101. *Molecular Volume and Structure. Parts VII and VIII.*

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Part VII.

Slight modification of two group values and one " interference correction " previously assessed is necessitated by recent determinations, and the parachors of aldehydes, ketones, and esters of fatty acids are reconsidered, as well as those of certain esters and ethers containing olefinic groups. Cyclic paraffins and olefins are considered in further detail. The variation of parachor with temperature in the case of certain normal liquids is discussed with special reference to the anhydrides of fatty acids.

Only in one instance have parachor determinations of the last few years necessitated the revision of " group values " calculated in the previous parts of this series: I and II, J., 1941, 299; III and IV, J., 1942, 661; V and VI, J., 1943, 146. Owen, Quayle, and Clegg (*J. Amer. Chem. Soc.*, 1942, **64**, 1294) measured the parachors of 15 alkyl ketones, seven of these being investigated for the first time. Their results, taken in conjunction with the earlier determinations, indicate that the values allotted in Part II for (C)·CO·(C) and (C)·CHO should each be increased by 0·1, thus becoming *51·0* and *67·4*, respectively. With these group values, calculated parachors for 41 normal liquids containing keto-groups agree with the mean observed values within 0·2% on the average. The " standard values " (S.V.) of the compounds containing the above groups (see Part III, pp. 664, 665; Part V, p. 148; Part VI, pp. 149, 150) each require the addition of 0·1 or 0·2 unit.

Sufficient data have now become available to show that the δ-carbon atom in the ethereal oxygen chain of alkyl fatty esters, as well as in the ethers themselves, is *−0·7* (Part V, p. 152). The table " Esters of Fatty Acids " (Part II, p. 307) thus requires extension and amendment as in Table I, in which are also included four esters and two ethers containing olefinic groups. For the last five compounds in this table, it has been assumed that the presence of a double bond in the ethereal oxygen chain does not appreciably affect the correction to be applied.

TABLE I.

Compound.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.
Methyl *iso*butyrate *	252·2	+0·6	252·8	253·3 [2]	+0·2	−2·0 : carb. β
*iso*Amyl formate	293·9	+0·8	294·7	293·65 [2]	−0·4	−0·7 : eth. δ
Butyl acetate	295·1	+0·8	295·9	295·45 [2]†‡	−0·1	,,
*iso*Amyl acetate	332·7	+1·0	333·7	334·35 [2]	+0·2	,,
Amyl acetate	334·9	+1·0	335·9	336·2 ‡	+0·1	,,
*iso*Amyl propionate	370·5	+1·3	371·8	372·1	+0·1	−2·7 : carb. β; eth. δ.
*iso*Amyl butyrate	409·5	+1·6	411·1	409·7 [2]	−0·3	−3·5 : ,, β, γ; ,,
*iso*Amyl stearate	965·0	+9·5	974·5	974·2	−0·0	−5·2 : ,, β, γ, δ; ,,
Allyl acetate	245·0	+0·6	245·6	245·2 §	−0·2	—
αγ-Dimethylallyl formate	282·5	+0·7	283·2	281·6 ‖	−0·6	−0·7 : eth. δ
αγ-Dimethylallyl acetate	321·3	+1·0	322·3	321·2 ‖	−0·3	,,
γ-Methyl-α-ethylallyl acetate	361·1	+1·3	362·4	362·3 §	−0·0	,,
αγ-Dimethylallyl methyl ether	276·4	+0·7	277·1	277·2 ‖	+0·0	,,
αγ-Dimethylallyl butyl ether	394·7	+1·5	396·2	393·8 ‖	−0·6	−1·4 : 2 eth. δ

* Inadvertently omitted from the original table (*q.v.*).

† Washburn and Shildneck (*J. Amer. Chem. Soc.*, 1933, **55**, 2354) : 294·3.

‡ Buehler, Gardner, and Clemens (*J. Org. Chem.*, 1938, **2**, 167), whose results include the following acetates: Et, 216·5; Pr, 257·0; Bu, 296·6; Am, 336·2.

§ Airs, Balfe, and Kenyon (J., 1942, 22).

