b = c = 18.201(20)$ Å, $\alpha = \beta = \gamma = 48.82(2)°$, and $Z = 4$. The three crystallographically independent molecules each have linear Si—N=C=N—Si chains lying along the crystallographic threefold axes; in two of the molecules the central carbon atom lies on a centre of symmetry. Principal mean bond lengths and angles are: Si—N, 1.696(25); Si—C, 1.846(20); N—C, 1.164(30); C—C, 1.387(14) Å; C—Si—N, 108.2(6); and C—Si—C, 110.8(6)°.

Introduction

As part of our study of the molecular structures of organo-silicon and -tin pseudohalides, we have determined the crystal structure of bis(triphenylsilicon) carbodiimide. It was of interest to determine whether this compound possessed a monomeric cyanimide or carbodiimide structure, with tetrahedrally coordinated silicon, or the intermediate structure adopted by $(Me_3SnN)_2C$ [1] in which planar trimethyltin groups are linked by linear N=C=N units in an infinite helical array. The interpretation of vapour phase electron diffraction data for silicon pseudohalides is complicated by the large amplitude low frequency Si—N—C bending vibration [2], but H_3SiNCS probably possesses a potential energy minimum in the linear conformation. On the other hand di-*p*-tolyl, di-*p*-nitrophenyl and digermyl-carbodiimides approximate to an allene conformation, with angles at nitrogen of 128° [3], 132° [4] and 138° [5] respectively.

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Experimental

Preparation and data collection

$(Ph_3SiN)_2C$ was prepared by refluxing freshly prepared Ph_3SiBr [6] with silver cyanimide in dry benzene. Colourless crystals were obtained by slow evaporation of a benzene solution and mounted in Lindemann glass capillary tubes. Intensities were determined on a Stoe Stadi-2 two-circle diffractometer (layers $h0l$ to $h16l$ inclusive) with Mo-K_α radiation ($\lambda = 0.71069$ Å) and graphite crystal monochromator from a crystal of approximate dimensions $0.12 \times 0.19 \times 0.12$ mm. 1504 Reflexions were measured in an approximately constant count mode, of which 36 were rejected because of background imbalance or because the net count was less than 3σ based on counting statistics. Lorentz and polarisation corrections were applied, and interlayer scale factors obtained by a linear least-squares analysis of equivalent reflexions in different layers. In view of the low absorption coefficient (μ(Mo-K_α) = 1.05 cm^{-1}) no absorption corrections were applied. Averaging of equivalent reflexions led to 593 unique observed data. Unit-cell dimensions were obtained by a least-squares fit to the observed omega measurements of 148 $h0l$ reflexions.

Crystal data

$C_{37}H_{30}Si_2N_2$, mol wt. 558.8, rhombohedral, $a = b = c = 18.201(20)$ Å, $\alpha = \beta = \gamma = 48.82(2)°$, $U = 3134$ Å^3, μ(Mo-K_α) = 1.05 cm^{-1}, $d_c = 1.18$ g cm^{-3} for $Z = 4$. No systematic absences were observed. Structure refinement was successful in space group $R\bar{3}$ (general positions: $\pm[x,y,z;\ y,z,x;\ z,x,y]$).

Structure solution and refinement

The structure was solved by a noval multisolution Σ-2 sign expansion [7], followed by successive difference electron density syntheses. All four silicon atoms and eighteen other atoms were located in the best E-map. The distribution of E-values implied that the crystal was centrosymmetric, and this was confirmed by successful refinement in the space group $R\bar{3}$. In the final full-matrix least-squares cycles, the hydrogen atoms were constrained to lie on the external bisectors of the C—C—C angles, with C—H fixed at 1.08 Å. A bonded hydrogen atom scattering factor was employed [8], with complex neutral atom scattering factors for the remaining atoms [9,10]; the weighting scheme was $w = \Sigma[\sigma^2(N) + 0.001N^2]^{-1}/[10.01 + |F_0| + 0.00644\ F_0^2]$, where N is the net peak count, and the summation is over equivalent reflexions. A total of 122 parameters were varied independently, including an overall isotropic temperature factor for the hydrogen atoms, anisotropic temperature factors for the silicon atoms and isotopic temperature factors for the remaining atoms. The refinement converged to $R = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_0| = 0.076$ with a corresponding unweighted index R 0.071. The highest peak in the final difference electron density synthesis was less than 0.5 electrons Å^{-3}. Atom coordinates and temperature factors are given in Tables 1 to 3, interatomic distances and angles in Tables 4 and 5. Structure factor tables may be obtained from the authors. The three crystallographically independent molecules are illustrated in Figs. 1 to 3.

