

Cette liaison O—H...O n'est pas symétrique contrairement à ce que pensait Williams & Rundle (1964) dans le cas de l'acide, où ils n'ont pas pu mettre en évidence les atomes d'hydrogène.

Dans le cas du composé deutéré les atomes d'oxygène et de carbone occupent sensiblement les mêmes positions dans la molécule. (Le Tableau 3 donne les distances interatomiques dans le cas de ce composé deutéré.)

Les distances O—H sont du même ordre de grandeur (1 Å) que dans le cas précédent. La seule modification sensible est la position du deutérium D(3) qui se trouve presque sur la droite O(8)...O(11) [angle O(11)—D(3)—O(8) = 176 (1)°, alors que le H(3) en est légèrement décalé [angle O(11)—H(3)—O(8) = 165 (1)°]. Et les distances O—D et O—H ne sont pas significativement différentes. La distance O(8)—O(11) reste constante.

L'ion K<sup>+</sup> est entouré par sept atomes d'oxygène (Tableau 3), un huitième atome d'oxygène se trouve également dans son voisinage mais la distance K—O est dans ce dernier cas nettement plus longue: 3,253 Å. Six de ces atomes (ceux dont les distances K—O sont les plus courtes) forment un prisme à base triangulaire. Ils appartiennent tous à six molécules différentes qui sont dans six mailles voisines. Le septième et le huitième atomes d'oxygène appartiennent à deux des molécules déjà liées au potassium (Fig. 2). Finalement le potassium échange des liaisons avec six molécules. Et c'est par l'intermédiaire de l'ion K<sup>+</sup> que les molécules sont reliées les unes aux autres.

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## The Crystal and Molecular Structure of Oxobis[triphenylgermanium(IV)]

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Crystals of oxobis[triphenylgermanium(IV)], O(Ph<sub>3</sub>Ge)<sub>2</sub>, are triclinic, space group  $P\bar{1}$ ,  $a = 15.553$  (2),  $b = 11.048$  (3),  $c = 9.708$  (2) Å,  $\alpha = 109.54$  (1),  $\beta = 92.68$  (1),  $\gamma = 103.08$  (2)°,  $Z = 2$ . The structure was solved by the Patterson method using diffractometer data, and refined by full-matrix least squares to  $R = 0.048$  for 4218 unique reflections. The principal geometrical parameters are:  $r(\text{Ge—O})$  1.767 (2) Å;  $\angle(\text{Ge—O—Ge})$  135.2 (2)°;  $r(\text{Ge...Ge})$  3.268 (1) Å;  $r(\text{Ge—C})$  1.942 (3) Å.

### Introduction

As part of a programme to test, and extend the application of, the hard-atom model of molecular

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### Conclusion

La résolution de ces structures a permis de déterminer avec précision les distances intermoléculaires et a montré que les deux groupements carboxyles sont très semblables.

D'autre part on a pu mettre en évidence que la liaison intramoléculaire n'est pas symétrique, aussi bien dans le cas du furanne-3,4-dicarboxylate acide de potassium que de son homologue deutéré; et que la distance O(8)—O(11) n'est pas modifiée par le remplacement de l'hydrogène par du deutérium.

Je remercie Mme G. Cassanas qui a préparé des cristaux des deux composés et M C. Dagron qui a isolé et taillé les deux cristaux utilisés dans ce travail.

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configuration at C, N and O (Glidewell, 1975, 1976, 1977) we have determined the molecular structure of oxobis[triphenylgermanium(IV)], O(Ph<sub>3</sub>Ge)<sub>2</sub>; our major interest in this structure was the geometry of the OGe<sub>2</sub> fragment, in particular the Ge...Ge distance. A structure determination of rather low precision (single-

