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THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIPHENYLSILICON ISOTHIOCYANATE

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Summary

The structure of Ph_3SiNCS has been determined by single crystal X-ray diffraction, and refined to $R = 0.055$ for 2841 diffractometer data. The crystals are monoclinic, $P2_1/c$, with $a = 9.402(8)$, $b = 18.735(16)$, $c = 11.350(9)$ Å, $\beta = 118.98(2)°$, and $Z = 4$. The structure consists of isolated molecules, with one molecule in the asymmetric unit. Some mean bond lengths and angles are: Si—N, 1.735(5); Si—C, 1.851(4); N—C, 1.156(4); C—S, 1.562(4); C—C, 1.381(8) Å; C—Si—N, 106.3(8); C—Si—C, 112.4(6); Si—N—C, 170.7(2); and N—C—S, 178.9(3)°.

Introduction

As part of our study of the molecular structures of silyl and organotin pseudohalides by X-ray and electron diffraction, we have determined the crystal structure of triphenylsilyl isothiocyanate. The crystal structures of the trimethyltin [1] and triphenyltin [2] analogues can be considered to be intermediate between structures based on tetrahedrally coordinated tin (NC_3) and on trigonal bipyramidal coordination (NC_3S), the extra Sn· · ·S interactions giving rise to =S· · ·Sn—N=C=S· · ·Sn— chains bent only at sulphur. The triphenyltin derivative is closer to idealised five coordination geometry, with Sn—N, 2.22(5); Sn· · ·S, 2.92(1) Å and C—Sn—N, 91.7(1.3)°. In contrast, in the structure reported here we find isolated Ph_3SiNCS molecules, with no short Si· · ·S interactions.

Experimental

Preparation

Ph_3SiBr was prepared by titrating bromine with Ph_3SiH in carbon tetrachloride; after removal of HBr, excess bromine and solvent, the product was dissolved in Na-dried benzene, excess dry AgNCS added, and the mixture refluxed under nitrogen. We find that this is a very convenient procedure for preparing silyl derivatives uncontaminated by hydrolysis products. Colourless crystals were obtained by slow evaporation of the benzene solution, and mounted in Lindemann glass capillary tubes.

Data collection

Intensities were determined on a Stoe Stadi-2 two-circle diffractometer (layers $0kl$ to $9kl$ and $h0l$ to $h23l$ inclusive) with Mo-K_α radiation (λ 0.71069 Å) and graphite crystal monochromator, from two crystals of approximate dimensions 0.20×0.19×0.14 mm and 0.23×0.52×0.44 mm respectively. The data were collected in an approximately 'constant count' mode; where a prescan indicated that the count could not be achieved within a specified time, the reflexion was ignored. A stationary background — omega scan — stationary background technique was employed, with variable reflexion width, and with the background measurement time proportional to the step measurement time. A total of 6876 reflexions was measured, of which 692 were rejected because the net count was less than 3σ based on counting statistics, because of background imbalance, or because of peak centering errors. Lorentz, polarisation and absorption corrections were applied, and interlayer scale factors obtained by a linear least-squares analysis of common reflexions; averaging equivalent reflexions led to 2841 unique observed reflexions. Unit cell dimensions were obtained by a least-squares fit to the median omega values for 319 $h0l$ and $0kl$ reflexions.

Crystal data

$C_{19}H_{15}SiNS$, mol. wt. 317.5, monoclinic, a = 9.402(8), b = 18.735(16), c = 11.350(9) Å, β = 118.98(2)°, U = 1749 Å^3, μ(Mo-K_α) 2.08 cm^{-1}, d_c 1.21 g cm^{-3} for Z = 4. Systematic absences: $0k0$ $k \neq 2n$; $h0l$, $l \neq 2n$. These uniquely determine the space group as $P2_1/c$. All the atoms occupy four-fold general positions of the set $\pm$ (x, y, z; x, ½ — y, ½ + z); the asymmetric unit is one formula unit.