(continued on p. 25)

TABLE 1

ATOM COORDINATES (X 10^4) AND ISOTROPIC TEMPERATURE FACTORS (Å^2 X 10^3)

	x/a	y/b	z/c	U
Si(1)	593(2)	593(2)	593(2)	
Si(2)	4406(2)	4406(2)	4406(2)	
Si(3)	1804(1)	1804(1)	1804(1)	
Si(4)	3001(1)	3001(1)	3001(1)	
N(1)	233(7)	233(7)	233(7)	174(13)
N(2)	4758(6)	4758(6)	4758(6)	159(12)
N(3)	2152(6)	2152(6)	2152(6)	122(10)
N(4)	2647(5)	2647(5)	2647(5)	118(11)
C(1)	0	0	0	172(27)
C(2)	5000	5000	5000	142(22)
C(3)	2404(8)	2404(8)	2404(8)	112(12)
C(11)	450(12)	1982(12)	—303(13)	79(5)
C(12)	—223(12)	2770(13)	89(12)	83(5)
C(13)	—347(13)	3829(14)	—564(13)	104(6)
C(14)	249(13)	4109(14)	—1660(13)	101(6)
C(15)	913(13)	3344(14)	—2055(13)	102(6)
C(16)	1012(13)	2305(13)	—1417(14)	96(6)
C(21)	4622(13)	2966(13)	5273(13)	85(5)
C(22)	3924(14)	2615(15)	5623(14)	124(6)
C(23)	4110(15)	1498(16)	6260(15)	143(7)
C(24)	4960(15)	870(14)	6488(13)	124(7)
C(25)	5634(15)	1179(16)	6177(15)	136(7)
C(26)	5506(15)	2256(15)	5535(14)	125(7)
C(31)	392(13)	2654(12)	2003(12)	79(5)
C(32)	—357(12)	2286(13)	2558(12)	84(5)
C(33)	—1430(14)	2974(14)	2678(13)	103(6)
C(34)	—1728(16)	4050(15)	2217(15)	128(7)
C(35)	—993(16)	4437(16)	1643(15)	139(7)
C(36)	80(15)	3769(15)	1512(14)	128(7)
C(41)	4362(12)	2103(12)	2907(13)	81(5)
C(42)	5191(12)	1892(13)	1990(12)	90(5)
C(43)	6245(13)	1213(13)	1898(14)	101(6)
C(44)	6493(14)	712(14)	2737(15)	113(6)
C(45)	5722(15)	902(13)	3624(14)	116(6)
C(46)	4649(12)	1584(13)	3745(13)	97(5)

TABLE 2

ANISOTROPIC TEMPERATURE FACTORS (Å^2 X 10^3) [a]

	$U11$	$U22$	$U33$	$U23$	$U13$	$U12$
Si(1)	122(6)	122(6)	122(6)	—57(3)	—57(3)	—57(3)
Si(2)	94(5)	94(5)	94(5)	—42(3)	—42(3)	—42(3)
Si(3)	93(5)	93(5)	93(5)	—43(3)	—43(3)	—43(3)
Si(4)	97(5)	97(5)	97(5)	—45(3)	—45(3)	—45(3)