axis data, isotropic refinement,  $R = 0.169$ ) has been reported (Kuz'mina & Struchkov, 1972) for this compound in which the Ge—C distances were found to range from 1.86 (4) to 2.03 (5) Å. Other Ge—C(aryl) distances have been reported for  $\text{Ph}_3\text{GeCOCH}_3$  (Harrison & Trotter, 1968) [1.945 (8) Å (mean), range 0.010 Å],  $(\text{Ph}_2\text{Ge})_2\text{Fe}_2(\text{CO})_7$  (Elder, 1969) [1.956 (7) Å (mean), range 0.029 Å],  $(\text{Ph}_2\text{GeOH})\text{PhPt}(\text{PEt}_3)_2$  (Gee & Powell, 1971) [1.975 (12) Å],  $\text{Ph}_4\text{Ge}$  [1.952 (1) Å (Chieh, 1971) and 1.954 (4) Å (Karipides & Haller, 1972)], and  $(\text{C}_6\text{F}_5)_4\text{Ge}$  (Karipides, Forman, Thomas & Reed, 1974) [1.957 (4) Å]. These data suggest that the range of 0.17 Å reported (Kuz'mina & Struchkov, 1972) for the Ge—C distances in  $\text{O}(\text{Ph}_3\text{Ge})_2$  is an artefact of an imprecise determination, and hence that little confidence may be placed in the accuracy of the values reported for the Ge—O and Ge...Ge distances. The present paper reports an accurate redetermination ( $R = 0.048$ ) of the structure of  $\text{O}(\text{Ph}_3\text{Ge})_2$  in which the Ge—C distances range from 1.934 (5) to 1.951 (5) Å, and the Ge...Ge distance of 3.268 (1) Å subtends an angle at O of 135.2 (2)°.

### Experimental

Bromotriphenylgermane was prepared (Johnson, Nebergall & Harris, 1957) from tetraphenylgermane, and converted to oxobis(triphenylgermanium) by the method of Morgan & Drew (1925). Recrystallization from petroleum (b.p. 60–80°C) yielded colourless prismatic crystals: a crystal of dimensions 0.30 × 0.12 × 0.10 mm was used for data collection.

Unit-cell parameters were determined by least-squares fits to the reflecting positions of 25 reflections each measured a total of 16 times during data collection using a Philips PW 1100 automatic four-circle diffractometer with graphite-crystal-monochromatized Mo  $K\alpha$  radiation. The intensities of 4712 reflections with  $3 \leq \theta \leq 27^\circ$  were measured using the diffractometer by the  $\omega/2\theta$  scan technique, with a scan width of  $(0.76 + 0.1 \tan \theta)^\circ$  in  $\omega$ , a scan speed of  $0.05^\circ \text{ s}^{-1}$  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 500). Backgrounds were measured at either end of the scan range for a time equal to  $(\text{scan time}/2)\sqrt{(I_{\text{BK}}/I_{\text{INT}})}$  or a minimum of 10 s, where  $I_{\text{BK}}$  = the background intensity scaled from an initial 10 s measurement and  $I_{\text{INT}}$  = integrated peak intensity. Three standard reflections were measured every five hours during data collection, and showed only random deviations from their mean intensities. Lorentz and polarization corrections were applied to the data, but no corrections for absorption were made.

### Results

#### Crystal data

$\text{C}_{36}\text{H}_{30}\text{Ge}_2\text{O}$ ,  $M_r = 623.82$ , triclinic,  $a = 15.553$  (2),  $b = 11.048$  (3),  $c = 9.708$  (2) Å (1 Å = 100 pm),  $\alpha = 109.54$  (1),  $\beta = 92.68$  (1),  $\gamma = 103.08$  (2)°,  $U = 1517.6$  Å<sup>3</sup>;  $Z = 2$ ,  $D_m = 1.371$  (by flotation),  $D_c = 1.365$  g cm<sup>-3</sup>;  $F(000) = 636$ ; Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 19.3$  cm<sup>-1</sup>. Space group  $P\bar{1}$  ( $C_i$ , No. 2) was verified by satisfactory refinement. All atoms occupy twofold general positions; the asymmetric unit consists of one molecule.