‖ Hills, Kenyon, and Phillips (J., 1936, 576).

Parachors of simple *cyclo*paraffins, C_nH_{2n}, and *cyclo*olefins, C_nH_{2n-2}, have been determined for $n = 5$—7, as well as parachors of several of their derivatives, and in Part III (*loc. cit.*) those of *cyclo*pentane and *cyclo*hexane and some of their derivatives were considered. So far, no values have been recorded for the parachors of the parent hydrocarbons in which $n = 3$ or 4, or for those of any of their homologues, but certain derivatives have been investigated. Table II gives probable values for (*a*) ring corrections, (*b*) S.V., and (*c*) parachor of the parent hydrocarbon in each case, but data are lacking for *cyclo*propene and *cyclo*butene rings. Parachors asterisked in this table were determined by Vogel (J., 1938, 1323).

TABLE II.

	*cyclo*Paraffins, C_nH_{2n}.			*cyclo*Olefins, C_nH_{2n-2}.		
n.	(*a*).	(*b*).	(*c*).	(*a*).	(*b*).	(*c*).
3	+ 5·9	131·9	132·0	—	—	—
4	+ 0·1	168·1	168·3	—	—	—
5	− 5·4	204·6	205·0 *	− 6·5	192·5	192·8 *
6	−10·7	241·3	241·8 *	−11·1	229·9	230·4 *
7	−15·9	278·1	278·8 *	−15·5	267·5	268·2 *

The above values of (*a*), (*b*), and (*c*) for *cyclo*paraffins lie smoothly on their respective curves, and the ring corrections (*a*) are determinable from the general formula $26{\cdot}1 - 7{\cdot}63n + 0{\cdot}35n^2 - 0{\cdot}016n^3$. The values for *cyclo*butane were obtained by interpolation, their approximate accuracy being indicated by good agreement of three of the four derivatives included in Table III, the calculated and observed parachors in which are supplementary to those given in Part III (*loc. cit.*, p. 662). The compounds in question are (A) methyl and (B) ethyl *cyclo*propane-1 : 1-dicarboxylate, (C) ethyl *cyclo*propane-1 : 2-dicarboxylate, (D) ethyl caronate, (E) *cyclo*-

TABLE III.

Derivatives of *cyclo*paraffins, C_nH_{2n}.

n.	Cpd.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.
3	(A)	337·9	+1·1	339·0	339·3	+0·1	−2·2 : // chains
,,	(B)	414·5	+1·7	416·2	417·1	+0·2	−4·4 : ,,
,,	(C)	421·1	+1·7	422·8	422·8	±0·0	—
,,	(D)	491·1	+2·4	493·5	493·2	−0·1	−5·4 : 2*o*-
,,	(E)	697·1	+4·9	702·0	701·1	−0·1	−14·2 : 2*o*-; // chains
4	(F)	312·7	+0·9	313·6	309·4	−1·3	—
,,	(G)	374·1	+1·4	375·5	374·8	−0·2	−2·2 : // chains
,,	(H)	450·7	+2·0	452·7	454·1	+0·3	−4·4; ,,
,,	(I)	360·7	+1·3	362·0	362·0 *	±0·0	—
				*cyclo*Olefins, C_nH_{2n-2}.			
5	(J)	231·3	+0·5	231·8	232·9	+0·5	—
6	(K)	268·7	+0·7	269·4	269·4	±0·0	—

* [*P*] increased from 358·1 at 13·5°, fairly rapidly at first (to 359·5 at 46°), later more slowly (361·1 at 84·5°, 361·5 at 111·5°) till it had reached 361·7 at 126·5°; extrapolation indicates the calc. value, 362·0.

propane-1 : 1 : 2 : 2-tetracarboxylate, (F) ethyl *cyclo*butanecarboxylate, (G) methyl and (H) ethyl *cyclo*butane-1 : 1-dicarboxylate, (I) ethyl 1-cyano*cyclo*butane-1-carboxylate, (J) 1-methyl-Δ^2-*cyclo*pentene, (K) 1-methyl-Δ^1-*cyclo*hexene. A correction of $-3{\cdot}2$ is made for attachment of a carbon atom to the ring; other corrections applied here or later include *o*-, *m*-, and *p*-corrections (as for the xylenes) and those for parallel chains of carbon atoms (as for alkyl malonates; see Part II, p. 309). Parachors recorded in Table III are by Sugden and Walters (J., **1927**, 139), except those of (A), (G), (J), and (K), which are by Vogel (J., **1934**, 333; **1938**, 1323).

