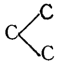
46. *Molecular Volume and Structure. Parts V and VI.*

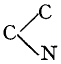
By T. W. Gibling.

Part V.

The parachors of the simpler organic compounds containing nitro-, nitrito-, azo-, diazo-, triazo-, cyano-, and *iso*cyano-groups are considered; group values are calculated, certain peculiarities of structure discussed, and the necessary " interference corrections " assessed. The polarity of the molecules of alkyl cyanides appears to produce an effect similar to that already observed in the case of carbonyl compounds.

From three concordant values recorded for the parachor of nitromethane, the standard value (S.V.) for the nitro-group, (C)·NO_2, can be assessed with reasonable certainty at *76·8*. This value is obtained by fixing S.V., CH_3– at 55·2 (see " Ethers," Part II, J., 1941, 304). Groupings (I) and (III) have been found to involve decreases in S.V. of 2·2 and 2·6, respectively (Parts I and II, J., 1941, 299, 304). It may be assumed that grouping (II) will require a correction of intermediate amount, *viz.*, *−2·4*. The ideal S.V. for –CH_2–, uncorrected for interference between the groups to which it is attached, has been assessed at 42·0. Hence the normal S.V. of (C)·CH_2·(N) is 42·0 − 2·4 = 39·6. Thus :


(I.)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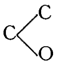
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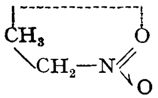

(IV.)

Nitroparaffin.	S.V., calc.	E.C.*	[*P*], calc.	[*P*], obs.†	Diff., %.
Nitromethane	132·0	+0·1	132·1	132·1 [3]	±0·0
Nitroethane	171·6	+0·3	171·9	171·2	−0·4

* " Expansion correction," see Part I, *loc. cit.*

† Observed values recorded here and in subsequent tables are, unless otherwise stated, taken from *Brit. Assoc. Rep.*, 1932, 265.

In the above calculation of the parachor of nitroethane, it is assumed that no extra interference is involved in the structure of the molecule, *i.e.*, that the plane of the –NO_2 group is approximately at right angles to that of (II). If both parts of the molecule were in the same plane, as in (IV), interference would occur between C and O (as indicated) with consequent reduction in S.V. of the order of 2·0, as for the carbonyl β correction (Part II, *loc. cit.*).*

Attachment of carbon and oxygen to the benzene ring has been estimated to involve the same corrections as for (I) and (III) (Part III, J., 1942, 661), so that of nitrogen is similarly assumed to be *−2·4*. Calculations are conveniently shortened by evaluating the groups phenyl, phenylene, etc. Since full group values, ununcorrected for outside interference, are : C_6H_5–, 192·4; –C_6H_4–, 179·2; $>C_6H_3$–, 166·0, normal S.V. are as follows :

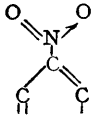
$C_6H_5\cdot$(C), 190·2
$C_6H_5\cdot$(N), 190·0
$C_6H_5\cdot$(O), 189·8

(C)·$C_6H_4\cdot$(C), 174·8
(C)·$C_6H_4\cdot$(N), 174·6
(C)·$C_6H_4\cdot$(O), 174·4

(N)·$C_6H_4\cdot$(O), 174·2
$\begin{matrix}(C)\\(C)\end{matrix}>C_6H_3\cdot(C)$, 159·4, and so on.

These values include the reduction in S.V. brought about by interference between the atoms of the ring and those atoms directly attached to it, but not reductions due to *o*-, *m*-, or *p*-substitution.

For –NO_2 attached to the benzene nucleus to give a structure as inset, we may expect, in addition to the above correction of −2·4, two further reductions of about 2·0 units each, due to interference of the oxygen atoms with atoms of the ring, each interference being supposed to be of the same order as that produced by the oxygen of a carbonyl group attached to the ring. Thus the total correction for attachment of –NO_2 is *−6·4*. This number agrees almost perfectly with that derived from the mean of four independent determinations of the parachor of nitrobenzene. For most of the compounds in Table I (in which halogenobenzenes are included for purposes of comparison), it is convenient to derive the calculated values from the S.V. of benzene (205·6) by addition of the amount corresponding to substitution of the required group, as obtained from the standard values of the parachors of toluene, anisole, chlorobenzene, etc. Increments required are : –CH_3, +39·8; –O·CH_3, +59·4 (Part III, *loc. cit.*, p. 664); –NO_2, +57·2; –Cl, +38·2; –Br, +52·1; –I, +74·5.



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* (*Note added in proof.*) The results of Boyd and Copeland (*J. Amer. Chem. Soc.*, 1942, **64**, 2540) for nitroparaffins as far as butyl, including *iso*propyl and *sec.*-butyl, which have just become available, show the effect of the strongly polar nitro-group in attracting the remainder of the alkyl chain. The extra corrections required appear to be : β, −1·0; γ, −2·7; δ, −0·5. For branching chains these corrections apply to only one of the branches.

TABLE I.

