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THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIPHENYLSILYLTHIIRANE

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Summary

Triphenylsilylthiirane, crystallized from anhydrous pentane, has the cell dimensions: a 16.452(6), b 11.440(2), c 19.192(7) Å; β 105.39(3)°; V 3483(2) Å³; Z = 8; space group $C2/c$. The structure was solved by direct methods and refined anisotropically down to R = 0.094. The triphenylsilyl group has a propeller conformation. The thiirane ring shows a significant thermal motion.

Introduction

We are engaged in a systematic study of the chemical properties, stereochemical stability and spectroscopic behaviour of organometallic derivatives of Si, Sn and Pb. In particular we are examining the influence exercised by the nature of the organic groups on the positional equilibrium around the metal atom. Such studies are given added interest by the fact that these organometallic compounds are widely used as intermediates in organic synthesis. Recently we have been concerned with the synthesis of organometallic derivatives containing small rings [1,2]. The chemical and physico-chemical properties of oxiranes bonded to Sn and Pb and the influence of the metal in the epoxidation of corresponding vinyl derivatives have been studied. The reaction of oxiranes with 3-methylbenzothiazole-2-thiene to give the corresponding thiiranes [3] has also been studied and has given the first metal-substituted thiirane. Within this context we now report the crystal and molecular structure of the title compound in order to contribute to knowledge of the conformation of this type of compound.

Experimental

Collection and reduction of X-ray data

The compound was synthesized as described previously [3] and recrystallized from anhydrous pentane.

A prismatic colourless crystal with dimensions of 0.14, 0.12, 0.33 mm was used for data collection. Preliminary cell parameters obtained by rotation and Weissenberg photographs were refined by a least-squares treatment of $(\vartheta, \chi, \varphi)_{hkl}$ values of seventeen reflections measured on a Siemens single-crystal diffractometer at room temperature. Cell dimensions and crystal data are given in Table 1. A total of 3108 independent reflections were measured using the $\omega - 2\vartheta$ scan technique and Ni-filtered $\text{Cu-K}\alpha$ radiation. 1697 of these were not used in the structure analysis since their intensities were less than twice their standard deviations (from counting statistics). During the refinement 35 of the remaining reflections were seriously affected by large non systematic errors, and were omitted in the last cycles of refinement. No absorption correction was applied.

Solution and refinement of the structure

The structure was solved by the multiresolution and phase permutation technique through the SHELX system [4]. All non-hydrogen atoms of the structure were located from the E map calculated with phases obtained by tangent formula refinement. A structure factor calculation carried out at this stage gave $R = 0.29$. The structure was refined by blocked full-matrix least-squares cycles, first with isotropic and then with anisotropic thermal parameters; R was reduced to 0.102. At this stage the calculated positional parameters of the hydrogen atoms were included with C—H bond length of 1.08 Å. A few least-squares cycles were then carried out including hydrogen atoms blocked in the calculated positions with isotropic thermal parameters and final value of $R = 0.094$ was obtained. The weighting scheme used in the last cycles was $w = 1/\sigma^2(F_0)$ where $\sigma^2(F_0)$ were determined from counting statistics. The atomic coordinates with their standard deviations are given in Table 2 and in Table 3 thermal parameters are reported. A list of observed and calculated structure factors is available from the authors on request.

Atomic scattering factors were from ref. 5 for non-hydrogen atoms and from ref. 6 for hydrogen.

All the calculations were carried out on a CDC Cyber 76 computer of Consorzio Interuniversitario per la gestione del Centro di Calcolo Elettronico per

TABLE 1
CRYSTAL DATA FOR $\text{C}_{20}\text{H}_{18}\text{Si}$

a 16.452(6) Å	Monoclinic
b 11.440(2) Å	Space group $C2/c$
c 19.192(7) Å	$\text{Cu-K}\alpha$ radiation
β 105.39(3)°	μ 21.3 cm^{-1}
V 3482.6 Å ³	$Z = 8$
	D_{calc} 1.21 g cm^{-3}

TABLE 2

ATOMIC COORDINATES ($\times 10^4$ for Si, S, C and $\times 10^3$ for H atoms) WITH STANDARD DEVIATIONS IN PARENTHESES