[a] The temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{\star 2} + U_{22}k^2b^{\star 2} + U_{33}l^2c^{\star 2} + 2U_{23}klb^{\star}c^{\star} + 2U_{13}hka^{\star}c^{\star} + 2U_{12}hka^{\star}b^{\star})$

TABLE 3

HYDROGEN ATOM COORDINATES (X 10^4) AND ISOTROPIC TEMPERATURE FACTORS (Å^2 X 10^3)

	x/a	*y/b*	*z/c*	*U*
H(12)	−667	2549	937	190(15)
H(13)	−891	4419	−231	190(15)
H(14)	187	4919	−2189	190(15)
H(15)	1378	3564	−2901	190(15)
H(16)	1520	1737	−1768	190(15)
H(22)	3239	3171	5421	190(15)
H(23)	3588	1193	6535	190(15)
H(24)	5107	36	6970	190(15)
H(25)	6297	603	6414	190(15)
H(26)	6067	2515	5260	190(15)
H(32)	−130	1438	2924	190(15)
H(33)	−2008	2652	3129	190(15)
H(34)	−2545	4585	2313	190(15)
H(35)	−1232	5288	1271	190(15)
H(36)	653	4103	1044	190(15)
H(42)	5009	2269	1330	190(15)
H(43)	6859	1083	1173	190(15)
H(44)	7300	172	2683	190(15)
H(45)	5929	519	4269	190(15)
H(46)	4052	1707	4475	190(15)

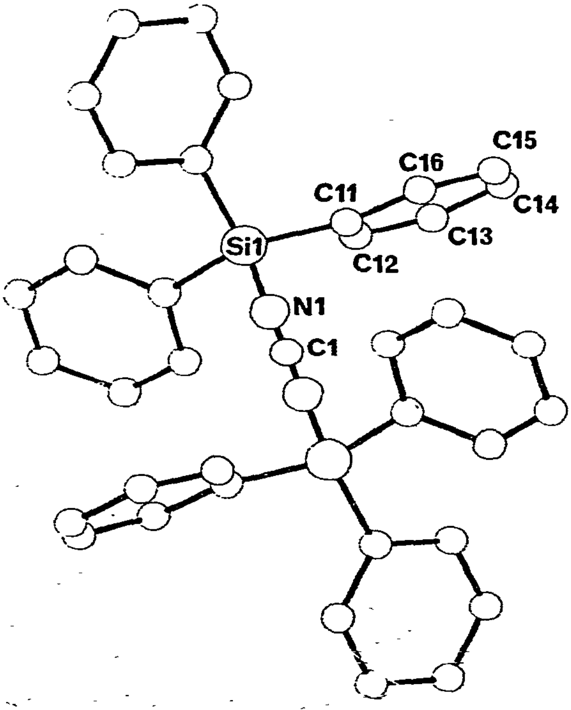

Fig. 1. Molecule 1 of $(Ph_3SiN)_2C$, with unique atoms labelled.

TABLE 4

BOND LENGTHS (Å)

Si(1)—N(1)	1.728(33)	Si(3)—N(3)	1.671(28)
Si(2)—N(2)	1.686(29)	Si(4)—N(4)	1.700(27)
Si(1)—C(11)	1.838(17)	Si(3)—C(31)	1.846(17)
Si(2)—C(21)	1.878(18)	Si(4)—C(41)	1.820(18)
N(1)—C(1)	1.120(33)	N(3)—C(3)	1.206(32)
N(2)—C(2)	1.163(29)	N(4)—C(3)	1.167(33)
C(11)—C(16)	1.412(21)	C(31)—C(36)	1.414(22)
C(11)—C(12)	1.397(18)	C(31)—C(32)	1.351(19)
C(12)—C(13)	1.392(19)	C(32)—C(33)	1.417(20)
C(13)—C(14)	1.398(21)	C(33)—C(34)	1.368(21)
C(14)—C(15)	1.370(21)	C(34)—C(35)	1.345(24)
C(15)—C(16)	1.375(20)	C(35)—C(36)	1.410(23)
C(21)—C(26)	1.395(20)	C(41)—C(46)	1.411(20)
C(21)—C(22)	1.379(20)	C(41)—C(42)	1.405(19)
C(22)—C(23)	1.448(23)	C(42)—C(43)	1.400(20)
C(23)—C(24)	1.327(22)	C(43)—C(44)	1.379(21)
C(24)—C(25)	1.310(22)	C(44)—C(45)	1.344(22)
C(25)—C(26)	1.414(22)	C(45)—C(46)	1.417(20)

