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GROUP IVB ORGANOMETALLIC SULPHIDES

VI*. CRYSTAL STRUCTURE OF TRIPHENYLGERMANIUM *p*-TERT-BUTYLPHENYL MERCAPTIDE

M.E. CRADWICK R.D. TAYLOR and J.L. WARDELL
Department of Chemistry, University of Aberdeen, Old Aberdeen, AB9 2UE (Great Britain)

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Summary

The crystal structure of $Ph_3GeSC_6H_4$-t-Bu-*p* has been determined using three dimensional X-ray diffractometer data by least squares methods, the final *R* being 0.069 for 2711 independent reflections. The crystals are monoclinic $P2_1/C$ *a* 13.64, *b* 9.28, *c* 19.62 Å, *β* 106.03°, *Z* 4. The compound is isostructural with its tin analogue, with a Ge—S bond length of 2.229 Å.

Introduction

Bonding between Group IVB elements and sulphur in organometallic sulphides, such as $R_{4-n}M(SR')_n$, $(R_3M)_2S$, $(R_2MS)_3$, and $(RM)_4S_6$ where $n = 1 \rightarrow 4$; M = Ge, Sn, Pb; R and R′ = alkyl or aryl, is the subject of argument. Particular controversy has concerned the suggestion of a $d_\pi \leftarrow p_\pi$ component in the metal—sulphur bond [2]. Various techniques, mainly spectroscopic, have been employed to investigate such bonding [2]; however only a few M—S bond lengths have been obtained from crystal structure data [3 - 8]. Among the crystal structures determined have been those of $Ph_3SnSPbPh_3$ [3] and $(Ph_2SnS)_3$ [4] (containing the Sn—S—M groupings), $Ph_3SnSC_6H_4$-t-Bu-*p* [5], $Me_3SnSC(S)NMe_2$ [6] and $Me_2ClSnS(S)CNMe_2$ [7] (containing the Sn—C—S grouping) and $(MeGe)_4S_6$ [8], which contains the Ge—S—Ge grouping. No crystal structure of an organogermanium mercaptide has as yet been published. In this paper, the structure of triphenylgermanium *p*-tert-butylphenyl mercaptide, $Ph_3GeSC_6H_4$-t-Bu-*p*, is reported.

Experimental

Triphenylgermanium *p*-tert-butylphenyl mercaptide was prepared from the metathetic reaction of triphenylgermanium bromide and *p*-tert-butylthio-

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[*] For Part V see ref. [1].

phenol in the presence of triethylamine. It was recrystallised from ethanol, m.p. 106 - 107.5°.

Crystal data

$C_{28}H_{28}SGe$, mol. wt. = 469.2, monoclinic, a 13.64(1) *, b 9.28(1), c 19.62(2) Å, β 106.03(4)°, U 2387 Å^3, d_c 1.31 for Z 4, $F(000)$ 976, Mo-K_α ($\lambda = 0.7107$ Å). Systematic absences: $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$ uniquely define the space group as $P2_1/c$.

The crystal chosen had a cross-section of dimensions (0.14 × 0.40) mm and was mounted about the b axis (0.70 mm) for data collection.

Intensity data for the layers $h0l$ to $h11l$ inclusive were collected on a Hilger and Watts, Y190 automatic diffractometer using an identical procedure to that previously described [5] giving a total of 2719 unique observed reflections. [A reflection was classified as observed if $I \geqslant 3\sigma(I)$].

The unit cell parameters were obtained from a least squares fit of 29 lines in a powder photograph taken with a Grandolf camera and Co-K_α radiation.

Structure solution and refinement

Since the structure of $Ph_3GeSC_6H_4$-t-Bu-*p* was thought to be similar to that of its tin analogue, the coordinates of the tin, sulphur and carbon atoms of $Ph_3SnSC_6H_4$-t-Bu-*p* were used initially for the germanium, sulphur and carbon atoms in the least squares refinement. Block diagonal approximation** was used throughout the refinement with R converging at 0.098 for the isotropic model, after interlayer scaling. In the final stages of refinement anisotropic thermal parameters were used for germanium, sulphur and the terminal tert-butyl carbon atoms [C(26), C(27), C(28)], resulting in convergence at R 0.069. A weighting scheme of the form $W = 1/[1 + (F - b/a)^2]^{½}$ ($a = 40$, $b = 25$) was used and scattering factors for the neutral atoms were taken from the International Tables [9]. A final difference synthesis showed fluctuations in electron density between ± 0.5 e · Å^{-3}.

Positional, thermal parameters and a table of observed and calculated structure factors may be obtained from the authors.

Results and discussion

Intramolecular distances (Part A bonded, Part B, selected non-bonded) and bond angles are given in Tables 1 and 2. Fig. 1 shows a view of the molecule perpendicular to the plane containing C(7), C(13) and C(19).