The unit-cell parameters reported previously (Kuz'mina & Struchkov, 1972) [ $a = 11.04$  (1),  $b = 9.71$  (1),  $c = 17.04$  (2) Å,  $\alpha = 106.45$  (33),  $\beta = 105.13$  (33),  $\gamma = 109.18$  (33)°] do not represent a reduced cell and consequently differ from the reduced

Table 2. Atomic coordinates ( $\times 10^4$ )

	x	y	z
Ge(1)	2502 (0)	1121 (0)	1226 (1)
Ge(2)	2333 (0)	4183 (0)	2491 (1)
O	2407 (2)	2666 (3)	1170 (4)
C(111)	2488 (3)	104 (4)	-833 (5)
C(112)	2280 (3)	-1275 (5)	-1336 (6)
C(113)	2262 (4)	-2014 (6)	-2827 (7)
C(114)	2446 (4)	-1381 (6)	-3811 (7)
C(115)	2643 (4)	-50 (7)	-3349 (8)
C(116)	2662 (4)	714 (6)	-1868 (6)
C(121)	3618 (3)	1301 (4)	2352 (5)
C(122)	4361 (3)	1101 (5)	1652 (6)
C(123)	5156 (4)	1181 (6)	2448 (7)
C(124)	5205 (4)	1450 (6)	3939 (7)
C(125)	4485 (4)	1663 (6)	4652 (7)
C(126)	3698 (4)	1605 (5)	3875 (6)
C(131)	1481 (3)	347 (4)	2020 (5)
C(132)	1540 (4)	-497 (5)	2794 (6)
C(133)	791 (4)	-1059 (6)	3337 (7)
C(134)	-7 (4)	-738 (6)	3111 (7)
C(135)	-62 (4)	90 (6)	2373 (7)
C(136)	671 (3)	627 (5)	1810 (6)
C(211)	1121 (3)	4301 (5)	2172 (5)
C(212)	601 (4)	3591 (5)	799 (6)
C(213)	-273 (4)	3683 (6)	577 (7)
C(214)	-623 (4)	4459 (6)	1677 (7)
C(215)	-126 (4)	5182 (6)	3044 (7)
C(216)	748 (4)	5095 (5)	3285 (6)
C(221)	3179 (3)	5524 (4)	2010 (5)
C(222)	2966 (4)	6663 (6)	1952 (6)
C(223)	3591 (4)	7617 (7)	1636 (8)
C(224)	4409 (4)	7438 (6)	1348 (7)
C(225)	4628 (4)	6318 (6)	1377 (7)
C(226)	4020 (4)	5360 (6)	1713 (6)
C(231)	2628 (3)	4283 (5)	4509 (5)
C(232)	3432 (4)	5097 (6)	5336 (7)
C(233)	3630 (4)	5185 (6)	6806 (7)
C(234)	3045 (4)	4451 (6)	7407 (8)
C(235)	2252 (4)	3624 (6)	6595 (6)
C(236)	2047 (3)	3549 (5)	5152 (6)

cell reported here. The matrix required to transform the earlier cell into the present reduced cell is

$$\begin{bmatrix} 1 & 1 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{bmatrix}.$$

### Structure solution and refinement

These were carried out using the *SHELX* program system (Sheldrick, 1976) with 4218 independent reflections having  $F_o > 6\sigma(F_o)$ .

The positions of the two independent Ge atoms were obtained from a Patterson synthesis, and a difference synthesis provided positions for all other non-hydrogen atoms. Three cycles of full-matrix least squares with the phenyl rings treated as rigid hexagons (C—C distance 1.395 Å) and individual isotropic temperature factors for all non-hydrogen atoms yielded a conventional  $R$  index ( $= \Sigma \Delta / \Sigma F_o$ , where  $\Delta = F_o - F_c$ ) of 0.069 and a generalized index  $R_G [= (\Sigma w\Delta^2 / \Sigma wF_o^2)^{1/2}]$  of 0.071. The introduction of a weighting scheme  $w = [\sigma(F)]^{-2}$  and of anisotropic temperature factors for the Ge and O atoms yielded, after three cycles of refinement, a reduction of  $R_G$  to 0.062 (significant at the 0.5% level). The contributions were then included of the H atoms placed in calculated positions about the rigid ring with the C—H distance = 0.96 Å, and of a common temperature factor: three cycles of refinement reduced

$R_G$  to 0.060. Finally the rigid constraints were removed from the phenyl rings; the H atom positions remained constrained along the bisectors of the external C—C—C angles with  $r(\text{C—H}) = 0.96$  Å: three cycles of refine-

Table 3. *Intramolecular distances* (Å)

