957. *Germanium Esters. Part I. Parachors and Molecular Structure.*

By D. C. BRADLEY, L. J. KAY, and W. WARDLAW.

The alkyl orthogermanates, $Ge(OR)_4$, where R = Me, Et. Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, n-C_5H_{11}, and CMe_2Et, have been prepared either by reactions involving the tetrachloride and the appropriate alcohol in the presence of ammonia or by alcohol interchange. The latter method failed to produce $Ge(OBu^t)_4$ from $Ge(OEt)_4$ owing to steric hindrance. The densities and surface tensions of the germanium esters were accurately measured between 20° and 40° and molecular volumes and parachors were calculated. The parachors, analysed by Gibling's method, showed considerable deviations from additivity which were identified by conformational analysis with volume losses caused by overlap of van der Waals fields in the preferred conformations. Parachor data on normal alkyl orthocarbonates and orthosilicates were similarly considered.

THIS work was initiated to try to establish the structural behaviour of compounds having the molecular formula $M(OAlk)_4$, where M is a central atom linked tetrahedrally to oxygen. In particular, information on systems containing no major intermolecular bonding between metal and oxygen was required and compounds of carbon, silicon, and germanium appeared to satisfy this requirement. Germanium esters were chosen first because little is known of their physicochemical properties and secondly because we were able to prepare esters containing primary, secondary, or tertiary alkyl groups whereas the preparation of branched-chain orthocarbonates or orthosilicates is difficult owing to steric hindrance.

The esters $Ge(OR)_4$, where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, n-C_5H_{11}, and CMe_2Et, were prepared and their densities and surface tensions were measured over the range 20—40°. Their preparation either from the tetrachloride by the ammonia method or by alcohol interchange has been mentioned in a preliminary note [1] but we have since discovered that the *tert.*-butoxide cannot be obtained by interchange from the ethoxide, the reaction stopping at the formation of $Ge(OEt)(OBu^t)_3$ which is resistant to further interchange with *tert.*-butyl alcohol, undoubtedly for steric reasons.

TABLE 1.

R in $Ge(OR)_4$ ...	Me	Et	Pr^n	Pr^i	Bu^n	Bu^i	Bu^s	Bu^t *	n-C_5H_{11}	CMe_2Et
d_{25}	1·3244	1·1288	1·0565	1·0245	1·0167	1·0054	1·0164	1·0574	0·9941	1·0425
γ_{25}	22·49	23·23	23·61	20·76	24·00	23·25	23·47	22·74	24·18	23·39
V_{25}	148·5	224·0	292·5	301·6	358·9	363·1	359·1	345·2	423·8	404·0
$[P]$	323·7	491·9	644·7	643·9	794·6	797·4	790·0	754·5	939·4	888·0
$[P]/V_{25}$	2·18	2·20	2·20	2·13	2·21	2·20	2·20	2·19	2·22	2·20

* M. p. 23·5°.

The densities and the surface tensions of each compound were linear functions of temperature whilst the parachor was independent of temperature. The densities (g./c.c.), molar volumes (c.c.), and surface tensions (dynes/cm.) at 25° together with the mean parachors $[P]$ and the ratio parachor : molar volume (at 25°) are presented in Table 1.

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[1] Bradley, Kay, and Wardlaw, *Chem. and Ind.*, 1953, 746.

The Eötvös constant, $k = -\mathrm{d}(\gamma V^{2/3})/\mathrm{d}T$, was independent of temperature for each compound and suggests that these liquids are unassociated. With regard to the *n*-alkyl orthogermanates, the expected decrease in density and increase in molar volume and parachor with increasing length of alkyl chain is evident in Table 1. The surface tension increases steadily with length of alkyl chain. The isomeric butyl esters form an exceptional group and it is noteworthy that the *iso*butyl derivative has the maximum molar volume and parachor. Moreover, although the surface tension of the *iso*propyl ester is lower than that of the *n*-propyl ester and the *tert.*-amyl ester has a lower value than the *n*-pentyl, there is not a steady change of surface tension with degree of branching in the butyl esters. It appears that some unusual structural factors are brought into operation in passing from the *n*-butyl to the *tert.*-butyl ester. Another feature of Table 1 is the constancy of the ratio $[P]/V_{25}$ since only the *iso*propyl ester differs appreciably from the average value of 2·19.

Although the early enthusiasm for Sugden's parachor diminished later there are signs [2] of renewed interest in this method of comparing molar volumes under standard conditions of intermolecular forces. In particular, Gibling's recent work [3] has shown the potentialities of the parachor as a means of revealing structural abnormalities in liquids. He suggests that the parachor value for an atom is affected by (i) the nature of other atoms bonded to it and (ii) interference from non-bonded neighbouring atoms, and instead of atomic parachors he uses group parachors; he successfully applied this method to a large number of compounds. Although we do not necessarily accept all of Gibling's postulates, in particular the view that interaction involving hydrogen atoms on hydrocarbons can be neglected, the fundamental idea of the group parachor seems reasonable and we have applied Gibling's method to the germanium esters. The following group of reduced parachors [4] were used: $CH_3(C) = CH_3(O) = 55·2$; $(C)CH_2(C) = 39·8$; $(C)CH_2(O) = 39·3$; $(C)_2CH(C) = 22·2$; $(C)_2CH(O) = 21·2$; $(C)_2C(C)_2 = 2·4$ and $(C)_3C(O) = 0·9$. The parachor of each germanium ester was used to determine the reduced parachor (R.P.) of the central group of germanium and four oxygen atoms, *i.e.*, R.P. $Ge[O(C)]_4$. First, the reduced parachor of the ester was calculated by subtracting from the parachor $[P]$ the value of the expansion correction (E.C.) obtained by interpolation from Gibling's table.[4] Then a summation of the group parachors of $CH_3(C)$, $(C)CH_2(C)$, etc., was made to give the reduced parachor of alkyl groups ($\sum$R.P. alkyl) which was then subtracted from the reduced parachor of the ester to give R.P. $Ge[O(C)]_4$. The relevant values are presented in Table 2.