Compound.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.*
Chlorobenzene	243·8	+0·5	244·3	244·35 [2]	+0·0	—
Bromobenzene	257·7	+0·6	258·3	258·8 [3]	+0·2	—
Iodobenzene	280·1	+0·7	280·8	281·5 [2]	+0·2	—
o-Chlorotoluene	280·9	+0·7	281·6	280·8	−0·3	−2·7 : *o*-
p- ,,	281·4	+0·7	282·1	283·6	+0·5	−2·2 : *p*-
p-Bromotoluene	294·8	+0·8	295·6	296·8	+0·4	,,
p-Iodotoluene	317·7	+1·0	318·7	318·6	−0·0	,,
p-Dichlorobenzene	279·8	+0·7	280·5	279·5	−0·4	,,
p-Chlorobromobenzene	293·7	+0·8	294·5	292·5	−0·7	,,
p-Chloroiodobenzene	316·1	+1·0	317·1	316·4	−0·2	,,
Nitrobenzene	262·8	+0·6	263·4	263·3 [4]	−0·0	—
o-Nitrotoluene	299·9	+0·8	300·7	301·1 †	+0·1	−2·7 : *o*-
m- ,,	300·9	+0·8	301·7	300·6 †	−0·4	−1·7 : *m*-
p- ,,	300·4	+0·8	301·2	301·6 †	+0·1	−2·2 : *p*-
o-Nitroanisole	319·5	+1·0	320·5	320·5 ‡	±0·0	−2·7 : *o*-
p- ,,	320·0	+1·0	321·0	322·0 ‡	+0·3	−2·2 : *p*-
o-Chloronitrobenzene	298·3	+0·8	299·1	299·9	+0·3	−2·7 : *o*-
m- ,,	299·3	+0·8	300·1	298·9	−0·4	−1·7 : *m*-
p- ,,	298·8	+0·8	299·6	300·0	+0·1	−2·2 : *p*-
o-Bromonitrobenzene	312·2	+0·9	313·1	312·9	−0·1	−2·7 : *o*-
m- ,,	313·2	+0·9	314·1	313·5	+0·2	−1·7 : *m*-
p- ,,	312·7	+0·9	313·6	313·5	−0·0	−2·2 : *p*-
2 : 5-Dichloronitrobenzene	332·6	+1·0	333·6	335·4	+0·5	−6·6 : *o*-, *m*-, *p*-
1-Chloro-2 : 4-dinitrobenzene	351·6	+1·2	352·8	see below		,,
1-Chloro-3 : 4-dinitrobenzene	351·6	+1·2	352·8			,,

* As for the xylenes (Part III, *loc. cit.*).

† For *o*- and *m*-: Sugden and Wilkins (J., 1925, 2517); for *p*-: Bhatnagar and Singh (*J. Chim. physique*, 1928, **25**, 21). Sugden (J., 1924, 1167, 1177) also gives *o*-, 297·7; *m*-, 297·0; *p*-, 302·8.

‡ Burawoy and Markowitsch-Burawoy (J., 1936, 36). Sidgwick and Bayliss (J., 1930, 2027) found *o*-, 322·1; *p*-, 322·6.

The parachors of the last two compounds both vary with temperature, *e.g.*,

2 : 4-Dinitro-compound.

Temp.	60·4°	76·2°	95°
[*P*]	347·2	348·2	349·4

3 : 4-Dinitro-compound.

Temp.	40°	50°	60°
[*P*]	346·0	347·8	349·3

Sickmann and Menzies (*J. Amer. Chem. Soc.*, 1930, **52**, 3328) recorded these results, but Mumford and Phillips (*ibid.*, p. 5295) found that the parachor of the 2 : 4-dinitro-compound continued to increase until it reached the calculated value, 352·8, at 173·5°, after which it began to decrease, having fallen to 351·5 at 204·2°, the highest temperature employed.

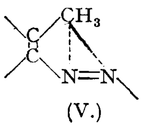
The ideal (uncorrected) S.V. of the nitrito-group, $\mathrm{(C){\cdot}O{\cdot}N{=}O}$, would be expected to be only slightly different from that of the nitro-group (cf. $CH_3{\cdot}CH_2{\cdot}OH$ and $CH_3{\cdot}O{\cdot}CH_3$, Part VI). Its normal value (*i.e.*, the S.V. corrected for interference among constituent and attached atoms) appears to be *75·3*.

Nitrite.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.
Methyl	130·5	+0·1	130·6	130·6 *	±0·0
Ethyl	169·9	+0·3	170·2	169·0 *	−0·7
Butyl	249·5	+0·6	250·1	251·8 †	+0·7
*iso*Amyl	287·1	+0·8	287·9	287·4 †	−0·2

* Noyes and Singh (*J. Amer. Chem. Soc.*, 1936, **58**, 802).

† Sugden, Reed, and Wilkins (J., 1925, 1525).

Azo-, diazo-, and triazo-groups are estimated to have the following normal S.V.: $\mathrm{(C){\cdot}N{=}N{\cdot}(C)}$, *51·8*; $\mathrm{(C){=}N\overset{\rightharpoonup}{-}N}$, *53·2*; $\mathrm{(C){\cdot}N{=}N\overset{\rightharpoonup}{-}N}$, *79·9*. In the assessment of interference corrections for compounds containing these groups, it has been assumed that the nitrogen atoms produce interferences of the same order as those given by carbon atoms: the nitrogen atom is rather smaller than the carbon atom, but the consequent closer association of the neighbouring atoms will tend to compensate for this. For aromatic *o*-compounds in which one of the substituted groups consists of two or more of these atoms in close association, *i.e.*, joined by a double or a triple bond, the ordinary *o*-correction appears to be *augmented* and to become *−4·7*. This is the case with $-N_2-$ (V), $-N_3$ (VI), and also with $-CN$ (VII) and $-NC$ (VIII). Details are given in Table II.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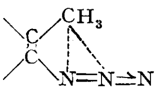
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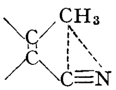
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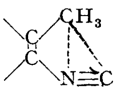

(VIII.)

TABLE II.

