137. *Molecular Volume and Structure. Parts III and IV.*

By T. W. Gibling.

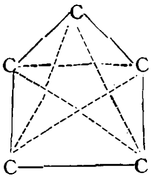
Part III.

The parachors of carbocyclic compounds are considered; ring corrections and interference corrections due to substitution and interaction of groups containing carbon, hydrogen, and oxygen are assessed, and group values calculated. Diminutions in the expected parachors of alkylbenzenes and aromatic ethers are attributed to the polarity of the molecules. The parachor of phenyl carbonate agrees with a structure similar to that of the methyl and the ethyl ester. The skew configuration recently suggested for benzil is confirmed by parachor evidence.

The parachor correction for ring formation may be taken to be the excess of the actual parachor standard value (S.V.) of a simple cyclic compound above the sum of the values of the constituent groups, these being allotted their full values uncorrected for interference. In Part I (J., 1941, 299) it was estimated that the ideal S.V. for $(C)\cdot CH_2\cdot(C)$, uncorrected for interference between the two carbon atoms to which it is attached, is 42·0. Then, for *cyclo*pentane :

S.V., obs.	204·6 (see table, later)
$5(C)\cdot CH_2\cdot(C)$, uncorrected, at 42·0	210·0
*cyclo*Pentane ring correction	−5·4

This correction is really the difference between two quantities : one, greater than 5·4 and of negative sign, representing the diminution in molecular volume caused by the interaction of those carbon atoms which are not linked to each other, and the second, a positive quantity, which measures the increase in volume due to the presence of the ring itself. It follows that in *cyclo*propane, in which all the carbon atoms are linked to each other, the ring correction will be positive. In *cyclo*pentane, with nucleus as inset, there are five equal interference effects, as indicated, and since the angles and distances are approximately those found in an open carbon chain, the total correction for these interferences should be about −2·2 × 5 = −11·0 (see Part I, *loc. cit.*, p. 302). Hence :



*cyclo*Pentane ring correction, observed	− 5·4
Total internal correction	−11·0
Difference due to presence of ring	+ 5·6

Careful determination, or redetermination, of the parachors of several cyclic paraffins and olefins and of certain of their derivatives has been undertaken by Vogel (J., 1928, 2010; 1938, 1323), and the various corrections adopted here are based mainly upon his most recent results. Thus, ring corrections: *cyclo*pentane, $-5{\cdot}4$; *cyclo*hexane, $-10{\cdot}7$. Assuming that no extra correction is required for the fusion of two simple rings (as appears from the parachors of naphthalene and quinoline, recorded later), we may use the following corrections for (*a*) decalin and (*b*) hexahydrohydrindene: (*a*) $-10{\cdot}7 \times 2 = -21{\cdot}4$; (*b*) $-10{\cdot}7 - 5{\cdot}4 = -16{\cdot}1$.

From consideration of the parachors of the simple 5- and 6-carbon *cyclo*-paraffins and olefins and those of their methyl derivatives, it is clear that substitution of CH_3 involves increase in S.V. of *38·8*, the corresponding interference correction being $-3{\cdot}2$ instead of the $-4{\cdot}4$ which might have been expected from comparison with open-chain compounds (see Part I, *loc. cit.*). Substitution of $CH_2{=}$ might be expected to necessitate a similar correction, but for five of the six methylene derivatives of *cyclo*paraffins for which parachors have been determined the correction required seems to be negligible, the increase in S.V. due to substitution of the methylene group being about *31·0*; for methylene*cyclo*hexane, however, the parachor calculated on this basis is 4·5 units above the observed value.

Parachors of cyclic hydrocarbons may be calculated as in the following example, *viz.*, methyl*cyclo*hexane:

$5(C){\cdot}CH_2{\cdot}(C)$, uncorrected, at 42·0	210·0	Σ group values	294·0
$\genfrac{}{}{0pt}{}{(C)}{(C)}{>}CH{\cdot}(C)$, ,, ,, 28·8	28·8	Ring correction	−10·7
$CH_3{\cdot}(C)$,, 55·2	55·2	Side-chain correction	− 3·2

Hence S.V., calc., 280·1; add E.C. ("expansion" correction) 0·7; [*P*], calc., 280·8.

(For group values, etc., used here and in other calculations, see p. 666.)