The following table is supplementary to that in Part III (p. 664) in which, as stated before, 0·1 should be added to each S.V.

Cyclic ketone.	S.V.; calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.
1-Methyl-Δ^1-*cyclo*hexen-3-one	277·2	+0·7	277·9	279·0 *	+0·4	−1·7 : *m*-
l-Menthone	400·8	+1·6	402·4	402·15 [2] †	−0·1	−6·6 : *o*-, *m*-, *p*-
dl-*iso*Menthone	400·8	+1·6	402·4	403·25 [2] †	+0·2	,,
dl-Angustione	440·8	+1·9	442·7	442 ‡	−0·2	−24·7 : 4*o*-, 3*m*-, 4*p*-

* Naves and Papazian (*Helv. Chim. Acta*, 1942, **25**, 1046).

† Carter (J., 1927, 1278) : *l*-, 403·2; *dl*-*iso*-, 405·3. Gillespie, Macbeth, and Mills (J., 1940, 280) : *l*-, 401·1; *dl*-*iso*-, 401·2.

‡ Evans and Soper (J., 1931, 289).

It may be noted that the parachor calculated for angustione (I), with its multiple *o*-, *m*-, and *p*-corrections, agrees well with the experimental value.

From the parachor of ethylene oxide, 112·5 (Sugden and Wilkins, J., 1927, 139), the ring correction in this appears to be $-1{\cdot}7$. Thus :

2-CH$_2$-, uncorr. at 42·0 (Part I, p. 302).........	84·0	S.V.	112·4
-O-, ,, 26·7 (Part VI, p. 150)	26·7	E.C.	+0·1
Σ group values	110·7	[*P*]	112·5
Ring correction	+1·7		

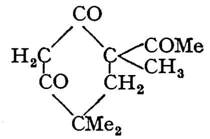
The fact that the parachor of water is greater the more fully its molecules are associated, in contrast to alcohols and phenols, whose parachors decrease with association (Part VI, p. 150), confirms the idea that H_2O molecules tend to associate in *small* rings, for which the increase in volume due to the presence of the ring itself is not swamped by a decrease brought about by interaction of the non-linked atoms of the ring (Part III, p. 661); an alcohol or a phenol, with carbon as well as hydrogen attached to the oxygen atom, tends to form open chains of molecules.

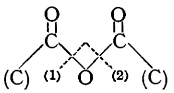
The earliest determinations of parachors showed clearly that those of non-associated substances, such as carbon tetrachloride, ether, ethyl acetate, and nitrobenzene, remained constant over wide temperature ranges. In certain cases, however, parachors of non-associated liquids have been found to vary considerably with temperature, the substances in question usually having molecules which are both polar and flexible.

Lewis's results (J., 1940, 32) show that the parachors of the anhydrides of four of the fatty acids all increase by just over a unit for a rise in temperature of 30° within the range of determination, *viz.*, 15° or 20° to 50°. He remarks that the presence of small traces of the associated acids would contribute to the anomaly, but Sugden's results (J., 1924, **125**, 37; " The Parachor and Valency," 1929, 167) for the parachor of acetic acid at different temperatures suggest that contamination of acetic anhydride with its acid should act in the reverse direction, *i.e.*, tend to reduce the anomaly. Thus, the parachor of acetic acid, treated as being in the dimeric state, increases from 262·6 at 10° to 263·4 at 50°, *i.e.*, only by 0·8, or 0·3%, for a temperature rise of 40°, whereas that of Lewis's acetic anhydride increases from 225·4 at 15° to 226·6 at 50°, *i.e.*, by 1·2, or 0·5%, for a rise of 35°. The parachor values of this series of anhydrides are consistent with each other at any one of the seven or eight temperatures used, and therefore the anomaly would appear to be connected with the structure of the –CO·O·CO·– grouping, the effective value of which seems to vary as follows :

Temp.	15°	20°	25°	30°	35°	40°	45°	50°
S.V.	114·5	114·6	114·7	114·9	115·1	115·3	115·5	115·7

(I.)





