equivalent, as would be expected, because interconversion would involve only slight positional shifts.

The crowding of the molecules can be viewed in an alternative way, considering the non-bonded O···O distances. The normal minimum for this is 2·75 to 2·8 Å, and in the acetate the minimum values for the four molecules are 2·69, 2·63, 2·74 and 2·79 Å, reflecting the overcrowding; in the nitrate, with shorter Sn—O, the minimum O···O is 2·72 Å.

The effect of further crowding can be seen in the structure of the $Sn(OAc)_5^-$ ion (Alcock & Tracy, 1976). For this to be eight-coordinate, it would need three bidentate and two unidentate acetate groups; compared to the tetraacetate, this would correspond to the replacement of one bidentate ligand of bite 2·23 Å with one of bite 2·8 Å (*i.e.* an unconstrained pair of donor atoms). This produces too much overcrowding; the effect is that one atom is extruded, and the coordination drops to seven with two bidentate and three unidentate ligands.

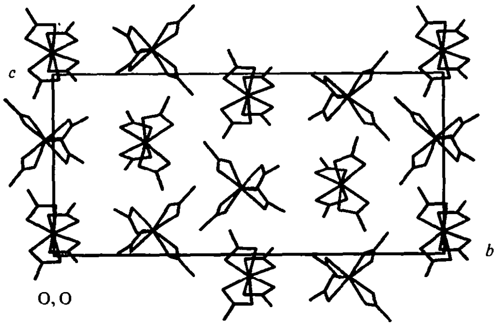

Fig. 2. Packing diagram, viewed down *a*.

Packing

Fig. 2 shows the packing. There are no very close interactions, and it is not possible to see just which interactions are responsible for the subtle difference in geometry between the four molecules, although these can certainly be attributed to packing effects. It also seems probable that it is the ability of the molecules to distort slightly in a variety of ways that causes the complex crystal structure with four different geometries, rather than the higher symmetry and more regular packing that would be usual.

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The Crystal and Molecular Structure of Triphenylgermanium Bromide

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Abstract

$(C_6H_5)_3GeBr$ is monoclinic, space group $P2_1/c$, a = 18·770 (4), b = 9·662 (3), c = 18·467 (4) Å, β = 106·84 (8)°, Z = 8. The structure was refined to R = 0·054 for 2304 counter reflections ($I > 3\sigma$). Eight discrete molecules are contained in the unit cell, comprising asymmetric units of two slightly distorted tetrahedral molecules, with slightly different orientations of the phenyl ligands. The principal geometrical parameters are: Ge—Br = 2·320 (3); Ge—C = 1·935 (10) Å; Br—Ge—C = 106·3 (4); C—Ge—C = 109·9 (4) to 114·5 (4)°.

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Introduction

As part of a study of coordinative and structural correlations in organocompounds of Group IV*b* elements we recently determined the structures of Ph_3PbX (Ph = C_6H_5, X = Cl, Br) (Preut & Huber, 1977). These compounds in the crystalline state are halide-bridged polymers with Pb showing coordination number 5 and with essentially planar Ph_3Pb units. This result prompted us to examine if X also links M atoms in analogous compounds of the lighter group-elements and how the geometry of the Ph_3M unit varies with M or X. The present paper reports the structure of Ph_3GeBr.

Experimental

Single crystals of Ph_3GeBr were obtained from Alfa Inorganics Ventron. A crystal 0·28 [101] × 0·37 [010] × 0·26 [10$\bar{1}$] mm was used for data collection. The observed absences 0*k*0 for $k = 2n + 1$ and *h*0*l* for $l = 2n + 1$ gave the space group $P2_1/c$. The cell parameters were determined at room temperature by a least-squares refinement of the angular settings of 23 reflections ($10 < \theta < 15°$, Hilger & Watts four-circle diffractometer, graphite monochromator, Mo $K\alpha$ radiation, λ = 0·70926 Å, scintillation counter). The intensities of 2304 reflections ($I > 3\sigma$) with $2 \leq \theta \leq 25°$ were measured by the $2\theta/\omega$ scan technique with a scan width $\Delta 2\theta$ (°) = 1·34 + 0·34 tg θ from background to background and a scan speed of 0·02° s^{-1} in 2θ. Backgrounds were measured at each end of the scan range for 7 s. Corrections were made for Lorentz and polarization effects but none for absorption.