Ge(1)—O	1.765 (3)	Ge(1)—C(111)	1.934 (5)
Ge(2)—O	1.769 (3)	Ge(1)—C(121)	1.941 (4)
Ge(1)···Ge(2)	3.268 (1)	Ge(1)—C(131)	1.946 (4)
		Ge(2)—C(211)	1.937 (5)
		Ge(2)—C(221)	1.944 (5)
		Ge(2)—C(231)	1.951 (5)
C(111)—C(112)	1.389 (6)	C(211)—C(212)	1.399 (7)
C(112)—C(113)	1.399 (7)	C(212)—C(213)	1.398 (7)
C(113)—C(114)	1.367 (8)	C(213)—C(214)	1.351 (8)
C(114)—C(115)	1.341 (8)	C(214)—C(215)	1.382 (8)
C(115)—C(116)	1.398 (8)	C(215)—C(216)	1.399 (8)
C(116)—C(111)	1.390 (7)	C(216)—C(211)	1.389 (7)
C(121)—C(122)	1.391 (7)	C(221)—C(222)	1.390 (7)
C(122)—C(123)	1.395 (7)	C(222)—C(223)	1.388 (8)
C(123)—C(124)	1.372 (8)	C(223)—C(224)	1.359 (8)
C(124)—C(125)	1.368 (8)	C(224)—C(225)	1.364 (8)
C(125)—C(126)	1.384 (7)	C(225)—C(226)	1.388 (8)
C(126)—C(121)	1.395 (7)	C(226)—C(221)	1.391 (7)
C(131)—C(132)	1.393 (7)	C(231)—C(232)	1.390 (7)
C(132)—C(133)	1.404 (8)	C(232)—C(233)	1.412 (8)
C(133)—C(134)	1.393 (8)	C(233)—C(234)	1.363 (8)
C(134)—C(135)	1.351 (8)	C(234)—C(235)	1.377 (8)
C(135)—C(136)	1.385 (8)	C(235)—C(236)	1.392 (7)
C(136)—C(131)	1.386 (6)	C(236)—C(231)	1.387 (7)

Table 4. *Intramolecular angles* (°)

C(111)—Ge(1)—C(121)	110.2 (2)	C(211)—Ge(2)—C(221)	111.8 (2)
C(111)—Ge(1)—C(131)	111.6 (2)	C(211)—Ge(2)—C(231)	110.4 (2)
C(121)—Ge(1)—C(131)	111.7 (2)	C(221)—Ge(2)—C(231)	111.6 (2)
O—Ge(1)—C(111)	102.3 (2)	O—Ge(2)—C(211)	106.7 (2)
O—Ge(1)—C(121)	111.4 (2)	O—Ge(2)—C(221)	103.8 (2)
O—Ge(1)—C(131)	109.3 (2)	O—Ge(2)—C(231)	112.3 (2)
Ge(1)—O—Ge(2)	135.2 (2)		
Ge(1)—C(111)—C(112)	120.7 (4)	Ge(2)—C(211)—C(212)	120.4 (4)
Ge(1)—C(111)—C(116)	121.8 (4)	Ge(2)—C(211)—C(216)	121.2 (4)
Ge(1)—C(121)—C(122)	120.7 (4)	Ge(2)—C(221)—C(222)	121.5 (4)
Ge(1)—C(121)—C(126)	121.5 (4)	Ge(2)—C(221)—C(226)	120.3 (4)
Ge(1)—C(131)—C(132)	121.6 (4)	Ge(2)—C(231)—C(232)	120.3 (4)
Ge(1)—C(131)—C(136)	119.7 (4)	Ge(2)—C(231)—C(236)	121.3 (4)
C(111)—C(112)—C(113)	120.9 (5)	C(211)—C(212)—C(213)	120.0 (5)
C(112)—C(113)—C(114)	120.0 (6)	C(212)—C(213)—C(214)	120.6 (6)
C(113)—C(114)—C(115)	120.0 (7)	C(213)—C(214)—C(215)	120.9 (6)
C(114)—C(115)—C(116)	121.2 (7)	C(214)—C(215)—C(216)	119.2 (6)
C(115)—C(116)—C(111)	120.4 (7)	C(215)—C(216)—C(211)	120.9 (5)
C(116)—C(111)—C(112)	117.5 (5)	C(216)—C(211)—C(212)	118.3 (5)
C(121)—C(122)—C(123)	120.9 (5)	C(221)—C(222)—C(223)	120.1 (6)
C(122)—C(123)—C(124)	119.7 (6)	C(222)—C(223)—C(224)	120.8 (6)
C(123)—C(124)—C(125)	120.3 (6)	C(223)—C(224)—C(225)	120.0 (6)
C(124)—C(125)—C(126)	120.4 (6)	C(224)—C(225)—C(226)	120.3 (6)
C(125)—C(126)—C(121)	120.8 (5)	C(225)—C(226)—C(221)	120.5 (5)
C(126)—C(121)—C(122)	117.9 (5)	C(226)—C(221)—C(222)	118.2 (5)
C(131)—C(132)—C(133)	120.5 (5)	C(231)—C(232)—C(233)	119.9 (6)
C(132)—C(133)—C(134)	118.7 (6)	C(232)—C(233)—C(234)	120.3 (6)
C(133)—C(134)—C(135)	120.7 (6)	C(233)—C(234)—C(235)	120.5 (6)
C(134)—C(135)—C(136)	120.8 (6)	C(234)—C(235)—C(236)	119.4 (6)
C(135)—C(136)—C(131)	120.5 (5)	C(235)—C(236)—C(231)	121.5 (5)
C(136)—C(131)—C(132)	118.7 (5)	C(236)—C(231)—C(232)	118.4 (5)