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>		<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Si	1987(1)	4949(2)	583(1)	H(1)	428	577	74
S	3809(2)	4830(3)	1704(2)	H(2)	348	660	96
C(1)	3745(7)	5740(12)	968(7)	H(3)	314	413	39
C(2)	3218(7)	4787(11)	813(6)	H(4)	84	685	-13
C(3)	1623(6)	6362(7)	897(4)	H(5)	26	860	33
C(4)	1036(6)	7064(7)	437(5)	H(6)	75	915	160
C(5)	722(8)	8066(8)	697(7)	H(7)	179	791	246
C(6)	991(9)	8367(9)	1399(8)	H(8)	236	613	200
C(7)	1589(8)	7675(10)	1894(7)	H(9)	54	466	119
C(8)	1901(7)	6670(7)	1633(5)	H(10)	-3	303	173
C(9)	1569(4)	3695(6)	1007(4)	H(11)	68	112	188
C(10)	853(6)	3820(6)	1244(4)	H(12)	189	82	138
C(11)	525(6)	2907(8)	1540(5)	H(13)	249	245	89
C(12)	916(7)	1832(6)	1618(6)	H(14)	230	637	-62
C(13)	1614(7)	1682(8)	1364(7)	H(15)	184	618	-195
C(14)	1937(6)	2592(7)	1077(5)	H(16)	85	462	-251
C(15)	1614(4)	4840(5)	-423(4)	H(17)	42	316	-175
C(16)	1888(5)	5664(9)	-863(5)	H(18)	84	335	-44
C(17)	1616(6)	5564(9)	-1611(5)				
C(18)	1073(6)	4677(9)	-1926(5)				
C(19)	821(5)	3875(8)	-1502(4)				
C(20)	1073(5)	3969(6)	-762(4)				

TABLE 3

THERMAL PARAMETERS ($\times 10^3$) WITH STANDARD DEVIATIONS IN PARENTHESES

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si	74(1)	82(1)	74(1)	-3(1)	16(1)	-10(1)
S	135(3)	178(3)	131(3)	-10(2)	16(2)	7(2)
C(1)	114(8)	152(11)	169(12)	-16(8)	17(8)	44(8)
C(2)	108(7)	158(10)	96(7)	-34(7)	-1(6)	-1(6)
C(3)	132(7)	70(4)	86(6)	-20(4)	45(5)	-14(4)
C(4)	122(7)	77(5)	110(7)	-4(5)	47(6)	2(4)
C(5)	158(10)	74(5)	150(10)	15(5)	74(8)	12(6)
C(6)	156(10)	79(6)	162(11)	-22(6)	81(9)	-28(7)
C(7)	162(11)	105(7)	141(10)	-43(7)	78(9)	-56(7)
C(8)	135(8)	83(5)	105(7)	-27(5)	47(6)	-24(5)
C(9)	77(4)	73(4)	73(4)	9(3)	5(3)	-7(3)
C(10)	93(5)	62(4)	91(5)	10(3)	29(4)	4(3)
C(11)	102(6)	90(5)	111(7)	6(4)	37(5)	10(4)
C(12)	131(8)	66(5)	128(8)	-7(4)	10(6)	18(5)
C(13)	116(8)	73(5)	177(10)	23(5)	31(7)	13(5)
C(14)	106(6)	81(5)	125(8)	23(4)	41(5)	-4(5)
C(15)	73(4)	72(4)	80(5)	7(3)	24(4)	-9(3)
C(16)	87(5)	98(5)	87(6)	-9(4)	25(4)	0(4)
C(17)	102(6)	117(7)	90(6)	-4(5)	34(5)	8(5)
C(18)	95(6)	124(7)	81(6)	20(5)	19(5)	-3(5)
C(19)	76(5)	104(6)	86(6)	4(4)	7(4)	-6(4)
C(20)	78(4)	75(4)	82(5)	7(3)	21(4)	-8(3)

Temperature factors are of the form: $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$

l'Italia Nord Orientale, Casalecchio, Bologna, with programs written by the authors and with the system SHELX-76 devised by Dr. Sheldrik of the University of Cambridge, U.K.

Results

Figure 1 shows a drawing of the structure in the plane of the three phenyl carbons attached to silicon with the arbitrary numbering scheme used in the analysis. Bond distances and angles and some torsional angles, together with their e.s.d.'s calculated with the full covariance matrix, are given in Table 4. Table 5 lists some least-squares planes and the dihedral angles between them.

The geometry of the thiirane ring has already been determined in the gas phase [7] and in the solid state [8]. In our compound the S—C and C—C bond distances are significantly shortened, and this can be associated with the significant thermal motion of the thiirane ring. Thus in this case is not possible to discuss the effect of the triphenylsilyl substituent on the geometry of the small

TABLE 4
BOND DISTANCES (Å) AND ANGLES (deg.)