Structure solution and refinement

The structure was solved by multisolution sigma-2 refinement, all 22 non-hydrogen atoms being located in the best E-map. The structure was refined by full-matrix least-squares with the final weighting scheme $w = \Sigma[\sigma^2(N) + 0.001\, N^2]^{-1}/[2.81 + |F_o| + 0.00991\, F_o^2]$, where N is the net peak count, and the summation is over equivalent reflexions. The hydrogen atoms were constrained to lie on the external bisectors of the CCC angles, with C—H 1.08 Å. In the final cycles a total of 215 parameters were varied independently, including isotropic temperature factors for the hydrogen atoms, anisotropic temperature factors for the remaining atoms, and a secondary extinction coefficient which refined to the value $10^5\, Q_o r^*$ 4(2) cm^{-1} [3]. A bonded hydrogen atom scattering factor was employed [4], with complex neutral atom scattering factors for the remaining atoms [5,6]. The refinement converged to R_w (= $\Sigma w^{1/2} \cdot |F_o - F_c| / \Sigma w^{1/2} \cdot |F_o|$) 0.064 with a corresponding unweighted index R 0.055. The final difference electron density synthesis had no peaks

TABLE 1

ATOM COORDINATES ($\times 10^4$)

	x/a	y/b	z/c
Si (1)	3896 (1)	3517	325 (1)
N (1)	2485 (3)	4149 (1)	−691 (3)
C (1)	1402 (3)	4525 (1)	−1320 (3)
S (1)	−39 (1)	5042 (1)	−2170 (1)
C (11)	5431 (3)	3471 (1)	−251 (2)
C (12)	6350 (3)	2860 (2)	−40 (3)
C (13)	7533 (4)	2831 (2)	−442 (4)
C (14)	7797 (5)	3423 (3)	−1044 (5)
C (15)	6909 (6)	4023 (3)	−1254 (4)
C (16)	5731 (4)	4053 (2)	−861 (3)
C (21)	2736 (3)	2677 (1)	60 (2)
C (22)	1461 (3)	2504 (2)	−1201 (3)
C (23)	588 (3)	1881 (2)	−1412 (3)
C (24)	966 (4)	1425 (2)	−362 (4)
C (25)	2237 (4)	1574 (2)	893 (3)
C (26)	3109 (3)	2198 (1)	1105 (3)
C (31)	4784 (3)	3833 (1)	2082 (2)
C (32)	3892 (3)	3808 (2)	2766 (3)
C (33)	4533 (4)	4035 (2)	4071 (3)
C (34)	6088 (4)	4297 (2)	4738 (3)
C (35)	6985 (4)	4352 (2)	4071 (3)
C (36)	6349 (3)	4112 (2)	2762 (3)

TABLE 2

ANISOTROPIC VIBRATIONAL AMPLITUDES ($Å^2 \times 10^3$)[a]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si (1)	52	52	58	1	26	−1
N (1)	72 (2)	69 (2)	80 (2)	14 (1)	28 (1)	12 (1)
C (1)	62 (2)	63 (2)	67 (2)	11 (1)	26 (1)	−7 (1)
S (1)	70 (1)	110 (1)	140 (1)	56 (1)	21 (1)	17 (1)
C (11)	64 (2)	61 (2)	58 (1)	−11 (1)	32 (1)	−12 (1)
C (12)	73 (2)	77 (2)	87 (2)	−9 (2)	44 (2)	0 (2)
C (13)	84 (2)	114 (3)	122 (3)	−29 (2)	59 (2)	4 (2)
C (14)	114 (3)	135 (4)	148 (4)	−41 (3)	99 (3)	−35 (3)
C (15)	144 (4)	117 (3)	131 (3)	−20 (3)	104 (3)	−39 (3)
C (16)	101 (2)	78 (2)	90 (2)	−10 (2)	65 (2)	−21 (2)
C (21)	50 (1)	60 (2)	59 (1)	−7 (1)	29 (1)	−4 (1)
C (22)	57 (1)	73 (2)	65 (2)	−7 (1)	22 (1)	−3 (1)
C (23)	58 (2)	84 (2)	82 (2)	−22 (2)	22 (2)	−13 (2)
C (24)	79 (2)	71 (2)	105 (3)	−23 (2)	56 (2)	−24 (2)
C (25)	103 (2)	65 (2)	83 (2)	−7 (2)	59 (2)	−16 (2)
C (26)	79 (2)	62 (2)	60 (2)	−5 (1)	33 (1)	−14 (1)
C (31)	54 (1)	46 (1)	63 (1)	−3 (1)	32 (1)	1 (1)
C (32)	73 (2)	66 (2)	84 (2)	−12 (1)	49 (2)	−8 (1)
C (33)	102 (2)	82 (2)	92 (2)	−18 (2)	66 (2)	−8 (2)
C (34)	97 (2)	96 (2)	72 (2)	−24 (2)	40 (2)	10 (2)
C (35)	63 (2)	107 (3)	87 (2)	−37 (2)	30 (2)	−5 (2)
C (36)	57 (2)	78 (2)	78 (2)	−17 (1)	35 (1)	−4 (1)