Table 5. *Least-squares planes and atom distances therefrom* ( $\text{\AA} \times 10^3$ )

Least-squares planes are defined in terms of the Cartesian coordinates by  $AX + BY + CZ + 1 = 0$ , where  $X$ ,  $Y$  and  $Z$  are related to the cell coordinates by:  $X = x + y \cos \gamma + z \cos \beta$ ,  $Y = y \sin \gamma - z \sin \beta \cos \alpha^*$ ,  $Z = z \sin \beta \sin \alpha^*$ . Planes are calculated from C atom positions only.

Ring, $ij$	$A$	$B$	$C$	$C(ij1)$	$C(ij2)$	$C(ij3)$	$C(ij4)$	$C(ij5)$	$C(ij6)$	$Ge(i)$
11	-0.2673	+0.0049	-0.0452	-6	+3	+1	-2	-2	+6	+12
12	-0.0530	-0.7727	-0.1220	+10	0	-8	+6	+3	-10	+89
13	-0.0185	-0.3510	-0.5862	0	-6	+6	0	-7	+7	+11
21	-0.0632	-0.0409	-0.3114	-5	+9	-5	-2	+5	-2	-26
22	-0.0528	-0.2981	+0.0953	+2	-3	+1	+2	-3	0	-5
23	+0.4180	-0.4328	-0.2090	-5	+9	-6	-2	+5	-1	-28

ment produced final values of  $R = 0.048$ ,  $R_w$  ( $= \sum w^{1/2} \Delta / \sum w^{1/2} F_o$ ) = 0.051, and  $R_G = 0.057$  (this decrease in  $R_G$  was significant at the 0.5% level).

An analysis of variance shows no significant dependence on the parity group,  $\sin \theta$ , or the magnitude of  $F_o$  (Table 1).<sup>\*</sup> Complex neutral-atom scattering factors (Cromer & Mann, 1968; Doyle & Turner, 1968) were

<sup>\*</sup> Lists of structure factors, thermal parameters and Table 1 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32973 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 6. *Selected intramolecular non-bonded distances* ( $\text{\AA}$ )

Ge(1)···C(112)	2.901	Ge(2)···C(212)	2.908
Ge(1)···C(116)	2.917	Ge(2)···C(216)	2.910
Ge(1)···C(122)	2.908	Ge(2)···C(222)	2.921
Ge(1)···C(126)	2.922	Ge(2)···C(226)	2.905
Ge(1)···C(132)	2.927	Ge(2)···C(232)	2.911
Ge(1)···C(136)	2.896	Ge(2)···C(236)	2.922
O···H(116)	2.66	O···C(111)	2.88
O···H(212)	2.79	O···H(136)	2.90
C(212)···H(136)	2.83	C(236)···H(126)	2.90

Table 7. *Selected intermolecular non-bonded distances* ( $\text{\AA}$ )