TABLE 2.

R in $Ge(OR)_4$	E.C.	R.P. Ester	ΣR.P. Alkyl	R.P. $Ge[O(C)]_4$	Δ	Δ′
Me	1·0	322·7	220·8	101·9	11·5	—
Et	2·3	489·6	378·0	111·6	1·8	—
Pr^{n}	4·1	640·6	537·2	103·4	10·0	8·2
Pr^{i}	4·1	639·8	526·4	113·4	0	—
Bu^{n}	6·3	788·3	696·4	91·9	21·5	11·5
Bu^{i}	6·4	791·0	687·6	103·4	10·0	—
Bu^{s}	6·3	783·7	685·6	98·1	15·3	—
Bu^{t}	5·6	748·9	666·0	82·9	30·5	—
n-C_5H_4	8·7	930·7	855·6	75·1	38·3	16·8
CMe_2Et	7·8	880·2	825·2	55·0	58·4	—

Ideally the value of R.P. $Ge[O(C)]_4$ should be constant irrespective of the ester and the remarkable variation shown in Table 2 suggests the presence of structural abnormalities associated with alkyl groups. Before interpreting these results it is convenient to give the values for R.P. $C[O(C)]_4$ and R.P. $Si[O(C)]_4$ which we have calculated from the parachor data for *n*-alkyl orthocarbonates and orthosilicates published by Arbusov and Vinogradova.[5] The values are given in Table 3 which also contains values for Δ, the

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[2] Mumford and Phillips, *J.*, 1929, 2112; Vogel *et al.*, *ibid.*, 1943, 333, 363; 1946, 143; 1948, 624; Quayle, *Chem. Rev.*, 1953, **53**, 439; Edward, *Chem. and Ind.*, 1956, 774.

[3] Gibling, *J.*, 1941, 298, 304; 1942, 661, 665; 1943, 146; 1944, 380, 383; 1945, 236.

[4] Gibling, "Molecular Volume and Structure," unbound M.S. presented to Library of Chemical Society, May, 1956.

[5] Arbusov and Vinogradova, *Doklady Akad. Nauk S.S.S.R.*, 1948, **60**, 799.

difference between R.P. $M[O(C)]_4$ for the methyl ester and any other ester, and Δ', which is the increment in ascending the homologous series $M(OC_nH_{2n+1})_4$.

The parachor for the *n*-pentyl orthosilicate was deduced by interpolation from the plot of parachor against number of carbon atoms in the alkyl group for the other esters. The values of Δ in Table 3 show a steady increase with increasing length of alkyl chain and Gibling [4] has previously pointed out a similar behaviour in the case of *n*-alkyl esters of dialkyl carbonates, sulphates, sulphites, phosphates, and phosphites. He attributed this to parallelism of the alkyl chains, and Arbusov and Vinogradova [5] appear to have applied Gibling's method and interpretation to the orthocarbonates and orthosilicates. It is noteworthy that in the dialkyl ethers the only anomaly found by Gibling [4] was a small reduction in parachor with the *n*-butyl groups which was interpreted as a bending back of the alkyl chain bringing the δ-carbon atom closer to the oxygen. It appears that the " parallelism " of *n*-alkyl chains occurs when they are linked by oxygen to another central atom, as in the ortho-esters, but not when linked to the same oxygen atom, presumably because in the latter case the zig-zag conformation of hydrocarbons is still maintained, *viz.*, (I). Returning to our results in Table 2, it is interesting to note that with the exception of the methyl ester, which is clearly anomalous, the *n*-alkyl germanates show a progressive reduction in R.P. $Ge[O(C)]_4$ with increase in number of carbon atoms in the alkyl chain {the values of Δ are relative to zero for the *iso*propyl ester which has the maximum value for R.P. $Ge[O(C)]_4$}. This behaviour is similar to that of the orthocarbonates and orthosilicates, but it is extremely interesting that in the isomeric butyl germanates reductions also occur in the order $\mathrm{Bu^t} > \mathrm{Bu^s} > \mathrm{Bu^n} > \mathrm{Bu^i}$ with branching of the alkyl group. Moreover, the reduction for the *tert.*-amyl ester is considerably greater than for the *n*-pentyl ester. On the other hand, the *iso*propyl ester (arbitrarily taken as $\Delta = 0$) has a smaller reduction than the *n*-propyl ester. Therefore it is clear that branching of the alkyl chain prevents the parallelism found in *n*-alkyl derivatives, but that extensive branching leads to another type of parachor reduction. With regard to methyl orthogermanate we suggest that this has an anomalous parachor because it gives a value for R.P. $Ge[O(C)]_4$ which is smaller than the corresponding value for $Si[O(C)]_4$ when, from a consideration of atomic radii, it should be greater. Two explanations are possible. Either the methyl orthogermanate molecules are able to pack more closely in the liquid state by virtue of being smaller and more nearly spherical than the higher esters or there may be some intermolecular association involving germanium and oxygen.

TABLE 3.