(II.)

Using the above group values at the corresponding temperatures, one finds that the 30 parachors calculated show excellent agreement with those recorded, the mean difference being less than 0·1%. Thus, at 20° :

Anhydride.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Diff. in S.V. for 2-CH$_2$-.*
Acetic	225·0	+0·5	225·5	225·6	+0·0	—
Propionic	300·7	+0·9	301·6	301·8	+0·1	2 × 37·8
Butyric	378·7	+1·4	380·1	379·2	−0·2	2 × 39·0
Valeric	454·9	+2·0	456·9	—	—	2 × 38·1
Hexoic	534·4	+2·8	537·2	536·8	−0·1	2 × 39·8

* See Part II, p. 306.

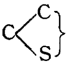
From consideration of the structure of the anhydride group, it is clear that its effective volume contribution will depend upon the relative positions in space of the two carbonyl groups attached to the ethereal oxygen atom, the different possible configurations being obtained by rotation of the attached groups round either of the axes (1) and (2) in (II). Configurations producing least interference (and therefore leading to greatest molecular volume) should be those in which the planes of the two halves of the anhydride group are approximately at right angles to each other (cf. the somewhat similar case of benzil; Part III, p. 665). The more nearly the structure of the group becomes planar, the greater will be the interference, and consequently the smaller the parachor contribution.

In some cases, notably with the *tert.*-alkyl chlorides investigated by Quayle, Owen, and Beavers (*J. Amer. Chem. Soc.*, **1939**, **61**, 3107), parachors of normal liquids have been found to *decrease* with rise in temperature, and in a few cases parachors seem to increase to a maximum value and then decrease with further rise in temperature (Part V, p. 147). Where parachors show a decided drift in one direction or the other, a mean value recorded over some arbitrary range of temperature can obviously have little significance.

PART VIII.

The parachors of alkyl sulphides, thiols, and disulphides are considered, and group values are estimated. It is suggested that the " interference corrections ", varying from member to member, which are required for the parachors of mercury alkylmercaptides, afford evidence as to the structure of these compounds. The structures of alkyl sulphites are similar to those of the corresponding alkyl carbonates, and those of sulphates and phosphates also appear to belong to the same type as the sulphites.

FROM the most recent determinations of the parachors of alkyl sulphides, thiols, and disulphides, standard values for groups have been estimated as follows : (C)·S·(C), *52·0*; (C)·SH, *68·2*; (C)·S·S·(C), *103·1*; (C)·CH_2·(S), *39·3*, whence the correction for the grouping (III) is *−2·7*. These values have been obtained by fixing S.V., $-CH_3$ at 55·2 (see Part II, p. 304). In all three classes of compound the alkyl chain would appear to bend backwards towards the sulphur atom to which it is attached. The " interference corrections " required extend as far as the fifth carbon atom, those for the disulphides necessarily including a correction for the β-carbon atom, due to interaction between this and the second sulphur atom.


(III.)

The CH_2 increments in the series are as follows :

	Et.	Pr.	Bu.	Am.	Hex.
Sulphides and thiols	39·3	38·8	39·2	38·8	39·8, normally
Disulphides...................................	38·4	38·5	39·2	38·8	—

Hence, if normal values are given to the alkyl groups [*viz.*, CH_3·(C), 55·2; (C)·CH_2·(C), 39·8; (C)·CH_2(S), 39·3; $\begin{matrix}(C)\\(C)\end{matrix}\!>\!CH\cdot(C)$, 22·2], the corrections required in the chain are as follows, these applying to only one of the branches in a divided chain :

