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## THE CRYSTAL AND MOLECULAR STRUCTURE OF OXO-BIS[TRIBENZYLGERMANIUM(IV)]

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### Summary

Crystals of oxo-bis[tribenzylgermanium(IV)],  $O[(PhCH_2)_3Ge]_2$ , are rhombohedral, space group  $R\bar{3}$ , having  $a = 9.621(2) \text{ \AA}$ ,  $\alpha = 85.48(3)^\circ$ . The structure was solved by Patterson methods using diffractometer data and refined by full-matrix least squares to  $R = 0.0876$ . The structure consists of molecules lying along the 3-fold axis of the unit cell, in which the GeOGe fragments are strictly linear and centrosymmetric. The Ge—O distance is  $1.730(1) \text{ \AA}$  and the Ge—C distance is  $1.980(5) \text{ \AA}$ .

### Introduction

As part of our structural study of organometallic oxo and hydroxo compounds, we recently reported the molecular structure of  $O(Ph_3Ge)_2$  [1], in which the GeOGe angle is  $135.2(2)^\circ$  and the Ge ... Ge distance  $3.268(1) \text{ \AA}$ . Seeking further support for the view that the wide angles in such  $\mu$ -oxo compounds are primarily limited by the non-bonded M ... M distances, we have determined the crystal and molecular structure of the benzyl analogue  $O[(PhCH_2)_3Ge]_2$  which turns out, unexpectedly, to contain a linear GeOGe fragment: a preliminary report of this structure and of that of the analogous tin derivative,  $O[(PhCH_2)_3Sn]_2$  has been published [2].

### Experimental

Oxo-bis[tribenzylgermanium(IV)],  $O[(PhCH_2)_3Ge]_2$ , was prepared from  $GeCl_4$  via  $(PhCH_2)_4Ge$  and  $(PhCH_2)_3GeBr$  [3].

### Data collection

Unit-cell parameters were determined by a least squares fit to the reflecting positions of 24 reflections measured on a Philips PW1100 automatic four-circle

diffractometer with graphite-monochromatized Mo- $K_{\alpha}$  radiation. The intensities of 3313 reflections with  $3 \leq \theta \leq 25^{\circ}$  were measured by the  $\omega/2\theta$  scan technique, with a scan width of  $[1.30 + 0.1 \tan \theta]^{\circ}$  in  $\omega$  and a maximum of two scans per reflection [a second scan was made if the total count obtained in the first scan was less than 100]. Backgrounds were measured at both ends of the scan range for a time equal to scan time/2. Three standard reflections were measured every 5 h during data collection and showed only small random deviations from their mean intensities. Lorentz and polarisation corrections were applied to the data, but no corrections for absorption were made.

### Crystal data

Oxo-bis[tribenzylgermanium(IV)],  $C_{12}H_{12}Ge_2O$ ,  $M_r = 707.94$ . Rhombohedral, space group  $R\bar{3}$  ( $C_{3i}$ , No. 148),  $a = 9.621(2)$  Å,  $\alpha = 85.48(3)^{\circ}$ ;  $U = 882.7$  Å<sup>3</sup>;  $Z = 1$ ;  $D_c = 1.332$  kg dm<sup>-3</sup>;  $F(000) = 366$ . Mo- $K_{\alpha}$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo-}K_{\alpha}) = 16.65$  cm<sup>-1</sup>.

### Structure solution and refinement

These were carried out using SHELX-76 [4].