Table 2. *Bond distances* (Å) *and angles* (°)

Ge(1)–Br(1)	2·318 (3)	Br(1)–Ge(1)–C(13)	106·1 (4)
Ge(1)–Br(2)	2·322 (3)	C(1)–Ge(1)–C(7)	112·8 (4)
Ge(1)–C(1)	1·939 (10)	C(1)–Ge(1)–C(13)	114·5 (4)
Ge(1)–C(7)	1·936 (10)	C(7)–Ge(1)–C(13)	109·9 (4)
Ge(1)–C(13)	1·927 (10)	Br(2)–Ge(2)–C(19)	106·9 (4)
Ge(2)–C(19)	1·934 (10)	Br(2)–Ge(2)–C(25)	105·2 (4)
Ge(2)–C(25)	1·933 (10)	Br(2)–Ge(2)–C(31)	106·7 (4)
Ge(2)–C(31)	1·941 (10)	C(19)–Ge(2)–C(25)	112·8 (4)
Br(1)–Ge(1)–C(1)	106·1 (4)	C(19)–Ge(2)–C(31)	110·9 (4)
Br(1)–Ge(1)–C(7)	106·9 (4)	C(25)–Ge(2)–C(31)	113·7 (4)

Table 1. *Final atomic positional parameters* (× 10^4) *with e.s.d.'s in parentheses*

	x	*y*	*z*
Ge(1)	495 (1)	601 (2)	1725 (1)
Ge(2)	5549 (1)	1818 (2)	1872 (1)
Br(1)	926 (1)	2369 (2)	1115 (1)
Br(2)	6011 (1)	−31 (2)	1344 (1)
C(1)	−579 (7)	780 (17)	1426 (6)
C(2)	−983 (7)	935 (17)	667 (6)
C(3)	−1754 (7)	1104 (17)	466 (6)
C(4)	−2121 (7)	1118 (17)	1024 (6)
C(5)	−1717 (7)	963 (17)	1783 (6)
C(6)	−946 (7)	794 (17)	1984 (6)
H(2)	−700 (7)	926 (17)	235 (6)
H(3)	−2068 (7)	1208 (17)	−120 (6)
H(4)	−2718 (7)	1228 (17)	869 (6)
H(5)	−2000 (7)	967 (17)	2216 (6)
H(6)	−631 (7)	685 (17)	2572 (6)
C(7)	943 (7)	870 (13)	2800 (7)
C(8)	1277 (7)	2114 (13)	3102 (7)
C(9)	1582 (7)	2257 (13)	3882 (7)
C(10)	1553 (7)	1155 (13)	4361 (7)
C(11)	1220 (7)	−88 (13)	4060 (7)
C(12)	914 (7)	−231 (13)	3279 (7)
H(8)	1298 (7)	2965 (13)	2729 (7)
H(9)	1840 (7)	3225 (13)	4114 (7)
H(10)	1791 (7)	1275 (13)	4967 (7)
H(11)	1199 (7)	−935 (13)	4435 (7)
H(12)	657 (7)	−1195 (13)	3051 (7)
C(13)	853 (7)	−1094 (13)	1407 (7)
C(14)	1620 (7)	−1288 (13)	1565 (7)
C(15)	1897 (7)	−2547 (13)	1395 (7)
C(16)	1409 (7)	−3612 (13)	1067 (7)
C(17)	643 (7)	−3418 (13)	908 (7)
C(18)	365 (7)	−2159 (13)	1078 (7)
H(14)	1997 (7)	−463 (13)	1822 (7)
H(15)	2493 (7)	−2688 (13)	1512 (7)
H(16)	1629 (7)	−4579 (13)	925 (7)
H(17)	269 (7)	−4245 (13)	647 (7)
H(18)	−226 (7)	−2020 (13)	957 (7)
C(19)	5919 (5)	3488 (10)	1529 (5)
C(20)	6686 (5)	3712 (10)	1740 (5)
C(21)	6969 (5)	4941 (10)	1539 (5)
C(22)	6485 (5)	5946 (10)	1126 (5)
C(23)	5718 (5)	5722 (10)	915 (5)
C(24)	5435 (5)	4493 (10)	1116 (5)
H(20)	7057 (5)	2936 (10)	2065 (5)
H(21)	7566 (5)	5109 (10)	1706 (5)
H(22)	6714 (5)	6887 (10)	961 (5)
H(23)	5353 (5)	6492 (10)	576 (5)
H(24)	4844 (5)	4320 (10)	935 (5)
C(25)	4478 (5)	1651 (12)	1499 (5)
C(26)	4142 (5)	1489 (12)	724 (5)
C(27)	3370 (5)	1385 (12)	444 (5)
C(28)	2933 (5)	1442 (12)	940 (5)
C(29)	3268 (5)	1604 (12)	1714 (5)
C(30)	4041 (5)	1708 (12)	1994 (5)
H(26)	4481 (5)	1446 (12)	342 (5)
H(27)	3111 (5)	1265 (12)	−156 (5)
H(28)	2333 (5)	1364 (12)	719 (5)
H(29)	2927 (5)	1643 (12)	2094 (5)
H(30)	4297 (5)	1824 (12)	2594 (5)
C(31)	5938 (6)	1623 (9)	2962 (5)
C(32)	6299 (6)	432 (9)	3312 (5)
C(33)	6566 (6)	368 (9)	4099 (5)
C(34)	6473 (6)	1494 (9)	4536 (5)
C(35)	6112 (6)	2684 (9)	4185 (5)
C(36)	5845 (6)	2748 (9)	3398 (5)
H(32)	6370 (6)	−438 (9)	2973 (5)
H(33)	6849 (6)	−553 (9)	4370 (5)
H(34)	6685 (6)	1442 (9)	5146 (5)
H(35)	6042 (6)	3553 (9)	4526 (5)
H(36)	5564 (6)	3669 (9)	3130 (5)