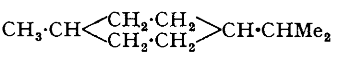
Calculations are often shortened, however, by using normal (corrected) group values for *cyclo*hexyl, etc., which may be obtained as follows:

S.V., methyl*cyclo*hexane	280·1
Deduct $CH_3{\cdot}(C)$ at 55·2	55·2
S.V., *cyclo*hexyl, $C_6H_{11}{\cdot}(C)$	224·9

This is 16·4 units less than S.V., *cyclo*hexane (241·3); hence S.V., *cyclo*hexylene, $(C){\cdot}C_6H_{10}{\cdot}(C)$, $= 224{\cdot}9 - 16{\cdot}4 = 208{\cdot}5$; and so on. Correction for interaction of the two substituted groups may have to be applied subsequently.

The corrections required for 1 : 2-, 1 : 3-, and 1 : 4-substitution by carbon atoms appear to be identical with the *o*-, *m*-, and *p*-corrections for aromatic compounds, *viz.*, *o*-(1 : 2), $-2{\cdot}7$; *m*-(1 : 3), $-1{\cdot}7$; *p*-(1 : 4), $-2{\cdot}2$ (see xylenes, later). In cyclic paraffins and their derivatives it seems probable that these corrections are inoperative if the substituted groups are in the *trans*-position to each other; Gillespie, Macbeth, and Mills (J., 1940, 280) investigated pairs of geometrical isomerides of the *cyclo*hexane series and, in the three cases in which they were dealing with non-associated *p*-substituted compounds, the parachor of the *trans*-compound was about 2 units greater than that of its *cis*-isomer; the actual differences recorded were as follows: *p*-menthane, 2·2; hexahydrocuminic ester, 1·9; dihydrocryptyl acetate, 1·9.

Calculation of the parachor of *cis*-*p*-menthane will serve to illustrate the alternative method suggested above:



$CH_3{\cdot}CH{<}\genfrac{}{}{0pt}{}{CH_2{\cdot}CH_2}{CH_2{\cdot}CH_2}{>}CH{\cdot}CHMe_2$

$(C){\cdot}C_6H_{10}{\cdot}(C)$ at 208·5	208·5	Σ group values	396·3
$3(C){\cdot}CH_3$,, 55·2	165·6	*p*-correction	−2·2
$\genfrac{}{}{0pt}{}{(C)}{(C)}{>}CH{\cdot}(C)$,, 22·2	22·2	S.V., calc.	394·1
		E.C. +1·5; [*P*], calc.	395·6

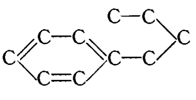
All the determinations in the following table were made by Vogel (J., 1938, *loc. cit.*), except those for 1 : 1-dimethyl*cyclo*hexane (Sugden, J., 1924, **125**, 1177) and the *p*-menthanes (as above). Earlier determinations for several of these hydrocarbons are recorded in Vogel's paper and *Brit. Assoc. Rep.*, 1932, 265.

Hydrocarbon.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.
*cyclo*Pentane	204·6	+0·4	205·0	205·0	±0·0	—
Methylene*cyclo*pentane	235·6	+0·5	236·1	235·3	−0·3	—
Methyl*cyclo*pentane	243·4	+0·5	243·9	243·8	−0·0	—
*cyclo*Hexane	241·3	+0·5	241·8	241·8	±0·0	—
Methylene*cyclo*hexane	272·3	+0·7	273·0	268·5	−1·6	—
Methyl*cyclo*hexane	280·1	+0·7	280·8	280·9	+0·0	—
1-Methyl-3-methylene*cyclo*hexane	309·4	+0·9	310·3	311·0	+0·2	−1·7 : *m*-
1-Methyl-4-methylene*cyclo*hexane	308·9	+0·9	309·8	310·1	+0·1	−2·2 : *p*-
1 : 1-Dimethyl*cyclo*hexane	316·7	+1·0	317·7	316·1	−0·5	— *
cis-*p*-Menthane	394·1	+1·5	395·6	395·6	±0·0	−2·2 : *p*-
trans-*p*-Menthane	396·3	+1·5	397·8	397·8	±0·0	—
2-Methylene-*trans*hexahydrohydrindene	363·1	+1·3	364·4	364·8	+0·1	−3·4 : 2*m*-
2-Methylene-*trans*decalin	399·3	+1·5	400·8	398·5	−0·6	−3·9 : *m*-, *p*-

* In calculating by the shorter method, note that a correction of −2·2 is required for the grouping $C{<}\genfrac{}{}{0pt}{}{C}{C}\}$.