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

TABLE 3

HYDROGEN ATOM COORDINATES AND ISOTROPIC VIBRATIONAL AMPLITUDES (Å^2 X 10^3)

	x/a	*y/b*	*z/c*	*U*
H (12)	6148 (3)	2402 (2)	439 (3)	87 (9)
H (13)	8240 (4)	2351 (2)	−286 (4)	144 (14)
H (14)	8720 (5)	3404 (3)	−1348 (5)	167 (17)
H (15)	7121 (6)	4480 (3)	−1729 (4)	125 (12)
H (16)	5031 (4)	4536 (2)	−1030 (3)	104 (10)
H (22)	1147 (3)	2865 (2)	−2033 (3)	88 (9)
H (23)	−390 (3)	1754 (2)	−2404 (3)	92 (9)
H (24)	262 (4)	944 (2)	−520 (4)	104 (10)
H (25)	2554 (4)	1204 (2)	1712 (3)	113 (11)
H (26)	4095 (3)	2316 (1)	2097 (3)	87 (9)
H (32)	2664 (3)	3604 (2)	2254 (3)	97 (10)
H (33)	3812 (4)	4007 (2)	4576 (3)	116 (11)
H (34)	6610 (4)	4458 (2)	5778 (3)	127 (12)
H (35)	8186 (4)	4584 (2)	4576 (3)	114 (11)
H (36)	7073 (3)	4142 (2)	2260 (3)	85 (9)

TABLE 4

BOND LENGTHS (Å)

Si (1)—N (1)	1.735 (5)	C (21)—C (26)	1.390 (5)
Si (1)—C (11)	1.852 (5)	C (21)—C (22)	1.388 (4)
Si (1)—C (21)	1.854 (5)	C (22)—C (23)	1.379 (5)
Si (1)—C (31)	1.846 (4)	C (23)—C (24)	1.367 (5)
N (1)—C (1)	1.156 (4)	C (24)—C (25)	1.373 (5)
C (1)—S (1)	1.562 (4)	C (25)—C (26)	1.380 (5)
C (11)—C (16)	1.392 (5)	C (31)—C (36)	1.391 (4)
C (11)—C (12)	1.384 (5)	C (31)—C (32)	1.393 (4)
C (12)—C (13)	1.393 (5)	C (32)—C (33)	1.369 (5)
C (13)—C (14)	1.386 (7)	C (33)—C (34)	1.371 (5)
C (14)—C (15)	1.350 (7)	C (34)—C (35)	1.383 (6)
C (15)—C (16)	1.381 (6)	C (35)—C (36)	1.381 (5)

TABLE 5

BOND ANGLES (°)