The positions of the atoms were obtained from Patterson and Fourier syntheses. The structure was refined by a full-matrix least-squares calculation. The phenyl rings were treated as rigid hexagons (C—C—C = 120°, C—C = 1·395, C—H = 1·080 Å) with individual isotropic temperature factors for C and H. With anisotropic temperature factors for the Ge and Br atoms the final R (= $\sum \Delta / \sum |F_o|$, where $\Delta = ||F_o| - F_c|$) = 0·054. 88 structural parameters were determined from 2304 intensities, a ratio of 16·5. The positional parameters are shown in Table 1, the bond lengths and angles in Table 2.*

The structure solution and refinement were carried out with *SHELX* (Sheldrick, 1976). In addition *ORTEP* (Johnson, 1965) was used. For Ge, Br, and C the scattering factors of Cromer & Mann (1968) and of Cromer & Liberman (1970), and for H of D. T. Cromer (personal communication to G. M. Sheldrick) were used.

Results

Crystal data are shown in Table 3. The cell contains eight discrete molecules. A stereoscopic view of the contents of the cell is presented in Fig. 1. A view of the two independent molecules and the atom numbering are presented in Fig. 2. The two independent molecules are essentially identical, if one considers only the geometry of the Ge atom and the atoms bound to it. From the slight deviations of the angles C—Ge—C and C—Ge—Br from the regular tetrahedral value it is apparent that more volume is required in the immediate bonding sphere around Ge by each phenyl group than by the Br ligand. The three phenyl groups are arranged

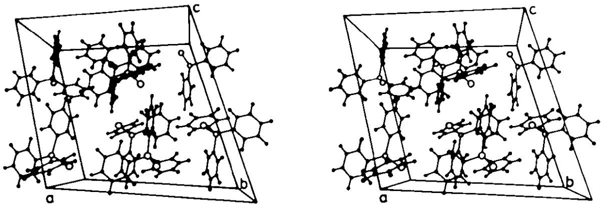

Fig. 1. The packing of the molecules in the unit cell of triphenylgermanium bromide (stereoscopic view).

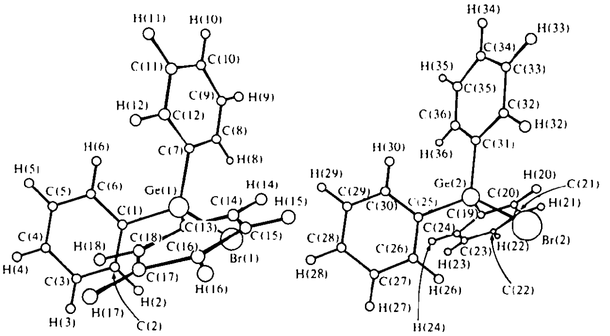

Fig. 2. A perspective drawing of the two molecules in the asymmetric unit of triphenylgermanium bromide and atom-numbering scheme.

Table 3. *Crystal data for* $(C_6H_5)_3GeBr$

a = 18·770 (4) Å
b = 9·662 (3)
c = 18·467 (4)
β = 106·84 (8)°
V = 3205 Å^3
Z = 8

Space group $P2_1/c$
$F(000)$ = 1520
μ(Mo $K\alpha$) = 2·15 mm^{-1}
M_r = 383·82
d_c = 1·59 Mg m^{-3}

Table 4. *Planes, distances of* Ge *therefrom and angles between planes*

Planes are defined in terms of the Cartesian coordinates by $Ax + By + Cz = D$, x parallel a, y in the plane ab and z parallel c^*.