R in $C(OR)_4$	R.P. $C[O(C)]_4$	Δ	Δ'	R in $Si(OR)_4$	R.P. $Si[O(C)]_4$	Δ	Δ'	R in $Si(OR)_4$	R.P. $Si[O(C)]_4$	Δ	Δ'
Me	77·3	0	—	Me	106·2	0	—	n-C_6H_{13}	86·8	19·4	3·6
Et	76·2	1·1	1·1	Et	105·0	1·2	1·2	n-C_7H_{15}	83·4	22·8	3·4
$\mathrm{Pr^n}$	71·8	5·5	4·4	$\mathrm{Pr^n}$	98·7	7·5	6·3	n-C_8H_{17}	81·2	25·0	2·2
$\mathrm{Bu^n}$ ...	66·8	10·5	5·0	$\mathrm{Bu^n}$	96·4	9·8	2·3	n-C_9H_{19}	74·1	32·1	7·1
				n-C_5H_{11}	90·4	15·8	6·0	n-$C_{10}H_{21}$	73·0	33·2	1·1

The enormous parachor reductions for the *tert.*-butyl and *tert.*-amyl esters prompted us to set up atomic models for germanium esters. The following bond lengths were used: C–C = 1·54 Å, C–O = 1·43 Å, and Ge–O = 1·72 Å, the last value being derived by application of the electronegativity correction [6] to the sum of the covalent atomic radii (Ge = 1·22 Å, O = 0·66 Å). It was further assumed that the angles ∠OGeO, ∠GeOC, and ∠OCC were all tetrahedral. These models showed clearly that in the highly branched esters rotation of alkoxide groups was severely restricted and that for all conformations of each molecule there was considerable overlap of the van der Waals volumes of the atoms. Accordingly we have attempted to measure the decrease in volume due to this overlap by measuring interatomic distances in these models in conformations of minimum intramolecular congestion. Using the van der Waals radii CH_3 = 2·0 Å, O = 1·4 Å, and Ge = 2·02 Å, we then calculated the volume of the two spherical caps produced by intersection of the van der Waals spheres of interacting atoms or groups and this gave the

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[6] Wells, " Structural Inorganic Chemistry," Oxford Univ. Press, 1945, p. 81.

volume (in Å^3) lost by overlap or interference of non-bonded atoms. An approximate relation between volume in Å^3 and parachor units was derived as follows. Gibling[4] has calculated the reduced parachor of methane to be 68·4 units. If it be assumed that methane consists of a hexagonal close-packed array of molecules of radius 2·0 Å then the volume occupied by a molecule is $5{\cdot}66 \times 2{\cdot}0^3 = 45{\cdot}3$ Å^3 $\equiv$ 68·4 parachor units, whence 1 Å^3 $\equiv$ 1·5 parachor units. Alternatively we may choose an imaginary germanium ester molecule occupying a volume = 1 Å^3 = 10^{-24} c.c. at 25°. Then 1 mole would occupy 0·6025 c.c. However, it is clear from Table 1 that for most germanium esters the ratio of the parachor to molar volume (at 25°, in c.c.) is 2·2 : 1 and hence 1 Å^3 = $2{\cdot}2 \times 0{\cdot}60$ = 1·3 parachor units. It appears that a value of 1 Å^3 $\equiv$ 1·4 parachor units is of the right order of magnitude.

Methyl Esters.—Inspection of models shows that rotation of alkoxide groups around the oxygen–central atom bond is restricted even in the methyl esters and especially for methyl orthocarbonate. For example, the conformation having the maximum separation of methyl groups from neighbouring alkoxide oxygen atoms on the same molecule is the one with the methyl group staggered with respect to two neighbouring oxygen atoms. The interatomic distances between carbon and oxygen are then : orthocarbonate, 2·75 Å; orthosilicate, 3·0 Å; and orthogermanate, 3·14 Å; all these are considerably less than the sum of the van der Waals radii of oxygen and the methyl group (3·4 Å). Moreover each methyl group interacts with two others since the intercarbon distance (*ca.* 3·5 Å) is less than the van der Waals distance (4·0 Å). Further interaction occurs between methyl groups and the central atom and it is clear that considerable " loss of volume " occurs in the methyl esters. The total loss of volume will not differ greatly between the staggered or the eclipsed methyl . . . oxygen conformations because the smaller specific loss involved in the former is offset by the existence of twice as many interactions as in the latter. Thus the calculated total volume losses in the methyl orthocarbonate are : staggered Me . . . O, 3·1 Å^3; eclipsed Me . . . O, 4·4 Å^3. For methyl orthogermanate the corresponding values are 0·59 Å^3 and 0·73 Å^3 and similar values would be expected for methyl orthosilicate. However, these values are automatically included in the values of R.P. $C[O(C)]_4$ and R.P. $Si[O(C)]_4$ and will not affect values of Δ in Table 3.

Normal Alkyl Esters.—Inspection of the increments Δ' in Tables 2 and 3 reveals some interesting differences between the *n*-alkyl ortho-carbonates, -silicates, and -germanates. A striking feature is the much greater increments for the orthogermanates than the corresponding increments in the other series. Furthermore, it is evident from the Δ' values for the orthosilicates that the increment is not constant for this series but shows a distinct alternation in value. The average value of Δ' (even number of carbon atoms in alkyl group) is 2·1 units whilst for Δ' (odd numbers) the average is 5·7 units and only in the step from *n*-hexyl to *n*-heptyl is there a discrepancy from alternation. It should be pointed out that an error of 0·1% in the parachor value will correspond to an error in R.P. $Si[O(C)]_4$ of 0·5 unit for $Si(OEt)_4$, 1·0 unit for $Si(OC_6H_{13})_4$ and 1·7 units for $Si(OC_{10}H_{21})_4$, so that the alternation in Δ' values is significant compared with probable experimental error. On the other hand the values of Δ' for the *n*-alkyl orthocarbonates and orthogermanates show a continuous increase in the increment with length of alkyl chain. Arbusov and Shavsa[7] have deduced from dipole-moment measurements that the rotation of the alkoxide groups is much more restricted in the orthocarbonates than in the orthosilicates whilst Moore, Gibbs, and Eyring[8] suggest that the straight-chain hydrocarbons up to $C_{10}H_{22}$ are essentially in the zig-zag conformation and rotating about the long axis above about room temperature. It seems likely that the restricted rotation in the orthocarbonates causes the alkyl chains to radiate from the central CO_4 group as zig-zag methylene chains sweeping out a smaller volume than the same number of methylene groups in the freely rotating hydrocarbons. This arrangement should lead to considerable intermolecular entanglement as the chain length increases. In the *n*-alkyl orthosilicates the alkyl chains are rotating more freely than in the orthocarbonates but the alternation in Δ' values suggests that a sinusoidal conformation (II) tends to occur. In this model the methyl groups in