	—S—	$\overset{\alpha}{CH_2}$	$\overset{\beta}{CH_2}$	$\overset{\gamma}{CH_2}$	$\overset{\delta}{CH_2}$	$\overset{\varepsilon}{CH_2}$—	
Sulphides and thiols				−1·0	−0·6	−1·0;	total, −2·6
Disulphides			−0·9	−1·3	−0·6	−1·0;	,, −3·8

In the following table the results for *iso*propyl and *sec.*- and *tert.*-butyl compounds are omitted, since the exact configurations of the molecules, and consequently the corrections required, are not obvious. The parachors of the sulphides and disulphides were measured by Vogel and Cowan (J., **1943**, 16) and those of the thiols by Mann and Purdie (J., **1935**, 1557), except ethylthiol and phenylthiol, whose parachors were recorded by Sugden, Reed, and Wilkins (J., **1925**, **127**, 1525). In the calculations for phenyl compounds it is assumed that interference between the sulphur atom and the benzene ring necessitates a correction of *−2·7*, *i.e.*, that S.V., C_6H_5·(S) is *189·7* (cf. Part III, p. 664 for oxygen attached to the ring).

Sulphides, R·S·R′.

R and R′.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.
Dimethyl	162·4	+0·2	162·6	163·1	+0·3	—
Methyl ethyl	201·7	+0·4	202·1	201·9	−0·1	—
Diethyl	241·0	+0·5	241·5	241·5	±0·0	—
Methyl *iso*butyl	278·1	+0·7	278·8	279·6	+0·3	−1·0 : Sγ
Methyl butyl	279·7	+0·7	280·4	280·1	−0·1	−1·6 : Sγ, δ
Dipropyl	318·6	+1·0	319·6	318·9	−0·2	−2·0 : S 2γ
Ethyl butyl	319·0	+1·0	320·0	320·3	+0·1	−1·6 : S γ, δ
Di*iso*butyl	393·8	+1·5	395·3	395·4	+0·0	−2·0 : S 2γ
Dibutyl	397·0	+1·5	398·5	399·3	+0·2	−3·2 : S 2γ, 2δ
Di*iso*amyl	472·2	+2·2	474·4	472·9	−0·3	,,
Diamyl	474·6	+2·2	476·8	477·0	+0·0	−5·2 : S 2γ, 2δ, 2ε
Dihexyl	554·2	+3·0	557·2	556·5	−0·1	,,
Diheptyl	633·8	+4·0	637·8	638·4	+0·1	,,
Dioctyl	713·4	+5·2	718·6	718·0	−0·1	,,
Diphenyl..........................	426·6	+1·8	428·4	428·0	−0·1	−4·8 : as 2EtPh

Thiols, R·SH.

R and R′.	S.V., calc.	E.C.	[*P*], calc.	]*P*], obs.	Diff., %.	Corrns. applied.
Ethyl	162·7	+0·2	162·9	162·9	±0·0	—
Amyl	279·5	+0·7	280·2	280·6	+0·1	−2·6 : S γ, δ, ε
Heptyl	359·1	+1·2	360·3	360·3	±0·0	,,
Octyl	398·9	+1·5	400·4	400·2	−0·0	,,
Phenyl	257·9	+0·6	258·5	257·0	−0·6	—

Disulphides, R_2S_2.

R and R′.	S.V., calc.	E.C.	[*P*], calc.	]*P*], obs.	Diff., %.	Corrns. applied.
Methyl	213·5	+0·4	213·9	213·9	±0·0	—
Ethyl	290·3	+0·8	291·1	291·1	±0·0	−1·8 : S_2 2β
Propyl	367·3	+1·3	368·6	368·5	−0·0	−4·4 : S_2 2β, 2γ
*iso*Butyl	441·5	+1·9	443·4	443·4	±0·0	,,
Butyl	445·7	+1·9	447·6	447·7	+0·0	−5·6 : S_2 2β, 2γ, 2δ
*iso*Amyl	520·9	+2·7	523·6	521·2 *	−0·5	,,
Amyl	523·3	+2·7	526·0	524·6 *	−0·3	−7·6 : S_2 2β, 2γ, 2δ, 2ε

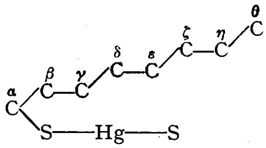
* These parachors increase rather rapidly with rise in temperature : 518·5 (13·4°) to 522·9 (120·2°) and 522·0 (18·5°) to 525·6 (120·7°), respectively.