Plane	Atoms	*A*	*B*	*C*	*D*	Ge distance (Å)
I	C(1) to H(6)⁽¹⁾	−0·0943	−0·9922	−0·0820	−0·7854	−0·042 (2)
II	C(7) to H(12)⁽¹⁾	0·9405	−0·3318	−0·0725	−0·3816	−0·026 (2)
III	C(13) to H(18)⁽¹⁾	0·2331	0·3478	−0·9081	−2·4332	−0·133 (2)
IV	C(19) to H(24)⁽¹⁾	0·3131	−0·4274	−0·8481	−0·5096	−0·101 (2)
V	C(25) to H(30)⁽¹⁾	−0·0357	0·9938	−0·1056	1·0320	0·028 (2)
VI	C(31) to H(36)⁽¹⁾	0·9262	0·3752	−0·0387	−9·2395	0·010 (2)
VII	Ge(1), Br(1), C(1)	0·1657	−0·6030	−0·7804	−2·7294	–
VIII	Ge(1), Br(1), C(7)	0·8211	−0·5695	−0·0372	−0·4390	–
IX	Ge(1), Br(1), C(13)	−0·6357	−0·0631	−0·7694	−2·3873	–
X	Ge(2), Br(2), C(19)	−0·6028	0·0284	−0·7974	−8·2637	–
XI	Ge(2), Br(2), C(25)	0·2372	0·5655	−0·7899	0·6127	–
XII	Ge(2), Br(2), C(31)	0·8380	0·5455	−0·0110	8·8110	–

Angles: (I, VII) = 49·7°, (II, VIII) = 15·4°, (III, IX) = 58·1°,
(V, XI) = 50·4°, (VI, XII) = 11·1°, (IV, X) = 61·6°.

(1) Sequence of atoms according to Table 2.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33975 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Comparison of bond distances and angles in phenylgermanium compounds*

In all examples Ge has coordination number 4 with essentially tetrahedral geometry (Et = C_2H_5, Ph = C_6H_5).

Compound	Ge—C (Å)	C—Ge—C (°)	References
$(C_6H_5)_4Ge$	1·957 (4)	109·0 (2)	Karipides & Haller (1972)
$(C_4H_3S)_4Ge$	1·94 (1)	111·5	Haller & Hayes (1977)
$(C_6F_5)_4Ge$	1·957 (4)	105·0 (2), 111·7 (1)	Karipides *et al.* (1974)
$(Et_3P)_2PhPtGePh_2(OH)$	1·975 (12)	104·7 (4)	Gee & Powell (1971)
$[Ge(C_6H_5)_2]_2Fe_2(CO)_7$	1·940 (8) to 1·971 (7)	106·5 (4), 109·3 (4)	Elder (1969)
$(C_6H_5)_3Ge.CO.CH_3$	1·945 (8)	107·4 (6) to 111·4 (6)	Harrison & Trotter (1968)
$O[(C_6H_5)_3Ge]_2$	1·934 (5) to 1·951 (5)	110·2 (2) to 111·8 (2)	Glidewell & Liles (1978)
$(C_6H_5)_3GeBr$	1·935 (10)	109·9 (4) to 114·5 (4)	Present work

in a propeller-like fashion. In Table 4, equations for the planes of the six phenyl rings and the six planes through the atoms Br, Ge and C_i (C_i = C atom through which the appropriate phenyl ring is bound to Ge) are given. The angles between corresponding planes demonstrate that the two molecules are distinguished only by a slightly different orientation of the phenyl rings. The Br ligand is involved in no interaction with a Ge atom of a neighbouring molecule; this is in contrast to Ph_3PbBr, in which the Ph_3Pb unit is essentially planar and each Br bridges two such units (Preut & Huber, 1977). In Ph_3GeBr no contacts between the molecules are less than the sum of the van der Waals radii.

The C—Ge—C angles (mean 112·4°) show significant differences, apparently caused by inter- and intramolecular non-bonding interactions, and agree with those in other Ph_3Ge compounds (Table 5).

Ge—C distances in Ph_3GeBr are essentially the same as in other phenylgermanium compounds (Table 5). The Ge—Br distance, 2·320 (3) Å, is a little shorter than the sum of the covalent radii, 2·36 Å (Pauling, 1960). It does not differ significantly from the Ge—Br distance in $(CH_3)_3GeBr$, 2·323 (1) Å (Li & Durig, 1973).

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