The ring correction for benzene, regarded as possessing the Kekulé structure, may be calculated as follows:

S.V., benzene (see table following)	205·6
6(C)·CH=(C), uncorrected, at 36·5 (Part I, *loc. cit.*, p. 303)	219·0
Benzene ring correction	−13·4



In benzene and its homologues both the lengths of the bonds and the angles beteeen them are different from those found in open-chain olefins. The increase in S.V. from benzene to toluene is *39·8*, instead of the 37·6 found when a primary olefin group is converted into a secondary grouping by substitution of CH_3, *i.e.*, the interference correction due to attachment of a carbon atom to the nucleus is *−2·2*, instead of −4·4. For the next three members in the series of *n*-alkylbenzenes, the Δ_{CH_2} values appear to be *37·4*, *39·2*, and *38·5*, respectively, after which the normal Δ value of 39·8 is found. It seems that the polarity of the molecule comes into play, causing the side chain to bend backwards towards the ring (see inset)—compare the similar effect supposed to be produced by the carbonyl group (Part II, *loc. cit.*, p. 306). For polyalkylbenzenes, *o*-, *m*-, or *p*-corrections are required, as mentioned before.

Group values for phenyl, phenylene, etc., may be obtained (as for *cyclo*hexyl, etc., before). Thus:

S.V., toluene	245·4	This is 15·4 less than S.V., benzene; hence S.V., $(C)\cdot C_6H_4\cdot(C)$, *174·8*; S.V., $\begin{matrix}(C)\\(C)\end{matrix}\!>\!C_6H_3\cdot(C)$, *159·4*.
Deduct $CH_3\cdot(C)$	55·2	
S.V., phenyl, $C_6H_5\cdot(C)$	190·2	

(*o*-, *m*-, or *p*-Corrections may have to be applied subsequently.)

The full group values, uncorrected for outside interference, are as follows: $C_6H_5\cdot(C)$, 192·4; $(C)\cdot C_6H_4\cdot(C)$, 179·2; $\begin{matrix}(C)\\(C)\end{matrix}\!>\!C_6H_3\cdot(C)$, 166·0.

If the normal group values are used (see p. 666), the corrections to be applied in an aromatic side chain will be as follows:

$$C_6H_5\text{———}\overset{\alpha}{C}\text{———}\underbrace{\underset{-2\cdot4}{\overset{\beta}{C}}\text{———}\underset{-0\cdot6}{\overset{\gamma}{C}}\text{———}\underset{-1\cdot3}{\overset{\delta}{C}}}_{\text{Total }-4\cdot3}\text{———}\overset{\epsilon}{C}\text{———}$$

These corrections for the β, γ, and δ carbon atoms are the differences between the Δ values recorded above (37·4, 39·2, 38·5) and the normal Δ value (39·8). Aromatic side-chain corrections, like carbonyl corrections, apply to only one branch in a divided chain.

All the experimental values quoted in the following table are taken from the British Association list (*loc. cit.*).

Aromatic hydrocarbon.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs. (mean).*	Diff., %.	Corrections applied.
Benzene	205·6	+0·4	206·0	206·0[4]	±0·0	—
Toluene	245·4	+0·6	246·0	246·0[5]	±0·0	—
Ethyl-benzene	282·8	+0·8	283·6	283·6[3]	±0·0	−2·4 : Ar.† β
Propyl- „	322·0	+1·0	323·0	322·6[2]	−0·1	−3·0 : Ar. β, γ
Butyl- „	360·5	+1·3	361·8	361·7	−0·0	−4·3 : Ar. β, γ, δ
Amyl- „	400·3	+1·6	401·9	402·0	+0·0	„ „
Hexyl- „	440·1	+1·9	442·0	442·0	±0·0	„ „
o-Xylene	282·5	+0·8	283·3	283·3[2]	±0·0	−2·7 : *o*-
m- „	283·5	+0·8	284·3	284·3[5]	±0·0	−1·7 : *m*-
p- „	283·0	+0·8	283·8	283·8[3]	±0·0	−2·2 : *p*-
Mesitylene	319·9	+1·0	320·9	320·7[2]	−0·1	−5·1 : 3*m*-
p-Ethyltoluene	320·4	+1·0	321·4	321·7	+0·1	−4·6 : Ar. β; *p*-
p-Cymene	358·0	+1·2	359·2	358·8	−0·1	„ „
Naphthalene	311·8	+0·9	312·7	312·5	−0·1	—

* The figures in brackets show the numbers of independent observations upon which the means are based.
† Aromatic side-chain correction (see above).