Compound.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.*
2 : 2′-Azobispropane	316·2	+0·9	317·1	318·4 †	+0·4	—
2 : 2′-Azobisbutane	395·8	+1·5	397·3	395·5 †	−0·5	—
Diethyl azoformate	373·8	+1·3	375·1	377·1 ‡	+0·5	—
Ethyl benzeneazoformate	400·4	+1·5	401·9	402·1 ‡	+0·0	− 2·4 : as EtPh
Azobenzene	427·0	+1·8	428·8	429·5 ‡	+0·2	− 4·8 : as 2EtPh
o-Methylazobenzene	462·1	+2·1	464·2	463·8 ‡	−0·1	− 9·5 : as 2EtPh; *o*- (aug.)
m- ,,	465·1	+2·1	467·2	467·3 ‡	+0·0	− 6·5 : as 2EtPh; *m*-
oo′-Dimethylazobenzene	497·2	+2·5	499·7	501·3 ‡	+0·3	−14·2 : as 2EtPh; 2*o*- (aug.)
mm′- ,,	503·2	+2·5	505·7	504·6 ‡	−0·2	− 8·2 : as 2EtPh; 2*m*-
o-Methoxyazobenzene	484·4	+2·3	486·7	486·9 §	+0·0	− 9·0 : as 2EtPh; ArOα; *o*-
m- ,,	485·4	+2·3	487·7	486·9 §	−0·2	− 8·0 : as 2EtPh; ArOα; *m*-
p- ,,	484·9	+2·3	487·2	485·0 §	−0·5	− 8·5 : as 2EtPh; ArOα; *p*-
Diazoacetone	191·4	+0·3	191·7	191·9 ‖	+0·1	− 2·0 : as carb. β
Methyl diazoacetate	206·9	+0·4	207·3	207·2 ‖	−0·0	,,
Ethyl ,,	246·3	+0·6	246·9	248·3 ‖	+0·6	,,
Butyl ,,	325·9	+1·0	326·9	326·0 ‖	−0·3	,,
Methyl diazomalonate	304·5	+0·9	305·4	305·4 ‖	±0·0	− 6·2 : as 2carb. β; // chns.
Ethyl ,,	381·1	+1·4	382·5	381·6 ‖	−0·2	− 8·4 : as 2carb. β; // chns.
Triazoacetone	221·2	+0·4	221·6	220·9 ¶	−0·3	− 2·0 : as carb. β
Triazoacetic ester	276·1	+0·7	276·8	277·0 ¶	+0·1	,,
Phenyl azide	267·5	+0·7	268·2	267·3 ¶	−0·3	− 2·4 : as EtPh
o-Tolyl azide	302·6	+0·9	303·5	303·8 ¶	+0·1	− 7·1 : as EtPh; *o*- (aug.)
p- ,,	305·1	+0·9	306·0	307·0 ¶	+0·3	− 4·6 : as EtPh; *p*-

* " as EtPh " = corrn. as for ethylbenzene (Part III, *loc. cit.*); ArOα = corrn. for the α-C atom in an ether chain (as in anisole); *o*- (aug.) = augmented *o*-corrn. (see above); as carb. β = corrn. as for the β-C atom in a chain attached to carbonyl (Part II, *loc. cit.*); // chns.—see alkyl malonates (Part II, p. 309).

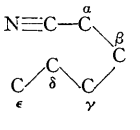
† Barricke, Drake, and Lochte (*J. Amer. Chem. Soc.*, 1936, **58**, 160).

‡ Lindemann and Groger (*Ber.*, 1930, **63**, 2572).

‖ Lindemann, Wolter, and Groger (*Ber.*, 1930, **63**, 702).

§ Burawoy and Markowitsch-Burawoy (*loc. cit.*).

¶ Lindemann and Thiele (*Ber.*, 1928, **61**, 1529).



It might be expected that, in consequence of the negative polarity of the nitrile and the *iso*nitrile group, the earlier part of an attached carbon chain would bend towards this group, just as it seems to do in the case of a carbonyl group (Part II, *loc. cit.*). This is confirmed by the parachors of the alkyl cyanides, in which the following extra corrections are suggested for alkyl groups involving carbon atoms constituting the chain attached to –CN : β, −*1·3*; γ, −*0·8*; δ, −*2·6*; ε, −*1·1*; total for the four, −*5·8* (see inset). In the case of a branching chain, the corrections apply to only one of the branches. From the parachor (mean value) of acetonitrile, S.V., (C)·CN = *66·6*. Detailed results are in Table III.

TABLE III.

R.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.
Cyanides, R·CN.						
Methyl	121·8	+0·1	121·9	121·9 [2]	±0·0	—
Ethyl	160·3	+0·2	160·5	160·5	±0·0	−1·3 : CN, β
Propyl	199·3	+0·4	199·7	199·8 [4]	+0·1	−2·1 : CN, β, γ
*iso*Butyl	236·9	+0·6	237·5	237·35 [2]	−0·1	,,
Butyl	236·5	+0·6	237·1	237·0 [2]	−0·0	−4·7 : CN, β, γ, δ
*iso*Amyl	274·1	+0·8	274·9	275·0	+0·0	,,
Amyl	275·2	+0·8	276·0	276·6	+0·2	−5·8 : CN, β, γ, δ, ε
Hexyl	315·0	+1·0	316·0	316·1	+0·0	,,
Heptyl	354·8	+1·3	356·1	356·0	−0·0	,,
Octyl	394·6	+1·6	396·2	395·2	−0·3	,,
Phenyl	256·8	+0·6	257·4	257·6 [3]	+0·1	—
o-Tolyl	291·9	+0·8	292·7	292·2 [4]	−0·2	−4·7 : *o*- (aug.)
m- ,,	294·9	+0·8	295·7	295·6	−0·0	−1·7 : *m*-
p- ,,	294·4	+0·8	295·2	295·2 [3]	±0·0	−2·2 : *p*-
Benzyl	292·9	+0·8	293·7	293·5 [2]	−0·1	−3·7 : EtPh; CN, β
iso*Cyanides*, R·NC.*						
Methyl	122·0	+0·1	122·1	122·1	±0·0	—
Ethyl	160·3	+0·2	160·5	164	+2·2	−1·3 : as CN β
Phenyl	256·8	+0·6	257·4	255·2	−0·9	—
o-Tolyl	291·9	+0·8	292·7	292·9	+0·1	−4·7 : *o*- (aug.)
p- ,,	294·4	+0·8	295·2	295·5 †	+0·1	−2·2 : *p*-
o-Methoxyphenyl	313·5	+0·9	314·4	314·1	−0·1	−2·7 : *o*-
p- ,,	314·0	+0·9	314·9	314·5 ‡	−0·1	−2·2 : *p*-