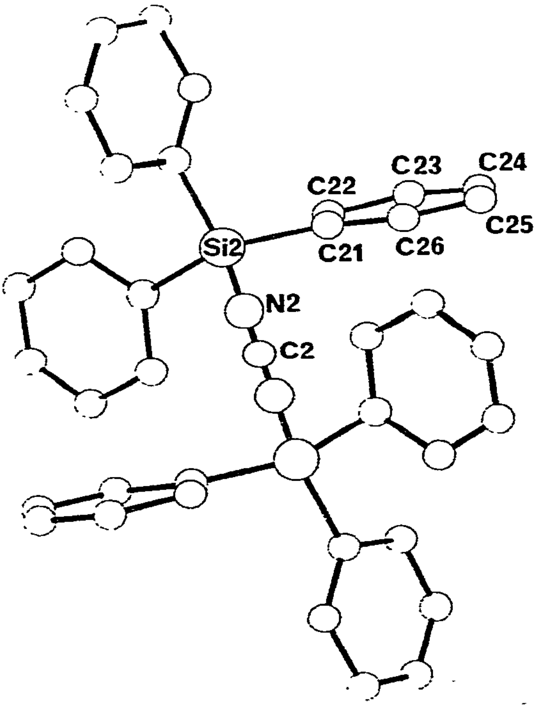

Fig. 2. Molecule 2 of $(Ph_3SiN)_2C$, with unique atoms labelled.

TABLE 5

BOND ANGLES (°)

C(11)—Si(1)—N(1)	107.6(6)	C(31)—Si(3)—N(3)	108.4(6)
C(21)—Si(2)—N(2)	107.7(6)	C(41)—Si(4)—N(4)	108.9(6)
C(11)—Si(1)—C(11′)	111.2(7)	C(31)—Si(3)—C(31′)	110.6(7)
C(21)—Si(2)—C(21′)	111.2(7)	C(41)—Si(4)—C(41′)	110.0(7)
C(12)—C(11)—Si(1)	121.4(13)	C(32)—C(31)—Si(3)	124.5(14)
C(16)—C(11)—Si(1)	121.9(14)	C(36)—C(31)—Si(3)	117.6(15)
C(16)—C(11)—C(12)	116.7(16)	C(36)—C(31)—C(32)	117.8(18)
C(13)—C(12)—C(11)	123.1(17)	C(33)—C(32)—C(31)	122.3(17)
C(14)—C(13)—C(12)	118.4(19)	C(34)—C(33)—C(32)	119.4(19)
C(15)—C(14)—C(13)	119.1(18)	C(35)—C(34)—C(33)	119.4(20)
C(16)—C(15)—C(14)	122.6(19)	C(36)—C(35)—C(34)	122.3(21)
C(15)—C(16)—C(11)	120.0(18)	C(35)—C(36)—C(31)	118.8(20)
C(22)—C(21)—Si(2)	119.9(15)	C(42)—C(41)—Si(4)	121.9(14)
C(26)—C(21)—Si(2)	119.6(15)	C(46)—C(41)—Si(4)	122.1(13)
C(26)—C(21)—C(22)	120.5(19)	C(46)—C(41)—C(42)	116.0(16)
C(23)—C(22)—C(21)	119.9(19)	C(43)—C(42)—C(41)	122.7(17)
C(24)—C(23)—C(22)	116.3(20)	C(44)—C(43)—C(42)	119.6(18)
C(25)—C(24)—C(23)	125.4(22)	C(45)—C(44)—C(43)	119.4(20)
C(26)—C(25)—C(24)	121.0(21)	C(46)—C(45)—C(44)	122.6(19)
C(25)—C(26)—C(21)	116.9(19)	C(45)—C(46)—C(41)	119.7(16)