With initial atom positions taken from the structure of the tin analogue [2] eight cycles of refinement (in space group  $R\bar{3}$ ) with the matrix blocked such that the O atom refined in every cycle, but the two crystallographically independent benzyl-Ge fragments refined in alternate cycles, the Ge and O atoms constrained to lie on the 3-fold axis, and individual isotropic temperature factors for all non-hydrogen atoms (63 variables) yielded  $R = 0.1476$ ,  $R_w = 0.1480$  and  $R_G = 0.1488$ , for 1697 reflections having  $F_o \geq 6\sigma(F_o)$ . The introduction of anisotropic temperature factors for the Ge atoms with 8 cycles of refinement (65 variables) reduced  $R_G$  to 0.1311. Difference syntheses revealed persistent electron density maxima which, from their positions, could only be ascribed to the carbon atoms of a *para*-methyl substituent on the benzyl groups. Eight cycles of refinement with these carbon atoms included, with temperature factors fixed at 0.09 Å<sup>-1</sup> and variable site occupation factors (SOF) (73 variables) reduced  $R_G$  to 0.0970. Eight further cycles with hydrogen atoms (except those of the *p*-methyl substituent) added in calculated positions and with separate common temperature factors for the phenyl and methylene hydrogen atoms (75 variables) reduced  $R_G$  to 0.0753.

At this stage of the refinement, the geometry of the molecule was unsatisfactory, with significant differences between chemically equivalent bond lengths, and therefore the refinement was continued in  $R\bar{3}$  using mean parameter values from the  $R\bar{3}$  refinement. Four cycles of full matrix least-squares refinement with the H atom positions allowed to refine (57 variables) yielded  $R_G = 0.0614$  for 1025 independent reflections having  $F_o \geq 6\sigma(F_o)$ . The introduction of anisotropic temperature factors for all non-hydrogen atoms (except the carbon atom of the *p*-methyl substituent, C(17), whose SOF was fixed at 0.60, with the isotropic temperature factor allowed to refine), in four cycles of refinement (93 variables) reduced  $R$  to 0.0876,  $R_w$  to 0.0509 and  $R_G$  to 0.0455. At each stage in the refinement the reduction of  $R_G$  was significant at the 99.5% level [5]. An equivalent refinement in  $R\bar{3}$  (182 variables) yielded  $R = 0.0803$ ,  $R_w = 0.0516$ , and  $R_G = 0.0461$ , and much worse agreement between chemically equi-

TABLE 1  
ATOM COORDINATES

	x	y	z
Ge	0.4035(0)	0.4035(0)	0.4035(0)
O	0.5000(0)	0.5000(0)	0.5000(0)
C(1)	0.4158(6)	0.2061(5)	0.4800(5)
C(11)	0.3787(5)	0.1834(4)	0.6332(5)
C(12)	0.2411(5)	0.1755(5)	0.6931(6)
C(13)	0.2138(6)	0.1541(5)	0.8353(6)
C(14)	0.3189(6)	0.1405(5)	0.9242(5)
C(15)	0.4543(6)	0.1493(5)	0.8684(6)
C(16)	0.4837(5)	0.1702(5)	0.7257(6)
C(17) <sup>a</sup>	0.2763(8)	0.1251(8)	1.0723(8)
H(1)	0.517(4)	0.167(4)	0.443(4)
H(2)	0.345(5)	0.176(5)	0.436(5)
H(12)	0.170(4)	0.192(4)	0.627(4)
H(13)	0.119(5)	0.151(4)	0.872(4)
H(15)	0.534(5)	0.141(4)	0.921(4)
H(16)	0.574(4)	0.174(4)	0.689(4)

<sup>a</sup> See text.

TABLE 2  
BOND DISTANCES AND ANGLES<sup>a</sup>

Bond distances (Å)		Bond angles (°)	
Ge—O	1.730(1)	Ge—O—Ge <sup>i</sup>	180.0(0)
Ge—C(1)	1.980(5)	O—Ge—C(1)	109.1(1)
C(1)—C(11)	1.492(6)	Ge—C(1)—C(11)	115.4(3)
C(11)—C(12)	1.406(6)	C(1)—C(11)—C(12)	124.1(5)
C(12)—C(13)	1.375(6)	C(1)—C(11)—C(16)	119.7(5)
C(13)—C(14)	1.367(6)	C(11)—C(12)—C(13)	121.3(5)
C(14)—C(15)	1.375(7)	C(12)—C(13)—C(14)	121.4(5)
C(15)—C(16)	1.382(7)	C(13)—C(14)—C(15)	118.5(5)
C(16)—C(11)	1.391(6)	C(14)—C(15)—C(16)	120.8(5)
C(1)—H(1)	1.06(4)	C(15)—C(16)—C(11)	121.7(5)
C(1)—H(2)	0.91(5)	C(16)—C(11)—C(12)	116.2(5)
C(aryl)—H(mean)	0.94(4)	C(aryl)—C(aryl)—H(mean)	120(4)