* All determinations are by Lindemann and Wiegrabe (*Ber.*, 1930, **63**, 1650), except that for the ethyl compound, which is by Hammick, New, Sidgwick, and Sutton, who also record the following: † 295; ‡ 315 (J., 1930, 1876).

The general agreement of calculated and observed parachors for aromatic nitriles confirms the approximate accuracy of the value used for the –CN group. The standard value of the *iso*nitrile group is naturally very little different from that of the nitrile group: S.V., (C)·NC *66·8*.

PART VI.

The parachors of hydroxy-compounds, amines, alkyl halides, and compounds containing ethereal oxygen atoms are discussed. For those substances which are associated at room temperature—alcohols and phenols, primary and secondary amines—parachors are estimated for the same substances existing as single molecules. As a general conclusion to the study of homologous series: the configuration of a carbon chain is determined primarily by the polarity of that part of the molecule to which it is attached.

The properties of most compounds containing hydroxyl, amino-, or imino-groups show that in the liquid state their molecules are more or less associated. It is generally accepted that the substances exist partly as chains of molecules, bound together by resonance and gradually dissociating as the temperature rises. This is confirmed by their parachors, which are usually considerably smaller than those of any non-associated isomers but steadily increase with rise in temperature: for aliphatic alcohols, the parachors at room temperature are some 5% smaller than those of isomeric ethers and the CH_2 parachor increment is also about 5% less than normal. The parachors of methyl and ethyl alcohols have been determined at a series of different temperatures (Sugden, "The Parachor and Valency," 1929, pp. 27, 207). The graphs for both alcohols take the same form and may be continued to infinite temperature. Assuming that these extrapolated values represent the true parachors of the fully-dissociated alcohols, we have:

[*P*],$CH_3\cdot OH$	94·5	[*P*],$C_2H_5\cdot OH$	134·0
E.C.	−0·1	E.C.	−0·2
S.V.,$CH_3\cdot OH$	94·4	S.V.,$C_2H_5\cdot OH$	133·8

From these results group values may be derived as follows:

S.V.,$CH_3\cdot OH$	94·4	S.V.,$CH_3\cdot CH_2\cdot OH$	133·8
Deduct CH_3–	55·2	S.V.,$CH_3\cdot OH$	94·4
S.V.,(C)·OH	*39·2*	S.V.,(C)·CH_2·(O)	*39·4*

S.V., (C)·CH_2·(O) here has a value identical with that found for the same group in carboxy-esters (Part II, J., 1941, 304).

The difference between the theoretical parachor of a hydroxy-compound, as calculated from group values and interference and expansion corrections, and the parachor determined experimentally at a given temperature may be regarded as a "packing correction," and is conveniently recorded as a percentage of the theoretical parachor. For instance, at the lowest and the highest temperature used in each case:

Methyl alcohol: [*P*], calc. = 94·5.

Temp.	[*P*], obs.	Diff.	Packing, %.
− 65°	86·7	−7·8	8·3
+190	91·9	−2·6	2·8

Ethyl alcohol: [*P*], calc. = 134·0.

Temp.	[*P*], obs.	Diff.	Packing, %
− 57°	124·2	−9·8	7·3
+200	131·0	−3·0	2·2

The parachor of phenol has been determined at a series of temperatures by Sidgwick and Bayliss (J., 1930, 2027) and by Buehler, Wood, Hull, and Erwin (*J. Amer. Chem. Soc.*, 1932, **54**, 2398), but the results do not lend themselves to accurate extrapolation. This parachor can be calculated as follows: S.V., C_6H_5·(O), 189·8 + (C)·OH, 39·2 = 229·0; E.C., +0·5; [*P*], calc., 229·5. From the former determinations:

Temp.	[*P*], obs.	Diff.	Packing, %.	Temp.	[*P*], obs.	Diff.	Packing, %.
49·6°	222·3	−7·2	3·2	147·5°	224·8	−4·7	2·1

In the other determinations, [*P*], obs., increased from 222·0 (50°) to 223·1 (150°).

Ring formation has been suggested by Sidgwick (J., 1924, 527; 1930, 2027; *Ann. Reports*, 1924, 104; "The Electronic Theory of Valency," 1927, 147) to account for the comparatively low value of the parachor, and for other anomalous properties, of the *o*-isomer among certain substituted phenols. The parachors of *o*-hydroxy-derivatives of benzaldehyde, methyl benzoate, and *p*-methoxybenzaldehyde are 2 or 3% less than the calculated values, whereas those of the *m*- and *p*-compounds are more nearly normal; *e.g.*, for *p*-hydroxybenzaldehyde:

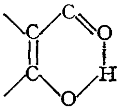
(C)·C_6H_4·(O)	174·4	Corrns.: carb. *β*	−2·0	Σ group values	280·9
(C)·CHO	67·3	*p*-	−2·2	corrns.	−4·2
(C)·OH	39·2	Total	−4·2	S.V., calc.	276·7

Compound.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Corrns. applied.
m-Hydroxybenzaldehyde	277·2	+0·7	277·9	274·5	−1·3	−3·7: carb. *β*; *m*-
p- ,,	276·7	+0·7	277·4	278·2 *	+0·2	−4·2: carb. *β*; *p*-
Methyl *p*-hydroxybenzoate	331·0 †	+1·0	332·0	331·8	−0·1	,,

---

* Burawoy and Markowitsch-Burawoy (*loc. cit.*) obtained values increasing from 275·6 at 117° to 277·2 at 145°.