The parachor of naphthalene agrees very closely with that calculated on the assumption that no appreciable interference effects are involved apart from those produced in ring formation. This assumption is confirmed by the parachors of other substances containing two simple fused-ring systems, *e.g.*, decalin and hexahydrohydrindene and derivatives (see elsewhere in this part), and also by comparison of the parachors of quinoline and pyridine with those of naphthalene and benzene:

	[*P*], obs.	E.C.	S.V., obs.		S.V., calc. (as above).
Quinoline	306·4	−0·9	305·5	Naphthalene	311·8
Pyridine	199·8	−0·5	199·3	Benzene	205·6
Difference			106·2		106·2

For cyclic ketones we have to consider the parachor value of the group (C)·CO·(C). The normal S.V., 50·9, derived from the parachor of acetone (Part II, *loc. cit.*, p. 307) includes two sets of interferences: (*a*) that between two methyl groups attached to a common carbon atom, (*b*) those between each of the methyl groups and the oxygen atom. The correction for (*a*) may be taken to be —2·2. In cyclic ketones, interference between the oxygen atom and the atoms constituting the ring is not likely to extend beyond those carbon atoms which are linked to the carbon of the carbonyl group, and therefore, when the ring angle does not differ greatly from the angle formed by the three carbon atoms in acetone, the reduction in parachor produced by the interference effects (*b*) may be taken to be substantially unchanged in such ring compounds. Hence, the partially corrected value of 53·1 (50·9 + 2·2) may be used for (C)·CO·(C) here. Parachors so calculated agree reasonably well with the experimental values, especially for cyclic ketones containing a six-carbon ring. The method of calculation is shown for *p*-benzoquinone :

4(C)·CH=(C), uncorr. at 36·5 .... 146·0
2(C)·CO·(C), part. corr. at 53·1 .... 106·2
Σ group values .... 252·2

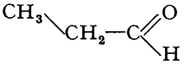
Ring corrn. (as benzene) .... —13·4
p- „ (as *p*-xylene) .... — 2·2
Hence S.V. = ... 236·6

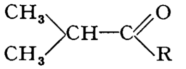
In the following table, observed values are each the mean of several concordant determinations made at different temperatures—the last two (quinones) by Sugden (J., 1927, 2880), the remainder by Vogel (1938, *loc. cit.*), who also records previous determinations for all the monoketones except *trans*-hexahydro-β-hydrindone.

Cyclic ketone.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns.* applied.
*cyclo*Pentanone	215·7	+0·4	216·1	214·1	—0·9	—
3-Methyl*cyclo*pentanone	252·8	+0·6	253·4	251·6	—0·8	—1·7 : *m*-
*cyclo*Hexanone	252·4	+0·6	253·0	252·2	—0·3	—
2-Methyl*cyclo*hexanone	288·5	+0·8	289·3	289·1	—0·1	—2·7 : *o*-
3- „	289·5	+0·8	290·3	290·3	±0·0	—1·7 : *m*-
4- „	289·0	+0·8	289·8	289·8	±0·0	—2·2 : *p*-
trans-Hexahydro-*β*-hydrindone	343·2	+1·1	344·3	344·5	+0·1	—3·4 : 2*m*-
trans-*β*-Decalone	379·4	+1·4	380·8	382·1	+0·3	—3·9 : *m*-, *p*-
p-Benzoquinone	236·6	+0·5	237·1	236·8	—0·1	—2·2 : *p*-
Toluquinone	272·0	+0·7	272·7	272·0	—0·3	—6·6 : *o*-, *m*-, *p*-

* *o*-, *m*-, and *p*-Corrections are taken to be the same as those found for the xylenes.

The interference effect due to attachment of a carbonyl group, —CO·R, to the benzene ring appears to be about the same as that found in the corresponding open-chain grouping, as in (I) or (II); *i.e.*, the correction may be taken as —2·0 (see Part II, *loc. cit.*, p. 305).