The interference corrections required by the parachors of mercury *n*-alkylmercaptides suggest, in the liquid state, zig-zag configurations of the alkyl chains on opposite sides of the S–Hg–S nucleus, itself known to have a linear structure (IV) [cf., however, Wells (*Z. Krist.*, 1937, *A*, **96**, 435) on the crystal structures]. Mann and Purdie (*loc. cit.*, p. 1562) recorded the parachors of six members of the series at two temperatures and that of the butyl compound at the higher temperature, 99°, only. Their results show an average increase in parachor of 2·9 per 22° rise in temperature. For purposes of comparison throughout the series, therefore, it is best to consider only the values measured at 99°. In the following table, " S.V., expd." is obtained by addition to the value for the ethyl compound of $2(n - 2) \times 39{\cdot}8$, where n is the number of carbon atoms in each alkyl chain. As might be expected from the configuration suggested, the corrections form two descending series—one for the odd-numbered carbon atoms (−6·1, −4·35, −3·55) and one for the even (−4·3, −3·0, −1·1)—and appear to diminish practically to zero when the eighth carbon atom is reached.

Mercury alkylmercaptides, $Hg(SR)_2$.

R.	[*P*], obs.	E.C.	S.V., obs.	S.V., expd.	Corrn.	Corrn. per C atom.
Ethyl	335·5	−1·1	334·4	(334·4)	—	—
Propyl	403·4	−1·6	401·8	414·0	−12·2	γ, −6·1
Butyl	475·0	−2·2	472·8	493·6	−20·8	δ, −4·3
Amyl	546·6	−2·9	543·7	573·2	−29·5	ε, −4·35
Hexyl	621·1	−3·8	617·3	652·8	−35·5	ζ, −3·0
Heptyl	694·5	−4·7	689·8	732·4	−42·6	η, −3·55
Octyl	773·1	−5·9	767·2	812·0	−44·8	θ, −1·1

The structure of alkyl sulphites (V) resembles that of the carbonates (Part II, p. 308), and the parachor corrections are identical, except that the β-carbon atom in each chain, by its interaction with the sulphite group (which is larger than the carbonate group), produces an interference for which the correction is *−0·8*. In the case of *iso*propyl sulphite, however, the correction is not operative, which suggests that each pair of methyl groups in this molecule is symmetrically arranged with respect to the plane of the SO_3 nucleus. In alkyl sulphates and phosphates, also, the alkyl chains beyond the β-carbon atoms seem to proceed parallel with each other, each pair of corresponding carbon atoms being at such a distance apart as to cause mutual interference necessitating a correction of *−2·2*. As the phosphates contain three alkyl chains, the correction for the interaction of each trio of corresponding carbon atoms beyond β will be *−6·6*. In both cases there is a correction for interference between the β-atom and the SO_4 or PO_4 group : for the former, *−1·1*, and for the latter, *−1·4*. The following are the S.V. of the sulphite, sulphate, and phosphate groups, respectively : (VI), *109·0*; (VII), *127·0*; (VIII), *119·8*. [N.B. S.V., (IX) = 39·4; S.V., (X) = 21·4—see Part II, p. 305]. All the parachor measurements are by Vogel and Cowan (*loc. cit.*, p. 22), who also give details of previous determinations in some cases.



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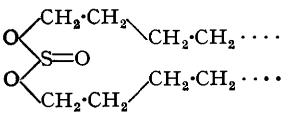

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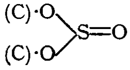

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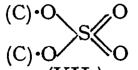
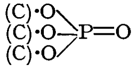


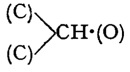
(VII.)



(VIII.)

$(C){\cdot}CH_2{\cdot}(O)$

(IX.)