The molecular and crystal structure of triphenylgermanium *p*-tert-butylphenyl mercaptide is essentially identical to the tin analogue [5].

The coordination of the germanium is approximately tetrahedral with

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* Throughout this paper the estimated standard deviation in parenthesis applies to the least significant digit.

** The computing programmes used were mainly those supplied by Dr. F.R. Ahmed and Collaborators, of the National Research Council of Canada, and adapted by Mr. J.S. Knowles of the Department of Computing, University of Aberdeen.

TABLE 1

INTRAMOLECULAR DISTANCES (Å)

A. Bonded					
Ge—S	2.229(2)		*C—CH$_3$ bonds*		
Ge—C(7)	1.925(7)	1.938^a	C(4)—C(25)	1.527(12)	1.545
Ge—C(13)	1.947(7)		C(25)—C(26)	1.577(14)	
Ge—C(19)	1.941(8)		C(25)—C(27)	1.538(15)	
S—C(1)	1.783(8)		C(25)—C(28)	1.539(14)	
Phenyl groups					
C(1)—C(2)	1.392(11)	1.388	C(7)—C(8)	1.388(10)	1.392
C(1)—C(6)	1.367(11)		C(7)—C(12)	1.412(11)	
C(2)—C(3)	1.408(12)		C(8)—C(9)	1.398(12)	
C(3)—C(4)	1.382(11)		C(9)—C(10)	1.384(13)	
C(4)—C(5)	1.377(11)		C(10)—C(11)	1.392(13)	
C(5)—C(6)	1.399(12)		C(11)—C(12)	1.375(13)	
C(13)—C(14)	1.389(11)	1.391	C(19)—C(20)	1.383(13)	1.389
C(13)—C(18)	1.381(12)		C(19)—C(24)	1.401(12)	
C(14)—C(15)	1.405(12)		C(20)—C(21)	1.414(14)	
C(15)—C(16)	1.375(14)		C(21)—C(22)	1.353(14)	
C(16)—C(17)	1.394(14)		C(22)—C(23)	1.366(15)	
C(17)—C(18)	1.404(13)		C(23)—C(24)	1.415(14)	
B. Selected non-bonded distances					
S—C(7)	3.47		S—C(19)	3.20	
S—C(13)	3.49		S—C(24)	3.29	

^{a}Mean values.

ranges of (100 - 113°) and (109 - 111°) for the S—Ge—C and C—Ge—C bond angles respectively. It seems likely that this distortion from regular tetrahedral geometry (greatest for the angle S—Ge—C(19)) is due to intermolecular interactions since the shortest Van der Waals contacts involve atoms of the tert-butylphenyl group attached to the sulphur atom, as with the tin analogue.

TABLE 2

BOND ANGLES (°)

S—Ge—C(7)	113.2(2)	109.4	C(4)—C(25)—C(26)	109.2(7)	109.5
S—Ge—C(13)	113.2(2)		C(4)—C(25)—C(27)	112.0(8)	
S—Ge—C(19)	99.9(2)		C(4)—C(25)—C(28)	109.0(7)	
C(7)—Ge—C(13)	108.9(3)		C(26)—C(25)—C(27)	106.9(8)	
C(7)—Ge—C(19)	110.0(3)		C(26)—C(25)—C(28)	109.6(8)	
C(13)—Ge—C(19)	111.4(3)		C(27)—C(25)—C(28)	110.1(8)	
Ge—S—C(1)	106.0(3)				
S—C(1)—C(2)	120.6(6)		Ge—C(7)—C(8)	122.7(6)	
S—C(1)—C(6)	119.7(6)		Ge—C(7)—C(12)	119.4(6)	
C(2)—C(1)—C(6)	119.3(7)	120.0	C(8)—C(7)—C(12)	117.8(7)	120.0
C(1)—C(2)—C(3)	119.2(8)		C(7)—C(8)—C(9)	120.3(7)	
C(2)—C(3)—C(4)	121.2(8)		C(8)—C(9)—C(10)	121.3(8)	
C(3)—C(4)—C(5)	118.5(7)		C(9)—C(10)—C(11)	118.6(8)	
C(4)—C(5)—C(6)	120.6(7)		C(10)—C(11)—C(12)	120.6(9)	
C(1)—C(6)—C(5)	121.1(7)		C(7)—C(12)—C(11)	121.4(8)	
C(3)—C(4)—C(25)	119.6(7)				
C(5)—C(4)—C(25)	121.8(7)				
Ge—C(13)—C(14)	120.9(6)		Ge—C(19)—C(20)	120.3(6)	
Ge—C(13)—C(18)	118.8(8)		Ge—C(19)—C(24)	120.9(6)	
C(14)—C(13)—C(18)	120.1(7)	120.0	C(20)—C(19)—C(24)	118.8(8)	120.0
C(13)—C(14)—C(15)	119.8(8)		C(19)—C(20)—C(21)	120.6(8)	
C(14)—C(15)—C(16)	119.6(8)		C(20)—C(21)—C(22)	120.1(9)	
C(15)—C(16)—C(17)	121.5(9)		C(21)—C(22)—C(23)	120.6(10)	
C(16)—C(17)—C(18)	118.3(9)		C(22)—C(23)—C(24)	120.6(9)	
C(13)—C(18)—C(17)	120.8(8)		C(19)—C(24)—C(23)	119.3(8)	