H(115)···H(126 <sup>iv</sup> )	2.50	C(224)···H(125 <sup>v</sup> )	3.01
H(134)···H(235 <sup>vii</sup> )	2.54	C(111)···H(135 <sup>v</sup> )	3.02
H(122)···H(224 <sup>viii</sup> )	2.56	C(126)···H(115 <sup>iv</sup> )	3.03
C(225)···H(125 <sup>v</sup> )	2.91	C(124)···H(232 <sup>x</sup> )	3.04
C(114)···H(124 <sup>v</sup> )	2.93	C(235)···H(214 <sup>ix</sup> )	3.07
C(121)···H(223 <sup>iii</sup> )	2.98	C(213)···C(213 <sup>vi</sup> )	3.41
C(122)···H(223 <sup>iii</sup> )	2.99	C(134)···C(134 <sup>i</sup> )	3.48
C(133)···H(213 <sup>i</sup> )	3.00	Ge(1)···H(223 <sup>ii</sup> )	3.74
C(236)···H(215 <sup>ix</sup> )	3.00		

Roman numerals as superscripts refer to the following transformations of the coordinates relative to the reference molecule at  $x, y, z$ :

(i) $-x, -y, -z$	(vi) $-x, 1 - y, -z$
(ii) $x, 1 + y, z$	(vii) $-x, -y, 1 - z$
(iii) $x, -1 + y, z$	(viii) $1 - x, 1 - y, -z$
(iv) $x, y, -1 + z$	(ix) $-x, 1 - y, 1 - z$
(v) $1 - x, -y, -z$	(x) $1 - x, 1 - y, 1 - z$

employed for all atoms. In the final refinement, 173 parameters were varied simultaneously (comprising 117 positional coordinates, 18 anisotropic temperature-factor components, 37 isotropic temperature factors, and one overall scale factor): all parameter shifts were less than  $0.18\sigma$  and a difference synthesis revealed no pronounced features. No correction for thermal motion has been applied to the bond lengths.

The results from the final least-squares cycle are given in Table 2. These, together with the full-covariance matrix and the e.s.d.'s in the unit-cell dimensions, were used to calculate the bond lengths and angles which are given with e.s.d.'s in Tables 3 and 4. Least-squares planes were calculated for each of the phenyl rings: these and the deviations of the atoms from them are given in Table 5. The shortest non-bonded distances are summarized in Tables 6 and 7. Fig. 1 is a perspective view of the molecule showing the numbering scheme (H atoms are numbered according to the C atoms to which they are bonded).

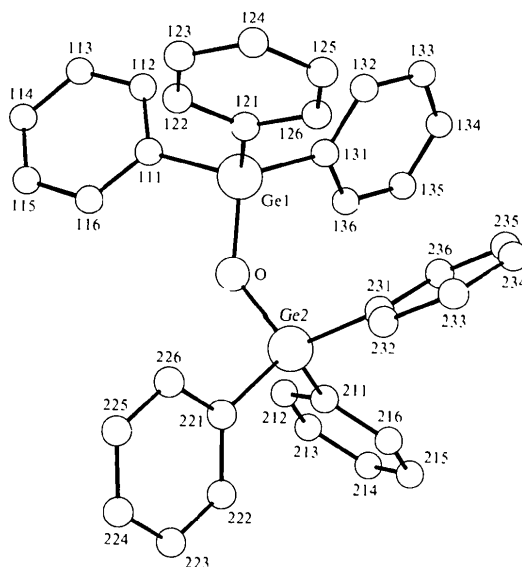


Fig. 1. Perspective view of the molecule, showing the numbering of the atoms.

### Discussion

The two crystallographically independent Ge—O distances are identical within experimental error [mean 1.767 (2) Å]; the Ge—O—Ge angle, 135.2 (2)°, is much greater than that anticipated from the VSEPR model, *ca* 110°.