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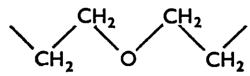
[7] Arbusov and Shavsa, *Doklady Akad. Nauk S.S.S.R.*, 1948, **69**, 599.

[8] Moore, Gibbs, and Eyring, *J. Phys. Chem.*, 1953, **57**, 172.

the *n*-propyl silicate come close to the oxygen atoms (the carbon–oxygen distance is 2·5 Å) causing a volume loss for four chains of 2·4 Å^3 ≡ 3·4 parachor units whilst in the longer chains there will be extra volume losses in the odd-numbered chains owing to the proximity of the carbon atoms (C . . . C, 2·75 Å). The maximum contraction for four groups at each odd-number chain due to the latter effect would be *ca.* 5·4 Å^3 ≡ 7·6 parachor units. An additional factor for the orthosilicates is the partial double-bond character in Si–O bonds due to overlap of a lone electron pair in an oxygen p_π orbital with a vacant d_π orbital of the silicon. This will tend to increase the ∠SiOC angle from the assumed tetrahedral value towards 120° required for sp^2 hybrid bonds between oxygen and its adjacent atoms in (III) and it will impose an added barrier to rotation about the Si–O bond. In fact, Yamazaki [9] has deduced from electron-diffraction studies on methyl orthosilicate that rotation is restricted and the ∠SiOC angle is widened to 113°. This widening will ease the congestion of alkyl groups for the lower alkyl chains and it is possible for reasons not immediately obvious that the partial double bonding is the cause of the alternation effect apparent in the Δ′ values for the orthosilicates. This is consistent with the lack of alternation in the orthocarbonates and orthogermanates because Gordy's [10] deductions from nuclear quadrupole coupling constants for the tetrahalides suggest that double-bonding tendencies are in the order Si > Ge > C. In addition to the sinusoidal tendency of the alkyl chains in alkyl orthosilicates there is the possibility of parallelism of pairs of chains as suggested by Arbusov and Shavsa [7] but in view of the small values of Δ′ compared with those for the germanates it appears that parallelism is much less marked in *n*-alkyl orthosilicates than in *n*-alkyl orthogermanates. Our interpretation of the steadily increasing values of Δ′ for the orthogermanates is that these molecules prefer a conformation in which the alkyl chains are aligned parallel in two pairs disposed in planes approximately at right angles giving an elongated molecule. In building the ethyl orthogermanate molecule from the methyl derivative it is clear that the preferred conformation (IV) of the terminal methyl group is transoid to the Ge–O–CH$_2$ system as shown (two Et groups omitted). The only additional volume loss in (IV) over that for the methoxide is a contribution caused by restricted rotation of the methyl group. Restricted rotation is severe because in conformation (V), with Ge·O·CH$_2$·CH$_3$ in a plane bisecting the line between the nearest two oxygen atoms the distance between methyl and oxygen is 2·66 and between methyl and germanium 2·46 Å. In conformation (VI) the distances are CH$_3$ . . . O, 1·86 and CH$_3$ . . . Ge, 3·0 Å. The total volume losses per molecule would be: (V), *ca.* 13·4 Å^3; (VI), *ca.* 11·8 Å^3. It is difficult to assess the volume loss in (IV) but if the methyl groups are " frozen " in this conformation, a loss of 5·8 Å^3 is estimated as follows. In a zig-zag polymethylene chain the maximum width of chain is 4·89 Å (including van der Waals radii) whilst the minimum width is 4·0 Å. The increment of length along the long axis due to each methylene group is 1·273 Å, hence for a normal hydrocarbon molecule rotating about the long axis a cylindrical volume is swept out and if the cylinders assume closest

(I)



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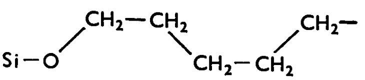

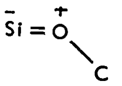

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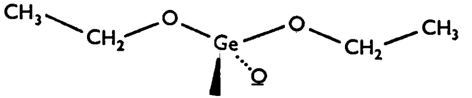

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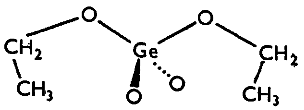

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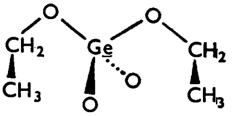

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[9] Yamazaki, Kotera, Yokoi, and Ueda, *J. Chem. Phys.*, 1950, **18**, 1414.

[10] Gordy, *Discuss. Faraday Soc.*, 1955, **19**, 27.