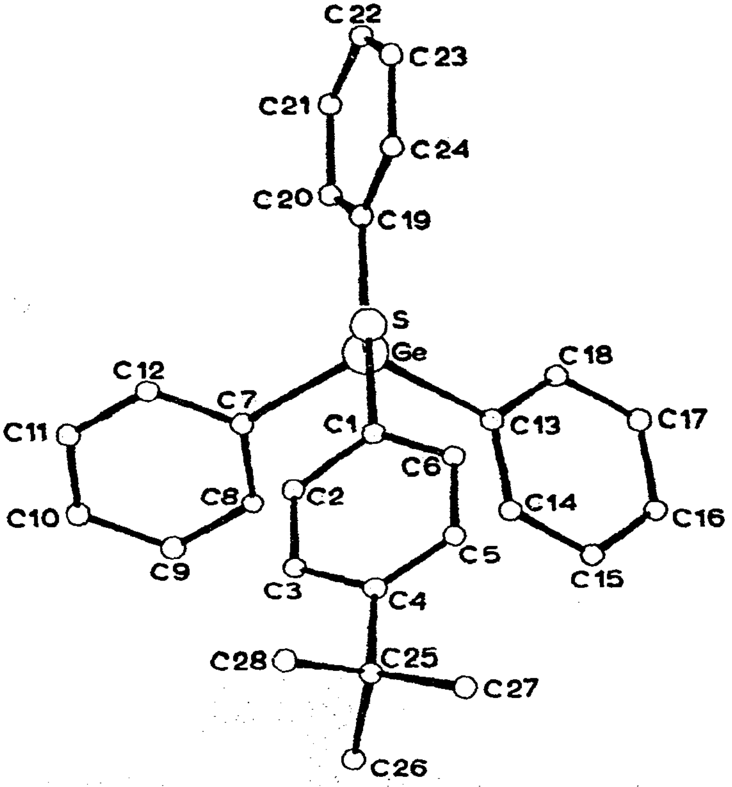

Fig. 1. View of the molecule perpendicular to the plane containing C(7), C(13) and C(19).

The average Ge—C bond of 1.938 Å compares with values reported for single covalent germanium—phenyl bonds; namely 1.945(8)Å in $Ph_3GeCOMe$ [10] and 1.953 Å in Ph_4Ge [11].

The sulphur atom exhibits normal sp^3 hybridisation, the angle at the sulphur being 106.0(3)° and the S—C bond of 1.783(8)Å being similar to that reported for other S—C single bonds [5].

The Ge—S bond length of 2.229(2) Å is slightly smaller (by ca. 0.03 Å) than the sum of the covalent radii [12] of Ge and S (2.26 Å) (in the tin analogue [5] the Sn—S bond length was 2.413(3) Å compared to the covalent radii sum of 2.43 Å). The Ge—S bond length [8] of 2.212(3) Å in the adamantane-like, $(MeGe)_4S_6$, is also comparable to the covalent radii sum. Structures of the binary germanium sulphides, GeS and GeS_2, have also been determined. While in GeS_2, the Ge—S bond length reported was 2.21 [13a] and 2.19 [13b], the different Ge—S bond lengths in GeS were considerably greater [14] at 2.47 and 2.64 Å. These values indicate, at least for the organogermanium sulphides, that the Ge—S bonds must essentially be single covalent bonds with very little, if any, $d_\pi \leftarrow p_\pi$ components. A similar finding was obtained for the Sn—S bond in organotin sulphides.

Each phenyl group is planar, the maximum deviation from the mean plane being 0.018 Å. As with the $-SnPh_3$ fragment in the tin analogue, the $-GePh_3$ residue has no overall symmetry. The rotations of the individual phenyl rings about their respective Ge—C bonds w.r.t. the normal to the plane containing the atoms C(7), C(13), C(19) are 130°, 127° and 157°. The corresponding rotations in the tin analogue are 126°, 123° and 157°. Three fold rotational symmetry would occur if the phenyl rings were rotated by equal amounts.

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