C (11)—Si (1)—N (1)	105.8 (2)	C (22)—C (21)—Si (1)	120.8 (3)
C (21)—Si (1)—N (1)	105.7 (2)	C (26)—C (21)—Si (1)	121.6 (3)
C (31)—Si (1)—N (1)	107.4 (2)	C (26)—C (21)—C (22)	117.6 (3)
C (21)—Si (1)—C (11)	113.6 (2)	C (23)—C (22)—C (21)	121.4 (4)
C (31)—Si (1)—C (11)	111.9 (2)	C (24)—C (23)—C (22)	119.7 (4)
C (31)—Si (1)—C (21)	111.8 (2)	C (25)—C (24)—C (23)	120.3 (4)
C (1)—N (1)—Si (1)	170.7 (2)	C (26)—C (25)—C (24)	119.9 (4)
S (1)—C (1)—N (1)	178.9 (3)	C (25)—C (26)—C (21)	121.0 (4)
C (12)—C (11)—Si (1)	120.3 (3)	C (32)—C (31)—Si (1)	120.8 (3)
C (16)—C (11)—Si (1)	121.3 (3)	C (36)—C (31)—Si (1)	121.6 (3)
C (16)—C (11)—C (12)	118.3 (4)	C (36)—C (31)—C (32)	117.6 (3)
C (13)—C (12)—C (11)	120.4 (4)	C (33)—C (32)—C (31)	121.7 (4)
C (14)—C (13)—C (12)	119.5 (5)	C (34)—C (33)—C (32)	120.1 (4)
C (15)—C (14)—C (13)	120.7 (4)	C (35)—C (34)—C (33)	119.7 (4)
C (16)—C (15)—C (14)	120.0 (5)	C (36)—C (35)—C (34)	120.2 (4)
C (15)—C (16)—C (11)	121.1 (4)	C (35)—C (36)—C (31)	120.7 (4)

TABLE 6

SELECTED INTRAMOLECULAR NON-BONDED DISTANCES (Å)

H (15)—H (34)	2.630	Si (1)—C (36)	2.834
N (1)—H (16)	2.701	Si (1)—C (16)	2.837
N (1)—S (1)	2.718	Si (1)—C (26)	2.841
C (11)—H (36)	2.797	N (1)—C (11)	2.862
N (1)—H (22)	2.800	N (1)—C (21)	2.862
Si (1)—C (12)	2.818	Si (1)—C (1)	2.882
Si (1)—C (32)	2.825	N (1)—C (31)	2.887
Si (1)—C (22)	2.829		

TABLE 7

SELECTED INTERMOLECULAR NON-BONDED DISTANCES (Å)

H (24)—H (35)	2.237	C (12)—H (26)	2.913
C (25)—H (33)	2.786	H (24)—C (35)	2.937
C (24)—H (33)	2.829	C (16)—H (25)	2.961

above 0.5 e Å^{-3}. The results of the final least-squares cycle are given in Tables 1-3, with the resulting interatomic distances and angles in Tables 4-7. Figure 1 shows the molecular geometry, and Fig. 2 the packing of the molecules. Lists of observed and calculated structure factors may be obtained from the authors.

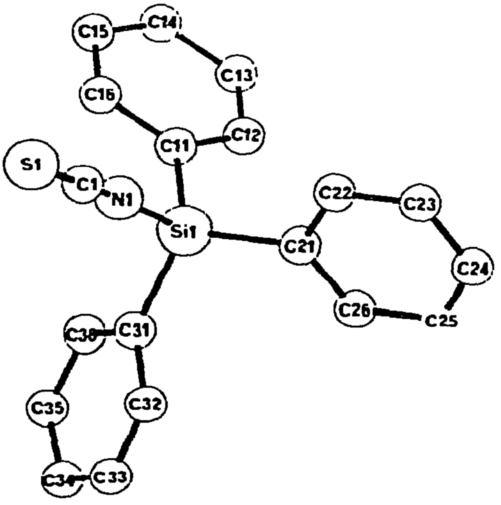

Fig. 1. The molecule of Ph_3SiNCS.