(I.)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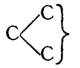
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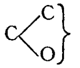
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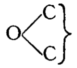

(V.)

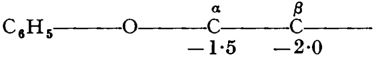
Carbonyl compound.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.
Benzaldehyde	255·5	+0·6	256·1	255·1*[3]	—0·4	—2·0 : carb. *β*
Acetophenone	291·9	+0·8	292·7	293·1†[2]	+0·1	—4·4 : carb. *β*; Ar. *β*
Methyl benzoate	309·8	+0·9	310·7	310·4	—0·1	—2·0 : carb. *β*
Ethyl phthalate	490·1	+2·4	492·5	491·0‡[2]	—0·3	—6·7 : 2 carb *β*; *o*-

* Mean of 254·0, 255·1, 256·2.

† Sugden (J., 1924, **125**, 1177), 293·8; Hammick and Andrew (J., 1929, 754), 292·4.

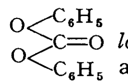
‡ Beck, Macbeth, and Pennycuick (J., 1932, 2258), 490·0; Bowden and Butler (J., 1939, 77), 492·0. The other references are given in the British Association list (*loc. cit.*).

Interferences between the nucleus and the oxygen side chains of aromatic ethers are likely to resemble those found in alkylbenzenes. Since substitution in the benzene ring by a carbon atom involves the same correction, —2·2, as the grouping (III), it is probable that for substitution of an oxygen atom a correction of *—2·6* will be required, *i.e.*, the same as for the grouping (IV). If this is correct, S.V., C_6H_5·(O) will be *189·8* [cf. S.V., C_6H_5·(C), 190·2]. From the parachors of anisole and its derivatives it appears that interference between the ring and the methyl group necessitates a correction of *—1·5*, while the mean parachor value, 303·3[3], observed for phenetole suggests that for the next carbon atom the extra correction is *—2·0*. No data are available to show the effects of further prolongation of the alkyl chain :


$$C_6H_5\text{———}O\text{———}\underset{-1\cdot5}{\overset{\alpha}{C}}\text{———}\underset{-2\cdot0}{\overset{\beta}{C}}\text{———}$$

Aromatic ether.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.
Anisole	265·0	+0·6	265·6	265·5[4]	—0·0	—1·5 : Ar·O**α*
o-Methoxybenzaldehyde ...	312·2	+0·9	313·1	312·4[2]	—0·2	—6·7 : Ar·O**α*; carb. *β*; *o*-
p- „ „ ...	312·7	+0·9	313·6	313·9	+0·1	—6·2 : Ar·O**α*; carb. *β*; *p*-

* Aromatic oxygen side chain correction (as above).

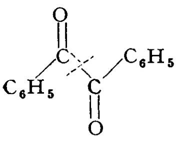


Phenyl carbonate may be presumed to have the structure inset (see alkyl carbonates, Part II, *loc. cit.*), in which case no extra interference is to be expected, either between the doubly-linked oxygen atom and the rings, or between the rings themselves. Then,

$2C_6H_5$·(O) at 189·8 .... 379·6
O=C[O(C)]$_2$ at 85·5 .... 85·5
S.V., calc. .... 465·1

Add E.C. 2·1; then [*P*], calc., 467·2; [*P*], obs., 467·4; Diff. %, +0·0

For aromatic and other cyclic compounds of more complicated type, as for other substances containing two or more groups with comparatively large polar or steric effects, estimation of the interference corrections required is often difficult, because the exact spatial relationships of the various groups are seldom determinable with certainty. Consideration of such compounds is better postponed until more data have been accumulated. The parachor of benzil, however, confirms the most recent views regarding its structure. If the two halves of the molecule (as inset) lie in the same plane, as was formerly suggested, a considerable amount of interference is to be expected; but the total correction, as derived from the parachor determined, is only −3·6. Caldwell and Le Fèvre (*Nature*, 1939, **143**, 803; J., 1614), from dipole-moment measurement of benzil in solution, and Knaggs and Lonsdale (*Nature*, *ibid.*, p. 1023), from *X*-ray measurements of the crystals, conclude that the molecule has a skew configuration in which the two benzoyl units lie in planes approximately at right angles to each other. If this is also the configuration in the pure liquid, then the extra interference in each half of the molecule will be the same as in benzaldehyde, *i.e.*, that between the carbonyl group and the ring to which it is attached. Adopting the skew configuration for benzil and its derivatives, one obtains the following results :