<sup>a</sup> The superscript *i* refers to the symmetry position  $1-x, 1-y, 1-z$ .

TABLE 3  
Anisotropic thermal parameters (Å<sup>2</sup>)<sup>a</sup>

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Ge	0.0571(3)	0.0571(3)	0.0571(3)	-0.0139(2)	-0.0139(2)	-0.0139(2)
O	0.078(2)	0.078(2)	0.078(2)	-0.025(2)	-0.025(2)	-0.025(2)
C(1)	0.082(4)	0.067(3)	0.076(4)	-0.014(3)	-0.019(3)	-0.012(3)
C(11)	0.068(3)	0.044(3)	0.076(3)	-0.003(2)	-0.013(3)	-0.012(2)
C(12)	0.060(3)	0.053(3)	0.096(4)	-0.005(3)	-0.018(3)	-0.015(2)
C(13)	0.062(3)	0.066(3)	0.100(5)	0.001(3)	0.005(3)	-0.019(3)
C(14)	0.078(4)	0.063(3)	0.082(4)	0.004(3)	-0.002(3)	-0.012(3)
C(15)	0.073(4)	0.070(3)	0.083(4)	0.006(3)	-0.022(3)	-0.009(3)
C(16)	0.054(3)	0.060(3)	0.092(4)	-0.006(3)	-0.010(3)	-0.004(3)

<sup>a</sup> The isotropic temperature parameter for H(1) and H(2) refined to 0.088(11) Å<sup>2</sup>. The isotropic temperature parameter for the aryl hydrogens refined to 0.082(7) Å<sup>2</sup>.

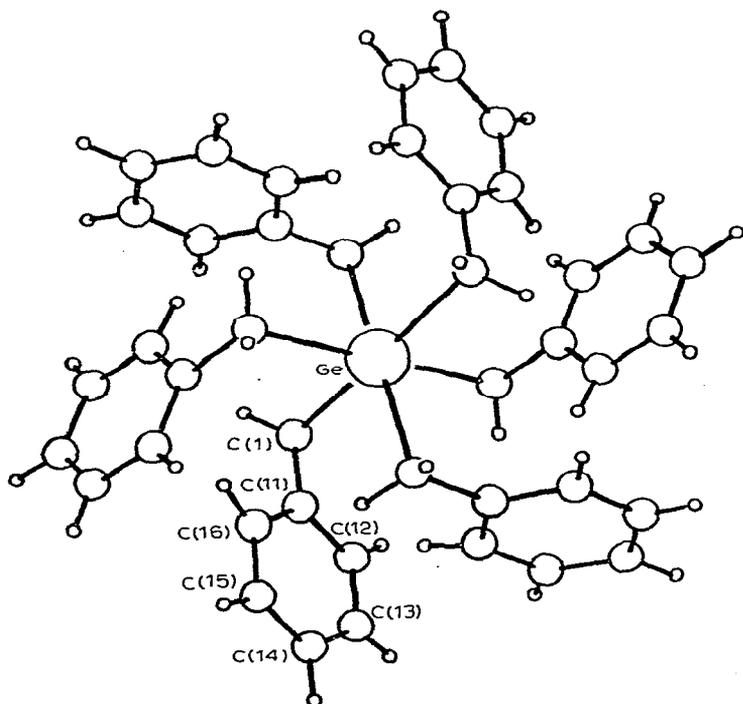


Fig. 1. The molecule of  $O[(PhCH_2)_3Ge]_2$  viewed down the 3-fold axis, showing the atom-numbering scheme.

valent bond lengths. The non-centrosymmetric space group was therefore rejected.