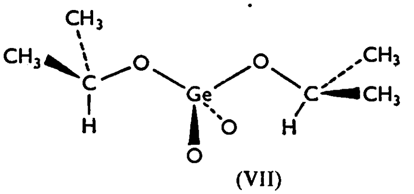
packing the volume per methylene group is $0{\cdot}866 \times 4{\cdot}89^2 \times 1{\cdot}273$ Å^3. When rotation about the long axis is completely restricted and the molecules take up simple cubic packing the volume per methylene group is $4{\cdot}89 \times 4{\cdot}0 \times 1{\cdot}273$ Å^3 and the loss in volume due to the restriction is thus 1·45 Å^3 per methylene group. Hence the major source of volume loss in the *n*-alkyl germanates, if they exist with the alkyl chains in two pairs of parallel zig-zags, will be due to the loss of rotation of these chains relative to free rotation in the hydrocarbons. This would require a volume loss of 5·8 Å^3 $\equiv$ 8·1 parachor units in passing from one homologue to the next whereas Δ' in Table 2 is not constant. This is not surprising because it is obvious from models that the chances of forming parallel chains increase steadily with length of chain. The values of Δ (Table 2) suggest that in the *n*-pentyl ester the chains are in fact close to parallelism since the difference in Δ between *n*-pentyl and ethyl is 36·5 units whereas a value of 32·3 units is calculated by assuming about half rotation of ethyl groups and no rotation of *n*-pentyl groups. Reasonable agreement is also found between experimental and calculated molecular volumes. In one case we have calculated the volume $V_1 = l \times 4{\cdot}9 \times 8{\cdot}0$ Å^3 of a parallelepiped formed by a non-rotating double-chain molecule of height 4·9 Å (for zig-zag polymethylene chain) and width 8·0 Å (for two parallel chains). The length l was measured from models and includes the van der Waals radii of the terminal methyl groups. This model neglects the constriction in the middle of the molecule caused by the GeO_4 grouping. In the second case we assume that the GeO_4 and α-methylene groups form a central box of volume $4{\cdot}78^2 \times 3{\cdot}92 = 89{\cdot}6$ Å^3 to which is added the volume $(2{\cdot}54n' + 4{\cdot}0) \times 8{\cdot}0 \times 4{\cdot}9$ Å^3 to give V_2 where $n' = 1, 2, 3,$ and 4 for Me, Pr^n, Bu^n, and *n*-C_5H_{11}. The results are shown in Table 4; V is the experimental molecular volume (at 25°).

TABLE 4.

R in $Ge(OR)_4$	n'	l (Å)	V_1 (Å^3)	V_2 (Å^3)	V (Å^3)
Et	1	10·46	410·1	346·0	372·0
Pr^n	2	13·00	509·6	445·6	485·4
Bu^n	3	15·54	609·1	545·1	596·0
n-C_5H_{11}	4	18·08	708·8	644·6	703·0

In all cases the experimental values are between V_1 and V_2 and support the theory that the *n*-alkyl germanates assume the non-rotating parallel double-chain conformation as deduced from parachor data. An interesting consequence of this double-chain conformation is that intermolecular entanglement will be minimised, whereas in the orthocarbonates and orthosilicates this effect should be more pronounced. We have already suggested that this entanglement of alkyl chains is responsible for the anomalous entropies of vaporisation of *n*-alkyl orthosilicates[11] and it will be interesting to obtain similar data for the alkyl orthogermanates.

Branched-chain Esters.—Inspection of molecular models shows that (VII) is the conformation having least intramolecular congestion in the molecule of *iso*propyl orthogermanate (two Pr^i groups omitted). In conformation (VII) there is no interference between methyl groups and oxygen whilst there are four methyl–methyl interactions (C . . . C = 3·25 Å) giving a volume loss of 2·16 Å^3 and eight methyl-CH interactions (C . . . C = 3·5 Å) with a loss of 1·92 Å^3 giving a total loss of *ca.* 4·1 Å^3 $\equiv$ 5·7 parachor units greater than in the methyl ester. Rotation of the *iso*propyl group to give conformation (VIII) introduces considerable interaction especially between germanium and the *cis*-methyl groups with a



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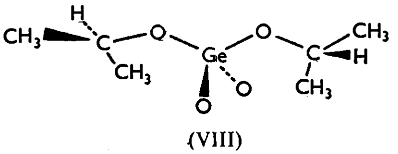

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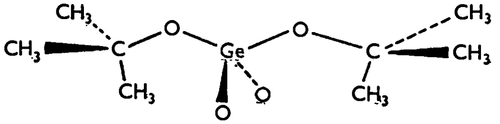
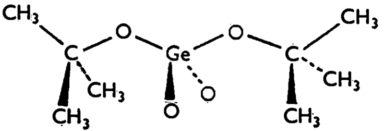
[11] Bradley, Mehrotra, Swanwick, and Wardlaw, *J.*, 1953, 2025.