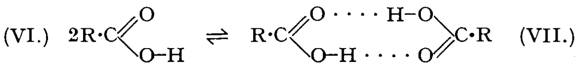


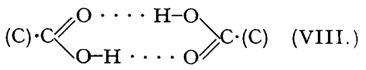
Compound.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.
Benzil	478·2	+2·2	480·4	480·8	+0·1	−4·0 : 2 carb. β
2 : 2′-Dimethoxybenzil	591·6	+3·5	595·1	596·8	+0·3	−12·4 : 2 carb. β; 2*o*-; 2Ar·Oα

PART IV.

The parachors of the normal fatty acids show that their molecules are mainly in the dimeric form at ordinary temperatures. A value for the parachor of dimeric acetic acid is determined by extrapolation to absolute zero of the parachors recorded at various temperatures. Values are calculated for the parachors of the dimers of carboxy-acids, and these are compared with the experimental values.

DETERMINATION of the mean standard values (S.V.) of the parachors of the normal fatty acids—derived, as explained in Part I (J., 1941, 299), from the observations recorded in *Brit. Assoc. Rep.*, 1932, 265—shows that, among the earlier members in the series, the Δ_{CH_2} value (*i.e.*, the increase in S.V. produced by addition of CH_2 to the structure) varies in much the same way as it does among the corresponding alkyl esters (Part II, J., 1941, 306). Thus, the average value of 38·3 (*i.e.*, 1·5 units less than the normal 39·8) between the second and the fifth member in the series agrees exactly with the results found for the corresponding esters, and is to be explained presumably by interference between the atoms of the carbonyl group and the neighbouring atoms in the attached carbon chain. From the fifth member onwards, however, as far as the eighteenth, the mean Δ value is 40·85, which is more than a whole unit *greater* than the normal value for Δ_{CH_2}, as found in the paraffins. Deviations from this normal value found among the members of the other classes of compounds already considered have been on the negative side and have been attributed to interference between atoms in the same molecule. Many of the physical properties of carboxy-acids show that in the liquid condition their molecules are associated. The association continues into the vapour state and is dependent upon the formation of a dimeric modification (VII) which exists in equilibrium with the monomeric form (VI), the proportion of the two kinds of molecule varying with the temperature. Obviously, the anomalous values of Δ_{CH_2} found among the higher fatty acids are due to the fact that, at the temperatures of parachor determination, these acids exist mainly in the dimeric form. Their parachors then lie, not between 365 and 778, as recorded, but between 730 and 1556, for which values of the parachor the difference for adjacent members in the series increases from twice 40·4 to twice 41·1 (see Part I, *loc. cit.*, Conversion Table, p. 304).

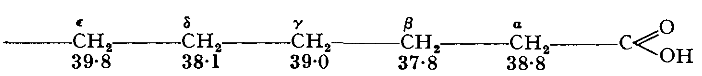

(VI.) (VII.)


(VIII.)

The parachor of acetic acid (as $C_2H_4O_2$) has been determined at a series of temperatures from 10° to 280° (Sugden, J., 1924, **125**, 37; "The Parachor and Valency," 1930, 167). A graph of [*P*] against *T* yields a curve which clearly represents the dissociation of the dimeric form into single molecules, and extrapolation to zero temperature gives [*P*] = 130·2. Thus, the parachor for the dimer appears to be 260·4, and since the "expansion correction" (E.C.) for this number is −0·6 (see Part I, *loc. cit.*), the "standard value" (S.V.) is 259·8.