Precise determinations of Ge—O distances are rare, and comprise 1.767 (4) Å in O(GeH<sub>3</sub>)<sub>2</sub> (Glidewell, Rankin, Robiette, Sheldrick, Beagley & Cradock, 1970), 1.838 (11) Å in (Ph<sub>2</sub>GeOH)PhPt(PEt<sub>3</sub>)<sub>2</sub> (Gee & Powell, 1971), and 1.739 (2) Å in quartz-like GeO<sub>2</sub> (Smith & Isaacs, 1964). Bridging Ge—O distances in oligogermanates range from 1.61 Å in K<sub>2</sub>Pb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> (Bassi & Lajzerowicz, 1965) to 1.81 Å in Gd<sub>4</sub>(GeO<sub>4</sub>)Ge<sub>3</sub>O<sub>10</sub> (Smolin, Shepelev & Butikova, 1971); and in pyroxene-like metagermanates they range from 1.791 Å in MnGeO<sub>3</sub> (Fang, Townes & Robinson, 1969) to 1.90 Å in BaGeO<sub>3</sub> (Hilmer, 1962). It is not possible to assert (Glidewell, Rankin, Robiette, Sheldrick, Beagley & Cradock, 1970) that the Ge—O distance in any of these species is 'short'. The additivity of covalent radii is so poor that the use of discrepancies between observed and calculated values to support particular models of chemical bonding is unsafe.

The Ge...Ge distance of 3.268 (1) Å in O(GePh<sub>3</sub>)<sub>2</sub> subtends an angle at O of 135.2°: these values may be compared with those in O(GeH<sub>3</sub>)<sub>2</sub> (3.156 Å, 126.5°) (Glidewell, Rankin, Robiette, Sheldrick, Beagley & Cradock, 1970), GeO<sub>2</sub> (3.154 Å, 130.1°) (Smith & Isaacs, 1964), K<sub>2</sub>Pb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> (3.21 Å, 180°) (Bassi & Lajzerowicz, 1965), Gd<sub>4</sub>(GeO<sub>4</sub>)Ge<sub>3</sub>O<sub>10</sub> (3.13 Å, 120°) (Smolin, Shepelev & Butikova, 1971), and Er<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> (3.256 Å, 136.0°) (Smolin, 1970). No simple rationalization in electronic terms seems possible.

The six independent Ge—C distances span the range 1.934 (5)–1.951 (5) Å with a mean of 1.942 (3) Å: consequently, the wide range of 0.17 Å of those reported by Kuz'mina & Struchkov (1972) (1.86, 1.93, 1.98, 1.99, 2.01 and 2.03 Å; mean 1.96, Å) must be regarded as an artefact of the imprecise determination. The values found here are closely comparable with those observed in Ph<sub>4</sub>Ge (Chieh, 1971; Karipides & Haller, 1972), (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Ge (Karipides, Forman, Thomas & Reed, 1974), Ph<sub>3</sub>GeCOCH<sub>3</sub> (Harrison & Trotter, 1968), (Ph<sub>2</sub>Ge)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>7</sub> (Elder, 1969), and (Ph<sub>2</sub>GeOH)PhPt(PEt<sub>3</sub>)<sub>2</sub> (Gee & Powell, 1971). The small overall range of Ge—C(aryl) distances (0.035 Å) is not mirrored by Ge—C(methyl) distances which range from 1.89 (3) Å in MeGeBr<sub>3</sub> (Drake, Hemmings, Hencher, Mustoe & Shen, 1976) to 2.08 (3) Å in (μ-Me<sub>2</sub>Ge)<sub>2</sub>[Fe(CO)<sub>3</sub>]<sub>2</sub> (Elder & Hall, 1969).

Within the phenyl groups, which are all strictly planar within experimental error (see Table 5), the C—C distances are not all equivalent: assuming local *mm*2 symmetry for each ring (Domenicano, Vaciago & Coulson, 1975a), and averaging the six rings together, C(1)—C(2)(mean) is 1.391 (1) Å, C(2)—C(3)(mean) is

1.395 (2) Å, and C(3)—C(4)(mean) is 1.366 (4) Å. The shortening of the C(3)—C(4) bond is a general phenomenon, usually ascribed to thermal motion (Goldstein, Seff & Trueblood, 1968). The internal angles at C(1) are all less than 120°, ranging from 117.5 (5) to 118.7 (5) [mean 118.2 (2)°]; similar values are found in Ph<sub>4</sub>Ge [117.9 (4) (Chieh, 1971) and 118.4 (4)° (Karipides & Haller, 1972)], Ph<sub>3</sub>GeCOCH<sub>3</sub> [118.3 (2)° (Harrison & Trotter, 1968)], and (Ph<sub>2</sub>GeOH)PhPt(PEt<sub>3</sub>)<sub>2</sub> [118.4 (11)° (Gee & Powell, 1971)]. The variation with substituent of the internal angle, α, at C(1) has been discussed in terms of the electronegativity coefficient χ of the substituent and a linear relationship derived (Domenicano, Vaciago & Coulson, 1975b). By contrast, the value of α in (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Ge is rather smaller, 115.6 (4)°, similar to values found in (C<sub>6</sub>F<sub>5</sub>P)<sub>4</sub> (Sanz & Daly, 1971) [115.3 (2)°], C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>Fe(CO)<sub>2</sub>C<sub>5</sub>H<sub>5</sub> (Redhouse, 1974) [114 (2)°], and C<sub>6</sub>F<sub>5</sub>COOH (Benghiat & Leiserowitz, 1972) [116.7 (10)°].