Si—C(2)	1.964(8)	C(9)—C(10)	1.397(7)
Si—C(3)	1.879(5)	C(9)—C(14)	1.390(6)
Si—C(9)	1.869(5)	C(10)—C(11)	1.366(7)
Si—C(15)	1.868(5)	C(11)—C(12)	1.377(8)
S—C(1)	1.735(8)	C(12)—C(13)	1.371(10)
S—C(2)	1.729(7)	C(13)—C(14)	1.352(8)
C(1)—C(2)	1.375(10)	C(15)—C(16)	1.417(7)
C(3)—C(4)	1.381(8)	C(15)—C(20)	1.379(6)
C(3)—C(8)	1.408(7)	C(16)—C(17)	1.391(7)
C(4)—C(5)	1.401(8)	C(17)—C(18)	1.381(9)
C(5)—C(6)	1.347(9)	C(18)—C(19)	1.361(8)
C(6)—C(7)	1.415(11)	C(19)—C(20)	1.373(7)
C(7)—C(8)	1.405(9)		
C(2)—Si—C(3)	114.0(3)	C(3)—C(8)—C(7)	120.7(7)
C(2)—Si—C(9)	107.8(3)	Si—C(9)—C(10)	120.6(3)
C(2)—Si—C(15)	105.3(3)	Si—C(9)—C(14)	122.5(4)
C(3)—Si—C(9)	109.6(2)	C(10)—C(9)—C(14)	116.8(5)
C(3)—Si—C(15)	110.2(2)	C(9)—C(10)—C(11)	121.6(4)
C(9)—Si—C(15)	109.9(2)	C(10)—C(11)—C(12)	120.2(5)
C(1)—S—C(2)	46.8(3)	C(11)—C(12)—C(13)	118.9(6)
S—C(1)—C(2)	66.4(5)	C(12)—C(13)—C(14)	120.4(5)
Si—C(2)—S	119.7(5)	C(9)—C(14)—C(13)	122.0(6)
Si—C(2)—C(1)	121.8(7)	Si—C(15)—C(16)	120.1(4)
S—C(2)—C(1)	66.8(4)	Si—C(15)—C(20)	122.0(4)
Si—C(3)—C(4)	121.6(4)	C(16)—C(15)—C(20)	117.9(5)
Si—C(3)—C(8)	119.4(5)	C(15)—C(16)—C(17)	119.6(5)
C(4)—C(3)—C(8)	118.8(6)	C(16)—C(17)—C(18)	120.4(6)
C(3)—C(4)—C(5)	120.6(6)	C(17)—C(18)—C(19)	119.9(6)
C(4)—C(5)—C(6)	120.7(7)	C(18)—C(19)—C(20)	120.6(5)
C(5)—C(6)—C(7)	121.0(6)	C(15)—C(20)—C(19)	121.6(5)
C(6)—C(7)—C(8)	118.2(7)		
C(3)—Si—C(2)—S	59.7	C(9)—Si—C(2)—C(1)	−141.9
C(3)—Si—C(2)—C(1)	−20.0	C(15)—Si—C(2)—S	−179.5
C(9)—Si—C(2)—S	−62.2	C(15)—Si—C(2)—C(1)	100.8

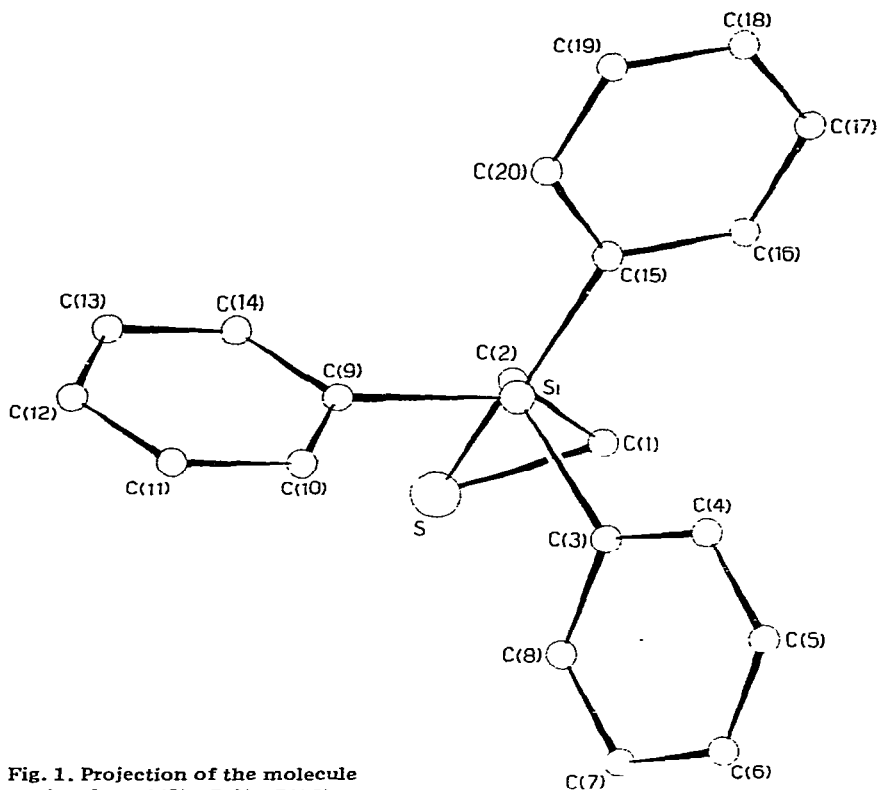


Fig. 1. Projection of the molecule on the plane C(3)—C(9)—C(15).