Then,	S.V., dimeric acetic acid (VII; R = CH_3)	259·8
	Deduct $2CH_3$– at 55·2	110·4
	S.V., $(CO{\cdot}OH)_2$ nucleus (VIII)	149·4

Assuming that the values for Δ_{CH_2} are the same as those for the corresponding esters (as the parachors of the earlier fatty acids indicate), one must use the following increments for replacement of H– by CH_3– at the points indicated in a carbon chain :


$$-\underset{39\cdot8}{\overset{\epsilon}{CH_2}}-\underset{38\cdot1}{\overset{\delta}{CH_2}}-\underset{39\cdot0}{\overset{\gamma}{CH_2}}-\underset{37\cdot8}{\overset{\beta}{CH_2}}-\underset{38\cdot8}{\overset{\alpha}{CH_2}}-C\langle^{O}_{OH}$$

or, taking the standard value for the $(CO{\cdot}OH)_2$ nucleus (VIII) to be 149·4 as above, one may allot to each alkyl group in the chain its normal value and then apply the following " carbonyl corrections " (which, in the case of a divided chain, refer to only one branch) : β, −2·0 ; γ, −0·8 ; δ, −1·7 : total for the three, −4·5 (see Part II, *loc. cit.*).

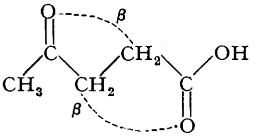
From the parachors determined by Hunten and Maass (*J. Amer. Chem. Soc.*, 1929, **51**, 153) for seven of the members between octoic and stearic acid, inclusive, it appears that, under experimental conditions, practically all the molecules of these substances were in the dimeric state. Two full " carbonyl corrections " of −4·5 have been applied to each of the calculated standard values in the following table.

Normal Fatty Acid Dimers, $(C_nH_{2n}O_2)_2$.

n.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.
8	728·4	+ 5·3	733·7	731·2	−0·3
10	887·6	+ 8·0	895·6	895·4	−0·0
12	1046·8	+11·2	1058·0	1065·6	+0·7
14	1206·0	+14·9	1220·9	1211·6	−0·8
16	1365·2	+19·2	1384·4	1386·4	+0·1
17	1444·8	+21·5	1466·3	1466·4	+0·0
18	1524·4	+24·0	1548·4	1556·4	+0·5

The reasonably good agreement of calculated and experimental parachors in the above table affords confirmation of the approximate accuracy of the parachor of dimeric acetic acid obtained by extrapolation, and also further confirmation of the accuracy of the correction used to counteract the " expansion effect " (see Part I, *loc. cit.*).

The parachors of undecylenic acid and lævulic acid (Mumford and Phillips, J., 1929, 2112) indicate that the molecules of these acids were also mainly in the dimeric form. For the former, two full carbonyl corrections of −4·5 are needed, as in the higher fatty acids above; for the latter, two carbonyl β corrections (−2·0 each) appear to be required for each half of the single molecule, which suggests that the configuration is planar (see inset).



Acid (dimer).	S.V., calc.	E.C.	*P*, calc.	*P*, obs.	Diff., %.
Undecylenic	945·2	+9·1	954·3	956·4	+0·2
Lævulic	512·8	+2·6	515·4	517·2	+0·3

Normal group values, determined in Parts I and II (J., 1941, 299), which have been used for calculations in Parts III and IV, are as follows :

$CH_3{\cdot}(C)$, 55·2 ; $(C){\cdot}CH_2{\cdot}(C)$, 39·8 ; $\genfrac{}{}{0pt}{}{(C)}{(C)}\!>\!CH{\cdot}(C)$, 22·2 ; $\genfrac{}{}{0pt}{}{(C)}{(C)}\!>\!C\!<\!\genfrac{}{}{0pt}{}{(C)}{(C)}$, 2·4. (Values uncorrected for mutual interference between the attached carbon atoms are 55·2, 42·0, 28·8, and 15·6, respectively.) $CH_2{=}(C)$, 49·7 ; $(C){\cdot}CH{=}(C)$, 34·3 ; $\genfrac{}{}{0pt}{}{(C)}{(C)}\!>\!C{=}(C)$, 16·7. (Uncorrected values : 49·7, 36·5, and 23·3, respectively.) $(C){\cdot}O{\cdot}(C)$, 21·5 ; $(C){\cdot}CHO$, 67·3 ; $(C){\cdot}CO{\cdot}(C)$, 50·9 ; $(C){\cdot}CO{\cdot}O{\cdot}(C)$, 66·4 ; $O{=}C[O(C)]_2$, 85·5. Interference corrections for simple groupings are as follows : $C\!<\!\genfrac{}{}{0pt}{}{C}{C}\Big\}$ and $C\!\ll\!\genfrac{}{}{0pt}{}{C}{C}\Big\}$ −2·2 ; $C\!<\!\genfrac{}{}{0pt}{}{C}{O}\Big\}$, −2·6.

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