† S.V., (C)·CO·O·(C) = 66·4.



According to Sidgwick, it is probable that in the corresponding *o*-hydroxy-compounds a closed chain is produced by means of a hydrogen-bond between two oxygen atoms. The reduction in parachor involved in the formation of the new six-membered ring (as inset) should be fairly large, because it would include not only the usual internal interference corrections but also the decrease in volume due to the union, or closer association, of the carbonyl oxygen atom with the hydrogen of the hydroxyl group. On the other hand, the new correction will also include those for interference between the carbonyl group and the benzene ring and for interference between hydroxyl and the ring, as well as the *o*-correction, none of which must therefore be counted again. The new correction appears to be about *−17·9*. For *o*-hydroxybenzaldehyde :

4 –CH=, uncorr. at 36·5	146·0	Σ group values	299·1
2 >C=, ,, ,, 23·3	46·6	Ring corrns. : −13·4 + −17·9 =	−31·3
(C)·CHO ,, 67·3	67·3	Hence S.V., calc.	267·8
(C)·OH ,, 39·2	39·2		

Compound.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.
Salicylaldehyde	267·8	+0·7	268·5	268·0	−0·2
Methyl salicylate	322·1	+1·0	323·1	322·9 [2]	−0·1
p-Methoxysalicylaldehyde	323·3 *	+1·0	324·3	325·1	+0·2

* Extra corrns. applied, −5·4 : ArO*a*; *m*-, *p*- (see Part III, *loc. cit.*).

The S.V. of methyl ether (131·9; see Part II, *loc. cit.*) is decidedly smaller than that of ethyl alcohol in the unimolecular state (133·8) on account of the comparatively large interference between two carbon atoms linked to the same oxygen atom. In order to estimate the magnitude of this effect, as compared with that of (III), which is considered to involve a correction of −2·6, one must know the parachor for H_2O. The parachor of water, regarded as H_2O, decreases slowly from 53·1 at 0° to 52·0 at 130° (Sugden, *op. cit.*, p. 169), and so is larger the *greater* the degree of association of its molecules, in contrast with the alcohols, for which the reverse holds. From Sugden's results it appears that the parachor for the substance existing as single molecules would be about 51·7, and, since the expansion correction for this value is negligible, S.V., H_2O is also 51·7. Consider the following :

Group.	S.V.	Diff.	Change in diff.	Ideal S.V.	Const. diff.
H·O·H	51·7	—	—	51·7	—
(C)·O·H	39·2	−12·5	—	39·2	−12·5
(C)·O·(C)	21·5	−17·7	−5·2	26·7	−12·5

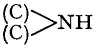
Supposing, as for the paraffins and olefins (Part I, *loc. cit.*), that the hydrogen atoms are too small to produce appreciable interferences, one finds that the correction due to grouping ·C·O·C· is *−5·2*. The ideal (uncorrected) S.V. of methyl ether will then be 131·9 + 5·2 = 137·1, whereas that of ethyl alcohol, uncorrected for interference (III), will be 133·8 + 2·6 = 136·4, *i.e.*, only 0·7 unit less. It was not expected that these ideal standard values would be identical, since the structures to which they correspond involve different linkages (see Part I, p. 300).

The parachors of methylamine and dimethylamine have been determined at different temperatures (Sugden, *op. cit.*, p. 170), but the ranges are too small for extrapolation. However, the probable parachor of the former, as a liquid consisting of separated molecules, can be obtained by comparison of the S.V. of corresponding compounds of carbon and oxygen with those of nitrogen : S.V., $CH_3{\cdot}OH$ is 42·7 units greater than S.V., H·OH (see above), and S.V., $CH_3{\cdot}CH_3$ (110·4) is 42·0 greater than S.V., CH_4 (which will be 55·2 + 13·2 = 68·4, since CH_4 may be regarded as the first member of the series CH_3, CH_2, CH, C; see Part I, p. 302, " Ideal S.V."). Then S.V., $CH_3{\cdot}NH_2$ should be about 42·4 units greater than S.V., $H{\cdot}NH_2$, 60·7 (Sugden, *ibid.*). Hence, S.V., $CH_3{\cdot}NH_2$, 103·1; deduct CH_3–, 55·2; S.V., (C)·NH_2 = *47·9*.

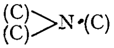
Of the parachor of trimethylamine, supposedly non-associated, the mean of three reasonably concordant values measured between −32° and −4° is 178·9 (Sugden, *ibid.*). Since E.C. is −0·3, S.V., $N(CH_3)_3$ is 178·6; deduct 3 CH_3– at 55·2, 165·6; S.V., (XII) = *13·0*.

NH_3
(IX.)

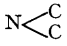
(C)·NH_2
(X.)



$\begin{matrix}(C)\\(C)\end{matrix}\!>\!NH$
(XI.)



$\begin{matrix}(C)\\(C)\end{matrix}\!>\!N{\cdot}(C)$
(XII.)



$N\!<\!\begin{matrix}C\\C\end{matrix}$
(XIII.)