A final difference synthesis showed no significant residual electron density. Attempts to allow the oxygen atom to refine off the 3-fold axis as a disordered atom led to unstable refinements with increases in  $R_G$ .

Complex neutral-atom scattering factors [6,7] were employed for all atoms.

The positional parameters from the final least-square cycles for this structure are given in Table 1: the bond lengths and angles are given with ESDS in Table 2. No correction for thermal motion has been applied to the bond lengths. Anisotropic temperature parameters, are given in Table 3.

The Figure shows a view of the molecule down the 3-fold axis, and the numbering of the atoms. In the Tables, the hydrogen atoms of the phenyl rings are given the numbers of the carbon atoms to which they are bonded.

## Discussion

In  $O[(PhCH_2)_3Ge]_2$ , as in  $O[(PhCH_2)_3Sn]_2$  [2], the molecules lie across the centre of inversion and along the 3-fold axis of the rhombohedral cell; in consequence the  $GeOGe$  fragment is linear. The refinement showed that the compound consisted of 40% of  $O[(PhCH_2)_3Ge]_2$  and 60% of  $O[(p-CH_3C_6H_4CH_2)_3Ge]_2$ : this was confirmed by NMR spectroscopy. The source of the methyl

groups was traced to the starting materials: the germanium compound was prepared using benzyl chloride (Hopkin and Williams) which was subsequently found to be an approximately 1/1 mixture of  $\text{PhCH}_2\text{Cl}$  and  $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$ ; the tin analogue had been prepared using benzyl bromide (Fisons) which contained no impurities. Since the presence of the methyl group does not prevent the close similarity of the two compounds, we do not feel that our structural conclusions are materially altered. The preparation of a new sample of the germanium compound and the re-analysis of its structure were not felt to be necessary.

The Ge—O distance  $1.730(1)$  Å is significantly shorter than that in the phenyl analogue  $\text{O}(\text{Ph}_3\text{Ge})_2$ ,  $1.767(2)$  Å [1], in which the GeOGe fragment is markedly non-linear. In a similar way the P—N distance in linear  $[\text{N}(\text{PPh}_3)_2]^+$ ,  $1.539(2)$  Å, is significantly less than that in the non-linear forms of this cation where the range of PNP angles is  $134.6^\circ$ — $141.8^\circ$  and the range of P—N distances is  $1.570$ — $1.586^\circ$  Å with a mean of  $1.575(2)$  Å. Apart from the single linear occurrence of the cation  $[\text{N}(\text{PPh}_3)_2]^+$  [8] the only other *p*-block analogues of the present molecules are the tin analogue  $\text{O}[(\text{PhCH}_2)_3\text{Sn}]_2$  [2] and the linear silicon species  $\text{O}(\text{Ph}_3\text{Si})_2$  [9]: however amongst *d*-block species, the titanium compound  $\text{O}[(\text{PhCH}_2)_3\text{Ti}]_2$  [10] is isostructural with  $\text{O}[(\text{PhCH}_2)_3\text{M}]_2$  ( $\text{M} = \text{Ge}, \text{Sn}$ ).

It has been suggested [11,12] that in molecules or ions of general type  $\text{O}(\text{MR}_n)_2$ , linearity at oxygen may be expected if M is of low electronegativity: when R is an electron donor, it will enhance the effect of the low electronegativity of M. The results for  $\text{O}[(\text{PhCH}_2)_3\text{M}]_2$  ( $\text{M} = \text{Ge}, \text{Sn}$ ) and those earlier reported for the analogous  $\text{O}(\text{Ph}_3\text{M})_2$  [1,13] are consistent with this suggestion.

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