TABLE 5. ANALYSIS OF THE PLANARITY

Equations of least-squares planes in the form $lX + mY + nZ = p$ where X , Y and Z are related to the crystallographic orthogonal axes by the transformation matrix

$$\|10 \cos \beta / 010 / 00 \sin \beta\|$$

Distances ($\text{\AA} \times 10^3$) of atoms from the planes are given in square brackets

Plane A: C(3)—C(8)

$$0.8187X + 0.5413Y - 0.1916Z = 5.4321$$

[C(3) 1(9), C(4) 0(9), C(5) -3(13), C(6) 4(14), C(7) -1(13), C(8) -1(11), Si -141(2)]

Plane B: C(9)—C(14)

$$-0.3404X - 0.2531Y - 0.9056Z = -3.4558$$

[C(9) -6(6), C(10) 3(8), C(11) 6(9), C(12) -18(11), C(13) 16(13), C(14) 3(9), Si 34(2)]

Plane C: C(15)—C(20)

$$-0.8145X + 0.5801Y - 0.0075Z = 0.8829$$

[C(15) -3(7), C(16) 0(9), C(17) -2(10), C(18) 11(10), C(19) -14(9), C(20) 8(7), Si -27(2)]

Plane D: S—C(1)—C(2)

$$-0.8156X + 0.5262Y + 0.2408Z = -0.7363$$

[Si 1.551(2)]

Plane E: C(3)—C(9)—C(15)

$$0.9603X - 0.0271Y + 0.2778Z = 2.3895$$

[Si 0.611(2)]

Angles between planes

$$A \wedge E = 44.1^\circ$$

$$B \wedge E = 124.9^\circ$$

$$C \wedge E = 143.1^\circ$$

$$D \wedge E = 136.9^\circ$$

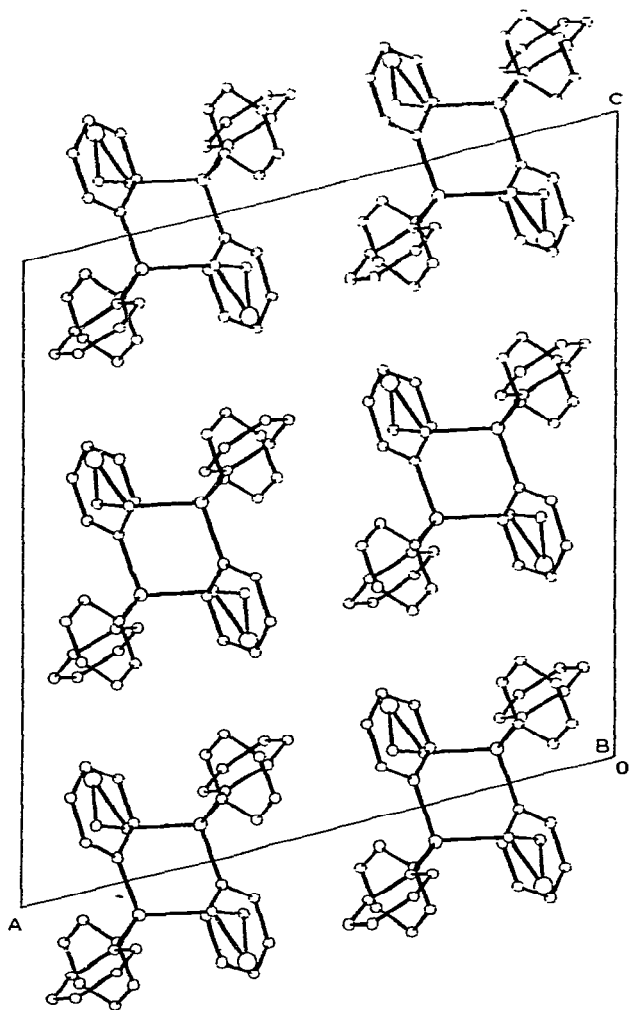


Fig. 2. Projection of the structure along $[0\ 1\ 0]$.

ring. The internal angles, which are slightly affected by thermal motion [9], agree with the gas phase values.

As usually found in similar structures, the triphenylsilyl group has a propeller conformation, with the phenyl planes oriented so as to minimize intramolecular interactions. Bond lengths involving silicon are as expected. The Si—C(2) bond forms an angle of 5.2° with the C(3)—C(9)—C(15) plane in the direction of the ring which is not involved in steric interactions with the thirane ring.

The packing, shown in Fig. 2, is consistent with Van der Waals interactions.

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