From the above group values one arrives at the following series :

Group.	S.V.	Diff.	Change in diff.	Ideal S.V.	Const. diff.
(IX)	60·7	—	—	60·7	—
(X)	47·9	−12·8	—	47·9	−12·8
(XI)	32·0	−15·9	−3·1	35·1	−12·8
(XII)	13·0	−19·0	−3·1	22·3	−12·8

If the hydrogen atoms produce no appreciable interference, correction for grouping (XIII) becomes *−3·1*. The ideal group values, uncorrected for interference, will then be as above.

The extent of the packing effect in some amines at different temperatures is shown in the following table :

Amine.	S.V., calc.	E.C.	[*P*], calc.	Temp.	[*P*], obs.*	Packing, %.	Corrns. applied.
Methylamine	103·1	+0·1	103·2	−70°	95·1	7·8	—
				−20	96·8	6·2	
Dimethylamine	142·4	+0·2	142·6	−78	133·4	6·5	—
				− 5	136·6	4·2	
Aniline	237·9	+0·5	238·4	50	235·2	1·3	—
				150	236·6	0·8	
o-Toluidine	275·0	+0·7	275·7	50	272·0	1·3	−2·7 : *o*-
				150	273·3	0·9	
m- ,,	276·0	+0·7	276·7	25	269·4	2·6	−1·7 : *m*-
				150	273·3	1·2	
p- ,,	275·5	+0·7	276·2	50	270·5	2·1	−2·2 : *p*-
				120	273·5	1·0	
m-4-Xylidine	310·9	+0·9	311·8	25	307·2	1·5	−6·6 : *o*-, *m*-, *p*-
				150	309·7	0·7	

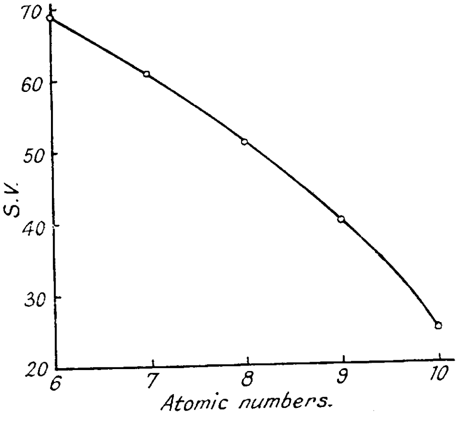
* Results of Buehler, Wood, Hull, and Erwin (*loc. cit.*), except that parachors of aliphatic amines are due to Sugden (J., 1924, 1167), from whose results also the following are derived: aniline, 234·2 (15°), 237·4 (164°); *p*-toluidine, 269·5 (51°), 275·9 (184°).

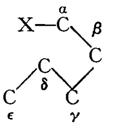
The parachors of some of the simpler compounds of carbon, nitrogen, oxygen, and fluorine can be roughly checked among themselves by plotting S.V. of series of substances like the following against atomic numbers of the elements: the S.V. of the members in each series should lie smoothly on a curve (see fig.). In Table I, S.V. are obtained from parachors recorded or calculated as in Parts I and II (*loc. cit.*) or in the present part, except that asterisked values have been interpolated.

TABLE I.

Subst.	S.V.	Subst.	S.V.	Subst.	S.V.
CH_4	68·4	$C(CH_3)_4$	223·2	$C(C_2H_5)_4$	382·4
NH_3	60·7	$N(CH_3)_3$	178·6	$N(C_2H_5)_3$	297·4
OH_2	51·7	$O(CH_3)_2$	131·9	$O(C_2H_5)_2$	210·7
FH	40·0 *	FCH_3	82·9 *	FC_2H_5	122·2 *
Ne	25·0	Ne	25·0	Ne	25·0

Subst.	S.V.	Subst.	S.V.	Subst.	S.V.	Subst.	S.V.
$CH_3{\cdot}CH_3$	110·4	$C_2H_5{\cdot}CH_3$	150·2	$CH(CH_3)_3$	187·8	$CH(C_2H_5)_3$	307·2
$CH_3{\cdot}NH_2$	103·1	$C_2H_5{\cdot}NH_2$	142·7	$NH(CH_3)_2$	142·4	$NH(C_2H_5)_2$	221·6
$CH_3{\cdot}OH$	94·4	$C_2H_5{\cdot}OH$	133·8	$CH_3{\cdot}OH$	94·4	$C_2H_5{\cdot}OH$	133·8
CH_3F	82·9	C_2H_5F	122·2	HF	40·0	HF	40·0





The parachors of the normal alkyl halides indicate that the earlier part of the alkyl chain tends to bend backwards towards the halogen atom. On the other hand, the parachors determined for the *iso*butyl and *iso*amyl halides suggest that in these molecules, which contain symmetrically branched chains, no such bending occurs, since each of the parachors agrees with that observed for the corresponding ethyl compound, *i.e.*, the S.V. may be obtained by allotting normal values to the alkyl groups in the carbon chain, *viz.*, $(C){\cdot}CH_3$, 55·2; $(C){\cdot}CH_2{\cdot}(C)$, 39·8; $\begin{matrix}(C)\\(C)\end{matrix}{>}CH{\cdot}(C)$, 22·2. The following appear to be the parachor values of the groups of type $(C){\cdot}CH_2X$: $(C){\cdot}CH_2Cl$, ***96·1***; $(C){\cdot}CH_2Br$, ***110·3***; $(C){\cdot}CH_2I$, ***131·6***. [Values for $(C){\cdot}X$ and $(C){\cdot}CH_2{\cdot}(X)$ cannot be determined with any certainty from existing data.] For normal alkyl bromides and iodides the extra interference effects extend as far as the 5th carbon atom in the chain. (The normal chlorides have not been investigated beyond amyl.) The corrections required for bromides and iodides seem to be about the same:

$$\begin{gathered}\text{X}—\overset{\alpha}{\text{C}}—\overset{\beta}{\text{C}}—\overset{\gamma}{\text{C}}—\overset{\delta}{\text{C}}—\overset{\epsilon}{\text{C}}— \\ \underbrace{-0{\cdot}7\quad -1{\cdot}5\quad -0{\cdot}6}_{\text{Total, }-2{\cdot}8}\end{gathered}$$