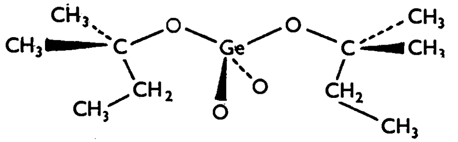
total volume loss of 15·7 $Å^3 \equiv$ 22 parachor units greater than in the methyl ester and it is obvious that conformation (VII) is preferred. It is interesting that the ethyl ester in conformation (IV) with half rotation of ethyl groups has a parachor reduction of 8·1 units which is 2·4 units greater than that of conformation (VII) for the *iso*propyl ester, in reasonable agreement with the experimentally deduced difference of 1·8 units (Table 2). Consideration of the models for the *tert.*-butyl ester shows that considerable intramolecular congestion is inevitable and is a minimum in conformation (IX) (two Bu^t groups omitted). This gives a disc-like molecule with eight "lateral" and four "lineal" methyl groups and the major volume loss occurs from interactions between oxygen and "lineal" methyls (O . . . C = 2·66 Å; volume loss 3·28 $Å^3$) and between lineal methyl groups and germanium (C . . . Ge = 2·46 Å; volume loss 8·97 $Å^3$). Additional smaller losses are caused by interaction between "lateral" methyl groups themselves, between "lateral" and "lineal" methyl groups, between tertiary carbon and "lateral" methyl groups and between tertiary carbon and "lineal" methyl groups giving a total volume loss of 19·5 $Å^3 \equiv$ 27·3 parachor units greater than in the methyl ester. In conformation (X) the volume loss has increased to 41 $Å^3$ = 57·4 parachor units and it is clear that the slightest rotation of either *tert.*-butyl or *tert.*-butoxide groups in conformation (IX) leads to a large decrease in effective volume. In fact the difference between the parachor losses of the *iso*propyl and *tert.*-butyl esters calculated on conformations (VII) and (IX) is 21·6 units compared with $\Delta' = 30{\cdot}5$ from Table 2. This higher value of Δ' may be due to oscillations of the alkyl groups which would cause a greater difference in parachor reductions, but alternatively the approximations involved in our calculations could account for the discrepancy. In either case it seems clear that the surprising parachor reduction in the *tert.*-butyl ester is closely related to the volume loss caused by interaction of the van der Waals fields of several of the atoms. The radial distance from the germanium atom to a "lateral" methyl group in conformation (IX) is *ca.* 5·5 Å (including van der Waals radius of methyl group) and in a freely rotating spherical molecule of this radius the molecular volume would be 942 $Å^3$ for hexagonal closest packing. For a disc-like molecule rotating about the polar (lineal) axis through the germanium atom, the molecular volume for close packing is 650 $Å^3$ (6·2 Å being taken as thickness of disc) compared with the experimental 573 $Å^3$ at 25°. It is clear from this that the *tert.*-butyl ester molecules are disc-like rather than spherical and that rotation of the molecule is severely restricted, although it must be remembered that the experimental molecular volume at 25° is close to the value at the m. p. (23·5°). Inspection of molecular models also confirms the further parachor reduction in passing from the *tert.*-butyl to the *tert.*-amyl ester. If the extra methylene groups are interposed at the "lineal" methyl positions in conformation (IX) of the *tert.*-butoxide, then the methyl groups must take up positions remote from the germanium atom as in (XI). Rotation of the "ethyl"-methyl group around the "lineal" carbon–carbon bond is restricted by the oxygen and germanium atoms and neighbouring "lateral" methyl



(IX)



(X)



(XI)

groups. Hence the methyl group is more or less frozen and this will cause a volume loss of *ca.* 5·8 Å^3 plus the loss of 8·8 Å^3 due to interaction of the " ethyl "-methyl group in the staggered position to the two " lateral " methyl groups, giving a total additional loss in parachor of *ca.* 20·4 units compared with the difference of 28·4 units between the R.P. Ge[O(C)]$_4$ values for *tert.*-amyl and *tert.*-butyl esters. Similar reductions are calculated when the " ethyl " methylene group is placed at a " lateral " position instead of " lineal " in conformation (IX) or in any alternative position in conformation (X) of the *tert.*-butyl ester.

It is also clear why the Δ values for the isomeric butyl orthogermanates are in the peculiar order Bu^t > Bu^s > Bu^n > Bu^i. Thus for the normal isomer the value of Δ (21·5) is near to that calculated for fixed parallel pairs of butyl chains (26·7 units). On the other hand the *iso*butyl derivative (Δ = 10·0) may be considered as built up from the *n*-propyl ester (Δ = 10·0) by adding a methyl group at the 2-position in the *n*-propyl chain without causing any further volume loss. The *sec.*-butyl ester is especially interesting because it appears that optical isomerism in the *sec.*-butoxide group will have an effect on the steric interactions in the *sec.*-butyl germanate. Let us consider the *sec.*-butyl ester as built up by addition of a methyl group to a " lateral " methyl in conformation (VII) of the *iso*propyl ester. If all the *sec.*-butoxide groups are optically of one sign, then however these groups are rotated into conformation (VII) the " ethyl "-methyl groups always clash in pairs. The interaction is minimised when the " ethyl "-methyl groups are nearly *cis* to the alcohol hydrogen and are equidistant (3·5 Å) from a neighbouring " ethyl "-methyl group, a neighbouring " lateral " methylene group and the " lateral " methyl of the same *iso*propyl group. This gives a loss in volume of 5·8 Å^3 to which should be added *ca.* 5·8 Å^3 for restricted rotation of the ethyl groups (as in *tert.*-amyl ester) to make a total of 11·6 Å^3 ≡ 16·2 parachor units of further volume loss compared with the *iso*propyl ester. On the other hand by bending back these ethyl groups the conformation becomes that of the *n*-propyl ester with parallel *n*-propyl chains with methyl substitution at the alcohol carbon atom. The 1-methyl groups interact with one another in two pairs, and with the germanium atom and the alcohol carbon atoms to give a volume loss 3·5 Å^3 ≡ 4·9 parachor units in addition to that of the *n*-propyl ester (10·0) to make a resultant Δ = 14·9 parachor units. The *sec.*-butyl ester used in our work will be a mixture of diastereoisomers with regard to optical sign of the *sec.*-butoxide group but it is interesting that a molecule containing two groups of one sign and two of the opposite sign can assume a conformation based on (VII) in which there is no interaction between " ethyl "-methyl groups and having Δ = 14·3 parachor units. There is another conformation for this molecule having interaction between one pair of " ethyl "-methyl groups which would require a calculated Δ = 15·2 which is near our observed Δ = 15·3 units. On the other hand this molecule cannot assume the parallel chain conformation of the *n*-propyl ester because the 1-methyl groups interfere. It seems possible that different diastereoisomers of the *sec.*-butyl ester might differ in their values of Δ by something of the order of one parachor unit. We intend to test this point experimentally.