The shortest intramolecular contacts (Table 6) are between O and *ortho* H atoms. All the shortest intermolecular distances (Table 7) involve at least one H atom: the shortest intermolecular distance not involving a H atom is C(213)...C(213<sup>v</sup>) (3.41 Å) through a centre of symmetry. There are no short (<3.4 Å) intermolecular distances involving O.

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## The Crystal and Molecular Structure of Oxobis[triphenylsilicon(IV)]

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Crystals of oxobis(triphenylsilicon),  $O(\text{SiPh}_3)_2$ , are triclinic, space group  $P\bar{1}$ ,  $a = 11.301(2)$ ,  $b = 9.539(2)$ ,  $c = 8.771(2)$  Å,  $\alpha = 66.34(1)$ ,  $\beta = 114.35(1)$ ,  $\gamma = 114.24(1)^\circ$ ,  $Z = 1$ . The structure was solved by direct methods using diffractometer data and refined by full-matrix least squares to  $R = 0.0374$ . The molecules are centrosymmetric, so that the SiOSi fragment is strictly linear: principal interatomic distances are Si–O 1.616(1) Å, and Si–C 1.864(5) Å; the central  $\text{C}_6\text{Si}_2\text{O}$  part of the molecule exhibits almost exact  $3m$  symmetry.

### Introduction

The bond angles at O in the Si ethers  $O(\text{SiH}_3)_2$  (Almenningen, Bastiansen, Ewing, Hedberg & Trætterberg, 1963),  $O(\text{SiF}_3)_2$  (Airey, Glidewell, Rankin, Robiette, Sheldrick & Cruickshank, 1970), and  $O(\text{SiCl}_3)_2$  (Airey, Glidewell, Robiette & Sheldrick, 1971) are 144.1, 155.7 and  $146^\circ$  respectively, each markedly greater than the value of  $ca\ 110^\circ$  expected from the VSEPR model. The structures were determined by gas-phase electron diffraction, and hence the angles quoted represent a mean over all the thermally populated vibrational states: in the case of  $O(\text{SiF}_3)_2$  [but not  $O(\text{SiH}_3)_2$ ] the possibility that the molecule has a linear ground vibrational state could not be ruled out, the observed non-linearity then being a consequence of a very low SiOSi bending frequency. It has been suggested (Glidewell, 1975) that the observed angles in these ethers are limited primarily by the non-bonded Si...Si distance. As part of a structural study of oxo and hydroxo compounds, we have investigated the

solid-state structure of a related Si ether, oxobis(triphenylsilicon),  $O(\text{SiPh}_3)_2$ , whose crystal and molecular structure is reported here.

### Experimental

#### Preparation

Oxobis[triphenylsilicon(IV)] was prepared by a method analogous to that used for the preparation of oxobis[ $\alpha$ -naphthylphenylmethylsilicon(IV)] (Sommer, Frye & Parker, 1964).

To a solution of hydroxotriphenylsilicon(IV) (2.0 g, 7.2 mmol) in dry toluene (30 cm<sup>3</sup>) was added excess powdered potassium hydroxide (7 g). The mixture was shaken vigorously for 10 min, then allowed to stand for several hours. The excess KOH was removed by filtration. A solution of chlorotriphenylsilicon(IV) (2.1 g, 7.2 mmol) in dry toluene (20 cm<sup>3</sup>) was added to the filtrate and the reaction was allowed to stand (2 h). The precipitate of KCl so formed was separated using a centrifuge. The supernatant solution was reduced in

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