The corresponding CH_2 increments from γ to ε are **39·1**, **38·3**, and **39·2**, respectively, after which the normal value of 39·8 holds. In Tables II values of [*P*], obs., are from Hennant-Roland and Lek (*Bull. Soc. chim.*, 1931, **40**, 177), except that for *iso*amyl chloride, recorded by Sugden (J., 1924, **125**, 1177).

From examination of the parachors of ethyl, propyl, butyl, and higher members of various homologous series of carbon, oxygen, nitrogen, and halogen compounds (many of which have been listed in Parts I—VI), as well as of a few substances containing other elements, such as sulphur and silicon, it is concluded that the

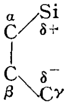
TABLE II.

Halide.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	
Ethyl chloride	151·3	+0·2	151·5	151·6	+0·0	—
*iso*Butyl chloride	228·7	+0·5	229·2	228·4	−0·4	—
*iso*Amyl chloride	268·5	+0·7	269·2	269·8	+0·2	—
Ethyl bromide	165·5	+0·2	165·7	165·7	±0·0	—
*iso*Butyl bromide	242·9	+0·5	243·4	243·8	+0·2	—
*iso*Amyl bromide	282·7	+0·7	283·4	282·9	−0·2	—
Ethyl iodide	186·8	+0·3	187·1	187·0	−0·1	—
*iso*Butyl iodide	264·2	+0·6	264·8	265·0	+0·1	—
Ethyl bromide	165·5	+0·2	165·7	165·7	±0·0	—
Propyl ,,	204·6	+0·3	204·9	205·3	+0·2	−0·7 : Hal γ
Butyl ,,	242·9	+0·5	243·4	243·5	+0·0	−2·2 : Hal γ, δ
Amyl ,,	282·1	+0·7	282·8	283·6	+0·3	−2·8 : Hal γ, δ, ε
Hexyl ,,	321·9	+1·0	322·9	322·8	−0·0	,,
Heptyl ,,	361·7	+1·3	363·0	363·0	±0·0	,,
Octyl ,,	401·5	+1·6	403·1	402·4	−0·2	,,
Ethyl iodide	186·8	+0·3	187·1	187·0	−0·1	—
Propyl ,,	225·9	+0·5	226·4	226·0	−0·2	−0·7 : Hal γ
Butyl ,,	264·2	+0·6	264·8	264·7	−0·0	−2·2 : Hal γ, δ
Hexyl ,,	343·2	+1·1	344·3	344·1	−0·1	−2·8 : Hal γ, δ, ε
Heptyl ,,	383·0	+1·4	384·4	384·5	+0·0	,,
Cetyl ,,	741·2	+5·5	746·7	748·9	+0·3	,,

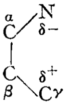
configuration of a carbon chain is determined primarily by the polarity of that part of the molecule to which it is attached; *e.g.*:

[*P*], $SiEt_4$, 412·1; E.C., −1·6; S.V., 410·5. [*P*], $SiPr_4$, 565·3; E.C., −3·1; S.V., 562·2.

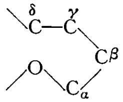
S.V., $SiPr_4$ would be expected to be 4 × 39·8 units greater than that of the ethyl compound, or 569·7; actually it is 7·5 less than this, whence the correction for interference between Si and the γ-C atom, as in (XIV), is about



(XIV.)



(XV.)



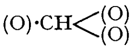
(XVI.)

−*1·9*. Similarly with tripropylamine, the calculated S.V. of which is 416·8: the mean of the two parachor values observed is 414·1; E.C. = −1·7, hence S.V., obs. = 412·4. This makes the γ-C correction in (XV) −*1·5*.

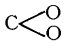
In alkyl ethers and esters of fatty acids, too, it appears that the polarity of the molecules comes into play, causing a bending of the alkyl chain towards the ethereal oxygen atom as in (XVI), just as in the other part of the fatty acid esters the acyl carbon chain has been supposed to bend towards the carbonyl oxygen (cf. Part II, *loc. cit.*, pp. 305, 307). From the parachors recorded for alkyl ethers, a correction of −1·4 units seems to be required for dibutyl and higher compounds, but the correction for propyl ethers is negligible, *i.e.*, there is no measurable interference between the oxygen atom and the γ-carbon atom, whilst that between the oxygen atom and the δ-carbon atom produces a decrease in S.V. of *0·7*. The latter part of the table of ethers (Part II, *loc. cit.*) should then be amended as follows:

Ether.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.	Ethereal O corrn.
Dibutyl	368·5	+1·3	369·8	369·9	+0·0	−1·4 : 2 Bu
Diamyl	448·1	+2·0	450·1	449·9	−0·0	,,
Di*iso*amyl	443·7	+2·0	445·7	445·7	±0·0	,,

The parachors of the five *iso*amyl esters of fatty acids listed in Part II are, on the average, 1·1 units less than the calculated values, but, in order to assess accurately the correction required, it will be necessary to know the parachors of butyl and higher formates, acetates, etc. From the parachor of ethyl orthoformate (Hammick


$(O)\cdot CH\!<\!\begin{matrix}(O)\\(O)\end{matrix}$

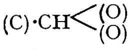
(XVII.)