Although it cannot be claimed that our analysis of the parachor data has completely elucidated the preferred conformations of these ortho-esters, we feel that this work demonstrates the value of the parachor as a means of interpreting molecular structure especially when Gibling's method of group parachors is applied.

EXPERIMENTAL

Determination of Germanium.—The accurate analysis of germanium presents some difficulties; the problem has been reviewed.[12] In the present work four methods were used and each compound was analysed by at least two of them.

Gravimetric methods. (*a*) The sample (0·05—0·1 g.) was weighed into a prepared silica crucible and hydrolysed with aqueous ammonia (*d*, 0·88; 3 c.c.) and alcohol (1 c.c.). Careful evaporation (under the infrared lamp) of the solution to dryness was followed by ignition (900°)

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[12] Kay, Ph.D. Thesis, London, 1955, 77.

and weighing as GeO_2. This method is only suitable for germanium esters which are chloride-free. (*b*) When chloride was present the germanium was precipitated from dilute sulphuric acid solution as the tannin complex by Holness's procedure.[13] The precipitate must be ignited to GeO_2 very carefully to avoid reduction of the germanium oxide by carbon.

Volumetric methods. (*a*) The sample (0·05—0·1 g.) was dissolved (the higher alkoxides required heating) in a freshly prepared aqueous solution of mannitol (5 g. in water, 20 c.c.) containing alcohol (1 c.c.). The solution was transferred to a potentiometric titration apparatus and the mannitol–germanic acid complex was titrated with sodium hydroxide (0·1—0·01N) with use of a glass electrode–calomel electrode cell. About 3 min. were allowed after each addition of alkali before the potential was measured and a small correction was applied for the acidity of the mannitol. Cluley's method[14] using an indicator did not give reproducible results.

(*b*) As an alternative to (*a*), the mannitol–germanic acid complex was titrated conductometrically with lithium hydroxide solution (*ca.* 0·05N), the end-point being deduced graphically. An advantage of this method was that chloride present could be detected and estimated on the same sample because two distinct end-points were detected.

Preparation of Alkyl Orthogermanates.—As germanium esters are readily hydrolysed, the same precautions were taken in drying apparatus and chemicals as described elsewhere.[15] Germanium tetrachloride [commercial (As $<0·1$ p.p.m.)] was used without further purification.

(a) *Preparation from the tetrachloride.* The alcohol and tetrachloride were dissolved in benzene (*ca.* 150 c.c.) and ammonia was passed in. Although a white cloud then appeared in the vapour space no precipitation occurred until after several minutes an exothermic reaction developed. Such behaviour has not been observed in the corresponding reactions involving titanium, zirconium, niobium, or tantalum chlorides and it appears that the reaction is initiated in the vapour phase. After the ammonium chloride had been filtered off the filtrate was evaporated to dryness and the germanium ester distilled under reduced pressure. In the preparation of the tertiary esters the procedure was modified as follows. The tetrachloride was added with stirring to a solution of the alcohol and pyridine (4 mol./mol. of $GeCl_4$) in benzene (150 c.c.), and reaction was completed by treatment with ammonia. The ester was then isolated as before. The details are given in Table 5 in which all except *n*-alkyl *esters* are new.

(b) *Preparation by alcohol interchange.* The mixture of lower ester, higher alcohol, and benzene (50—100 c.c.) was azeotropically distilled in a column (70 cm.) packed with Fenske glass helices and fitted with a total condensation variable take-off stillhead. A reflux ratio of *ca.* 10 : 1 was used. After removal of solvent, the germanium ester was distilled under reduced pressure. The details are given in Table 5.

TABLE 5.

R in $Ge(OR)_4$	ROH taken (g.)	Starting material		Yield of $Ge(OR)_4$ (g.)	Ge (%)	
		Compd.	Taken (g.)		Found	Calc.
Me	15	$GeCl_4$	20	13	37·0	36·9
Et	20	,,	17	16	28·7	28·7
Pr^n	31	,,	15	18	23·5	23·5
Pr^i	20	$Ge(OMe)_4$	12	17	23·2	23·5
Bu^n	40	$GeCl_4$	14	20	19·9	19·9
,, ...	20	$Ge(OEt)_4$	15	20	19·9	,,
Bu^i	50	$GeCl_4$	16	21	19·9	,,
,, ...	20	$Ge(OPr^i)_4$	14	15	19·9	,,
Bu^s	45	$GeCl_4$	12	17	19·9	,,
Bu^t	50	,,	14	19	19·9	19·9
,, ...	30	$Ge(OEt)_4$	10	12	21·4 *	,,
n-C_5H_{11}	40	$GeCl_4$	11	19	17·2	17·2
,, ...	17	$Ge(OPr^n)_4$	11	13	17·3	,,
CMe_2Et	40	$GeCl_4$	15	23	17·2	,,

* Calc. for $Ge(OEt)(OBu^t)_3$: Ge, 21·5%.

The yields given in Table 5 are based on the distilled ester.

Density Determinations.—An all-glass dilatometer with two limbs of " Veridia " capillary tubing (bore *ca.* 1 mm.) terminating in standard joints (B 10) was used. Each limb (5 cm.

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[13] Holness, *Analyt. Chim. Acta*, 1948, **2**, 254.

[14] Cluley, *Analyst*, 1951, **76**, 523.