(X.)

Alkyl sulphites, R_2SO_3.

R.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.
Methyl	219·4	+0·4	219·8	219·7	−0·0	—
Ethyl	296·6	+0·8	297·4	297·6	+0·1	−1·6 : SO_3 2*β*
*iso*Propyl	372·8	+1·3	374·1	374·5	+0·1	—
Propyl	374·0	+1·4	375·4	375·4	±0·0	−3·8 : SO_3 2*β*; // chns.
*iso*Butyl	447·0	+2·0	449·0	450·6	+0·4	−6·0 : ,, ,,
Butyl	451·4	+2·0	453·4	452·5	−0·2	,, ,, ,,
*iso*Amyl	524·4	+2·7	527·1	525·7	−0·3	−8·2 : ,, ,,
Amyl	528·8	+2·8	531·6	532·0	+0·1	,, ,, ,,

Alkyl sulphates, R_2SO_4.

R.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.
Methyl	237·4	+0·5	237·9	237·9	±0·0	—
Ethyl	314·0	+0·9	314·9	316·4	+0·5	−2·2 : SO_4 2*β*
Propyl	391·4	+1·5	392·9	392·2	−0·2	−4·4 : ,, ; // chns.
Butyl	468·8	+2·1	470·9	469·9	−0·2	−6·6 : ,, ,,

Alkyl phosphates, R_3PO_4.

R.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.
Methyl	285·4	+0·8	286·2	286·2	±0·0	—
Ethyl	399·5	+1·5	401·0	399·9	−0·3	− 4·2 : PO_4 3*β*
Propyl	512·2	+2·6	514·8	515·9	+0·2	−10·8 : ,, ; // chns.
Butyl	625·0	+3·9	628·9	629·2	−0·0	−17·4 : ,, ,,

The three pairs of methyl groups at the end of the molecule of an *iso*-alkyl phosphate will presumably take up a symmetrical structure about the axis of the PO_4 group, but the interference corrections involved are not calculable from present data; from the parachors determined for *iso*propyl phosphate (509·9) and *iso*butyl phosphate (625·2), the corrections required (−8·9 and −14·5, respectively) seem to be intermediate between those calculated for the normal isomer and the preceding normal homologue in each case.

New or amended group values recorded in these two parts are as follows : S.V., (C)·CO·(C), 51·0; (C)·CHO, 67·4; (C)·CO·O·CO·(C), varying from 114·5 at 15° to 115·7 at 50°; (C)·S·(C), 52·0; (C)·SH, 68·2; (C)·S·S·(C), 103·1; (C)·CH_2·(S), 39·3; C_6H_5·(S), 189·7; $[(C)\cdot O]_2SO$, 109·0; $[(C)\cdot O]_2SO_2$, 127·0; $[(C)\cdot O]_3PO$, 119·8.

Correction for the grouping $\mathrm{C}{<}^{\mathrm{C}}_{\mathrm{S}}\}$, −2·7.

Corrections for carbon atoms in alkyl chains attached to :

–O– : δ, −0·7. –S– : γ, −1·0; δ, −0·6; ε, −1·0 (total, −2·6).
–S·S– : β, −0·9; γ, −1·3; δ, −0·6; ε, −1·0 (total, −3·8).
–O·SO·O– : β, −0·8 (−2·2 extra for each following pair of C atoms).
–O·SO_2·O– : β, −1·1(−2·2 extra for each following pair of C atoms).
$^{-\mathrm{O}}_{-\mathrm{O}}{>}$PO·O– : β, −1·4 (−6·6 extra for each following trio of C atoms).

Ring corrections : Derivatives of *cyclo*paraffins, C_nH_{2n}, with $n = 3$, +5·9; 4, +0·1; 5, −5·4; 6, −10·7; 7, −15·9; *i.e.*, $26{\cdot}1 - 7{\cdot}63n + 0{\cdot}35n^2 - 0{\cdot}016n^3$. Derivatives of *cyclo*olefins, C_nH_{2n-2}, with $n = 5$, −6·5; 6, −11·1; 7, −15·5.

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