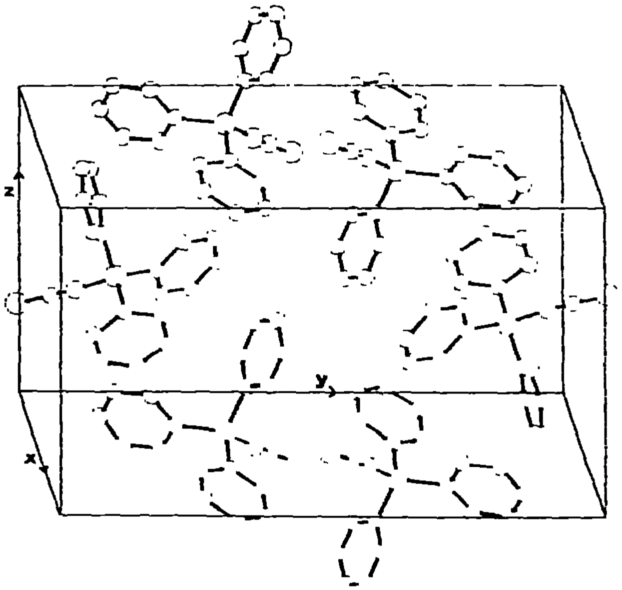

Fig. 2. One unit cell of Ph_3SiNCS, illustrating the molecular packing.

Discussion

The triphenylsilyl group adopts the propeller conformation found in other triphenylsilyl derivatives; the C—Si—C angles are all a little greater than the tetrahedral angle, and the N—Si—C angles a little less, presumably a consequence of H· · ·H repulsions between the *ortho* hydrogen atoms. There is little difference in the Si—C(Ph) bond lengths reported for triphenylsilyl derivatives; Ph_3SiNCS, 1.851(4); $Ph_3SiC(O)Me$, 1.864(8) [7]; $Ph_3SiC(N_2)Ph$, 1.865(16) [8]; $Ph_3SiC(H)(Ph)OC(O)C_6H_4Br$, 1.86(1)[9] and Ph_4Si, 1.872(7) Å [10]. The small increase along this series is consistent with the decrease in electronegativity of the fourth substituent.

Electron diffraction investigations of H_3SiNCS in the vapour phase [11] indicate that this molecule has a potential energy minimum at the linear conformation of the Si—N—C—S chain, but with a low frequency large amplitude Si—N—C bending vibration; very little energy would be required to change the Si—N—C angle. Thus the Si—N—C angle of 170.7(2)° found here is not inconsistent with a linear potential energy minimum for this molecule also; using the potential function derived for H_3SiNCS, about 0.9 kJ mol^{-1} would be required for a 10° deformation; this could easily be accomodated in minimising the crystal packing energy. The C—S lengths are similar in H_3SiNCS [1.563(6)] and Ph_3SiNCS [1.562(4) Å], but there are significant differences in the N—C [1.197(7) and 1.156(4) Å] and Si—N distances [1.704(6) and 1.735(5) Å respectively]; this may be caused by N· · ·H repulsions.

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References

1 R.A. Forder and G.M. Sheldrick, J. Organometal. Chem . 21 (1970) 115.
2 A.M. Domingos and G.M. Sheldrick, J. Organometal. Chem., 67 (1974) 257.
3 A.C. Larson, in F.R. Ahmed (Ed.), Crystallographic Computing, Munksgaard, Copenhagen, 1970.
4 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
5 D.T. Cromer and J.B. Mann, Acta Crystallogr. Part A, 24 (1968) 321.
6 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.
7 P.C. Chieh and J. Trotter, J. Chem. Soc. A, (1969) 1778.
8 C. Glidewell and G.M. Sheldrick, J. Chem. Soc. Dalton, (1972) 2409.
9 K.T. Black and H. Hope, J. Amer. Chem. Soc., 93 (1971) 3053.
10 C. Glidewell and G.M. Sheldrick, J. Chem. Soc. A, (1971) 3127.
11 C. Glidewell, A.G. Robiette and G.M. Sheldrick, Chem. Phys. Lett., 16 (1972) 526.