[15] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 4204, 5020.

long) had a fiduciary mark about 1 cm. from the lower end of the capillary, and the dilatometer was calibrated with pure mercury to give the volume v_0 below the fiduciary marks and the average volume per cm. length of capillary (weights were corrected for buoyancy). Before each measurement the dilatometer was cleaned first with nitric–chromic acid, next distilled water, then aqueous sodium hydroxide (10% w/v), and finally it was steamed for $\nless$ 1 hr. It was then dried for 1 hr. at 130° and allowed to cool at 0·05 mm. and dry air was then admitted. After storage in a desiccator (30 min.) it was kept in the balance for 30 min. before being weighed. It was essential to adhere to this rigid procedure to obtain accurately reproducible results. The dilatometer was then connected through a B 10 joint (lubricated with high-vacuum Silicone grease) to an all-glass fractional distillation apparatus and the middle fraction of germanium ester was collected under reduced pressure (0·1 mm.). Enough sample (6·5 c.c.) was collected to bring the level of the meniscus in each capillary just above the fiduciary mark. After admission of dry air the dilatometer was detached, the joints were immediately degreased with trichloroethylene, and the apparatus was reweighed. Experiments on the empty dilatometer showed that the greasing and degreasing procedure did not significantly affect the weight of the dilatometer. The joints were then regreased and the dilatometer was completely immersed in a water-bath thermostatically controlled to ±0·1° for 1 hr. before measurement of the heights of the menisci above the fiduciary marks. Measurements were then made at different temperatures in the following order: 20, 25, 30, 35, 40, 45, 42·5, 37·5, 32·5, 27·5, and 22·5°, 1 hr. being allowed at each temperature for attainment of thermal equilibrium. At least two samples of each compound were used and the reproducibility of the results was about 1 in 10^4. Within this limit of accuracy the densities were exactly linear functions of temperature and the results are presented in Table 6 in the form $d_t = d_0 - \alpha t$ where d_t is the density (g./c.c.) at t° and d_0 and α are constants. Our results are in good agreement with the values at 25° reported by Johnson and Fritz[16] for the *n*-alkyl germanates.

Surface Tensions and Parachors.—The apparatus is shown in the Figure. The "Veridia" capillaries were found by the mercury-thread method to be uniform in bore within 0·01%. The cleaning procedure was similar to that used for the dilatometer except that dry steam was found to be better in the steaming out while in the final drying at 0·05 mm. the apparatus was cautiously "flamed." The sample was collected by distillation at 0·1 mm. and the difference in levels of the menisci was measured at the same temperatures as used for the densities. The apparatus was calibrated with pure benzene. At least two samples of each ester were measured, giving meniscus levels in different regions of the capillaries, and the reproducibility was better than 0·5%. Slight exposure of the sample to the atmosphere gave no visible signs of hydrolysis but the surface tension was markedly affected. Within the experimental error the surface tension of each sample was exactly a linear function of temperature and the results in Table 7 are expressed in the form $\gamma_t = \gamma_0 - \beta t$, where γ_t is the surface tension at t° and γ_0 and β are

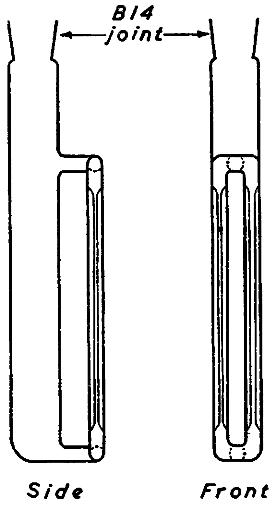

TABLE 6.

R in Ge(OR)$_4$	d_0	α	R in Ge(OR)$_4$	d_0	α
Me	1·3599	0·00142	Pr^i	1·0515	0·00108
Et	1·1592	0·00122	Bu^i	1·0281	0·00091
Pr^n	1·0820	0·00103	Bu^s	1·0396	0·00093
Bu^n	1·0400	0·00093	Bu^t	1·0844	0·00108
n-C_5H_{11}	1·0156	0·00086	CMe_2Et	1·0662	0·00095

TABLE 7.

R in Ge(OR)$_4$	γ_0	β	R in Ge(OR)$_4$	γ_0	β
Me	24·51	0·0810	Pr^i	22·80	0·0815
Et	25·43	0·0880	Bu^i	25·41	0·0865
Pr^n	25·85	0·0895	Bu^s	25·79	0·0930
Bu^n	26·26	0·0905	Bu^t	24·74	0·0800
n-C_5H_{11}	26·43	0·0890	CMe_2Et	25·76	0·0950

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[16] Johnson and Fritz, *J. Amer. Chem. Soc.*, 1953, **75**, 718.

constants. The results for the parachor, $[P] = V_m \gamma^{\frac{1}{4}}$, at different temperatures are given in Table 8 together with the root-mean-square percentage deviations (σ) from the mean values given in Table 1.

From the probable error of up to 0·5% in the surface-tension measurements we should expect error in the parachors to be up to 0·1% and it is clear from Table 8 that for each compound the parachor is independent of temperature within the expected error. It is noteworthy that for the *n*-alkyl esters σ decreases with increase in chain length. This trend is not surprising because the ease of hydrolysis appears to decrease with increase in chain length and it is undoubtedly the susceptibility of these compounds to hydrolysis which is the main cause of experimental error.

TABLE 8.

R in	[P]					
Ge(OR)$_4$	20°	25°	30°	35°	40°	σ
Me	323·2	323·4	323·7	324·0	324·2	±0·11
Et	491·2	491·7	492·0	492·3	492·4	0·09
Pr^n	644·7	644·9	645·0	644·9	644·0	0·06
Bu^n ...	794·8	794·8	794·6	794·4	794·2	0·03
n-C$_5$H$_{11}$	939·9	939·7	939·3	939·3	938·7	0·04
Pr^i ...	643·6	643·9	644·1	643·6	644·3	0·04
Bu^i ...	797·2	797·2	798·7	797·2	796·6	0·09
Bu^s ...	790·8	790·4	790·0	789·8	789·2	0·07
Bu^t ...	—	753·9	754·3	754·0	755·7	0·09
CMe$_2$Et	888·9	888·6	888·0	887·5	886·9	0·08

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