$C\!<\!\begin{matrix}O\\O\end{matrix}$

(XVIII.)

$(O)\cdot CH_2(O)$

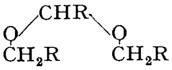
(XIX.)


$(C)\cdot CH\!<\!\begin{matrix}(O)\\(O)\end{matrix}$

(XX.)

and Wilmut, J., 1935, 207), it appears that S.V., (XVII) = *17·7*, whence the mutual interference of two oxygen atoms attached to a carbon atom, as in (XVIII), is −*3·7*; also S.V., (XIX) = *38·3*; S.V., (XX) = *19·9* (see Parts I and II, *loc. cit.*). Hence, the parachor of this ester is calculated as follows:

(XVII)	at 17·7	17·7	S.V., calc.	366·0
3(C)·O·(C)	,, 21·5	64·5	E.C.	+1·3
$3(O)\cdot CH_2\cdot(C)$	,, 39·4	118·2	[*P*], calc.	367·3
$3(C)\cdot CH_3$	,, 55·2	165·6	[*P*], obs.	367·2



If one assumes that acetals have a (non-planar) structure of the type inset, it seems probable that the two outer carbon atoms are at such a distance from each other as to produce a decrease in S.V. of 2·2 (see similar cases in previous parts). Then for methylal:

$$\left.\begin{array}{lll} 2\mathrm{CH_3\cdot(O)} & \text{at } 55{\cdot}2 \ \ldots\ldots & 110{\cdot}4 \\ 2\mathrm{(C)\cdot O\cdot(C)} & ,,\ 21{\cdot}5 \ \ldots\ldots & 43{\cdot}0 \\ \mathrm{(O)\cdot CH_2\cdot(O)} & ,,\ 38{\cdot}3 \ \ldots\ldots & 38{\cdot}3 \end{array}\right\} \begin{array}{ll} \Sigma \text{ group values } \ldots\ldots & 191{\cdot}7 \\ \text{Corrn., as above } \ldots\ldots & \underline{-2{\cdot}2} \\ \text{S.V., calc. } \ldots\ldots & 189{\cdot}5 \end{array}$$

Acetal.	S.V., calc.	E.C.	[*P*], calc.	[*P*], obs.	Diff., %.
Methylal	189·5	+0·3	189·8	189·8	±0·0
Dimethylacetal *	226·3	+0·5	226·8	226·0	−0·4
Diethylacetal *	305·1	+0·9	306·0	306·3 [2]	+0·1

* N.B.—Group (XX) occurs in these compounds.

The chief group values and corrections deduced in these two parts are as follows: $\mathrm{(C)\cdot CH_2\cdot(N)}$, 39·6; $\mathrm{(C)\cdot NO_2}$, 76·8; $\mathrm{(C)\cdot O\cdot N{=}O}$, 75·3; $\mathrm{(C)\cdot N{=}N\cdot(C)}$, 51·8; $\mathrm{(C){=}N{\rightleftharpoons}N}$, 53·2; $\mathrm{(C)\cdot N{=}N{\rightleftharpoons}N}$, 79·9; $\mathrm{(C)\cdot CN}$, 66·6; $\mathrm{(C)\cdot NC}$, 66·8; $\mathrm{(C)\cdot NH_2}$, 47·9; $\begin{smallmatrix}\mathrm{(C)}\\ \mathrm{(C)}\end{smallmatrix}\!>\!\mathrm{NH}$, 32·0 (ideal S.V., 35·1); $\begin{smallmatrix}\mathrm{(C)}\\ \mathrm{(C)}\end{smallmatrix}\!>\!\mathrm{N\cdot(C)}$, 13·0 (ideal S.V., 22·3); $\mathrm{(C)\cdot OH}$, 39·2; $\mathrm{(C)\cdot O\cdot(C)}$, 21·5 (ideal S.V., 26·7); $\mathrm{(C)\cdot CH_2\cdot(O)}$, 39·4; $\mathrm{(O)\cdot CH_2\cdot(O)}$, 38·3; $\begin{smallmatrix}\mathrm{(O)}\\ \mathrm{(O)}\end{smallmatrix}\!>\!\mathrm{CH\cdot(C)}$, 19·9; $\begin{smallmatrix}\mathrm{(O)}\\ \mathrm{(O)}\end{smallmatrix}\!>\!\mathrm{CH\cdot(O)}$, 17·7; $\mathrm{(C)\cdot CH_2Cl}$, 96·1; $\mathrm{(C)\cdot CH_2Br}$, 110·3; $\mathrm{(C)\cdot CH_2I}$, 131·6; $\left.\mathrm{C}\!<\!\begin{smallmatrix}\mathrm{C}\\ \mathrm{N}\end{smallmatrix}\right\}$, −2·4; $\left.\mathrm{N}\!<\!\begin{smallmatrix}\mathrm{C}\\ \mathrm{C}\end{smallmatrix}\right\}$, −3·1; $\left.\mathrm{C}\!<\!\begin{smallmatrix}\mathrm{C}\\ \mathrm{O}\end{smallmatrix}\right\}$, −2·6; $\left.\mathrm{C}\!<\!\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}\right\}$, −3·7; $\left.\mathrm{O}\!<\!\begin{smallmatrix}\mathrm{C}\\ \mathrm{C}\end{smallmatrix}\right\}$, −5·2. Corrections in alkyl chains: CN: β, −1·3; γ, −0·8; δ, −2·6; ε, −1·1 (total, −5·8); Br and I: γ, −0·7; δ, −1·5; ε, −0·6 (total, −2·8). Various group values and corrections required for aromatic compounds with nitrogen and oxygen attached to the ring are in the text.

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