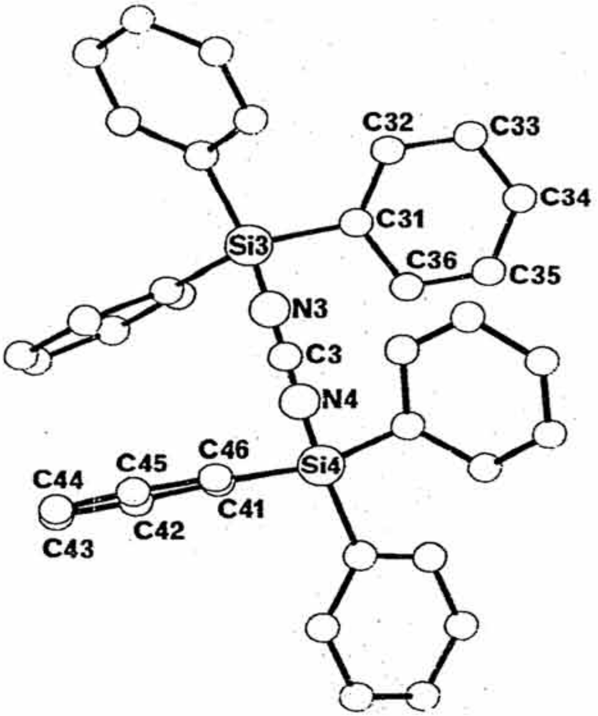

Fig. 3. Molecule 3 of $(Ph_3SiN)_2C$, with unique atoms labelled.

Discussion

Molecules 1 and 2 possess point group symmetry $\bar{3}$ (S_6), but molecule 3 possesses only 3 (C_3) symmetry. All Si—N=C=N—Si units lie along crystallographic threefold axes, and hence are constrained to be linear; the first two necessarily adopt the staggered conformation of carbon atoms bonded to silicon, and this conformation is also found in the third molecule. The triphenylsilicon moieties adopt the usual propeller conformation; in molecules 1 and 2 propellers of opposite hand have been combined to give molecules of exact $\bar{3}$ symmetry, but in molecule 3 two propellers of the same hand have been combined to give a molecule of approximately symmetry 32 (D_3). Taking the multiplicities of the special positions into account, the crystal thus contains *d*, *meso*, and *l* conformers in the ratio 1/2/1, exactly consistent with a random distribution and restricted rotation about the Si—C bonds. The C—Si—C angles (mean 110.8(6)°) are consistently slightly larger than the C—Si—N angles (mean 108.2(6)°), presumably a consequence of H···H repulsions between the *ortho* hydrogen atoms. The mean Si—C distance of 1.846(20) Å is not significantly different from the values in Ph_3SiNCS [6] 1.851(4) Å and in Ph_3SiNNN [11] 1.85(1) Å.

The linear Si—N=C=N—Si skeleton, in contrast to the aryl and germyl derivatives, and the short Si—N and N—C bond lengths (compared with N—C 1.21(1) aryl [3,4] and 1.184(8) germyl [5]) are consistent with delocalisation of nitrogen lone pair and N—C antibonding π electrons into the vacant silicon 3*d* orbitals. In view of the relatively large temperature factors and the probability of a low frequency large amplitude Si—N—C bending vibration, it is also possible that some of the apparent shortening of the Si—N and N—C bonds may be a vibrational averaging effect. The considerable thermal motion also plausibly accounts for the relatively high *R* index obtained. Apart from the conformational differences, there are no significant differences in the bond lengths and angles in the three crystallographically independent molecules, and no unusually short intra- or intermolecular contacts.

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