273. *Studies in Dielectric Polarisation. Part XXIII. The Dipole Moments of Some Aliphatic and Aromatic Aldehydes and of Anthrone.*

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The dipole moments of a number of aldehydes have been measured. The moments of the lower aliphatic aldehydes are discussed from the point of view of the series effect. From the moments of benzaldehyde and its substituted derivatives an angle of 55° between the axis of the ring and the C=O direction is found. Allowance for interaction moment in the *p*-substituted compounds is made by a comparison with the corresponding acid chlorides, and by an application of these results a value of 125° is found for the angle between the axes of the rings in benzophenone. The —CHO groups in *p*-phthalaldehyde are found to exhibit completely free rotation.

In Parts XVI—XVIII (J., 1936, 158, 1175, 1178) the dipole moments of a number of acid chlorides were recorded. The work has now been extended to measurements on aldehydes and their derivatives, *viz.*, some aliphatic aldehydes, chloral, bromal, benzaldehyde, and some *p*-substituted benzaldehydes. (A preliminary note on the results for aliphatic aldehydes was given in *Nature*, 1937, **139**, 510.) The compounds listed in Table I have been investigated in benzene solution at 20°, and the results are given in Debye units together with those of previous measurements on aldehydes.

TABLE I.

Acetaldehyde	2·49 [1]	Trichloroacetaldehyde	1·58 [1]
Propaldehyde	2·54,[1] 2·4 [2]	Tribromoacetaldehyde	1·69 [1]
n-Butaldehyde	2·57,[1] 2·46 [3]	Phenylacetaldehyde	2·48 [1]
*iso*Butaldehyde	2·58 [1]	Benzaldehyde	2·96,[1] 2·75,[6] 2·77 [7]
n-Valeraldehyde	2·57 [1]	*p*-Tolualdehyde	3·30 [5]
*iso*Valeraldehyde	2·60 [1]	*p*-Bromobenzaldehyde	2·19 [5] (dioxan 25°)
Heptaldehyde	2·56 [4]	*p*-Chlorobenzaldehyde	2·03 [1]
α-Ethylhexaldehyde	2·64 [5]	*p*-Nitrobenzaldehyde	2·41,[1] 2·4 [6]
		p-Phthalaldehyde	2·35 [8]
		Anthrone	3·66 [1]

[1] Present research. [2] Herold and Wolf, *Z. physikal. Chem.*, 1931, *B*, **12**, 165. [3] Hassel and Naeshagen, *ibid.*, 1929, *B*, **6**, 152. [4] Errera and Sherrill, *J. Amer. Chem. Soc.*, 1930, **52**, 1993. [5] Pearce and Berhenke, *J. Physical Chem.*, 1935, **39**, 1005. [6] J. W. Williams, *J. Amer. Chem. Soc.*, 1928, **50**, 2350. [7] Goebel and Wenzke, *ibid.*, 1937, **59**, 2301. [8] Hassel and Naeshagen, *Z. physikal. Chem.*, 1930, *B*, **6**, 441.

The moments of the following compounds have also been measured, but owing to experimental difficulties experienced by reason of the great tendency of the substances to polymerise, the results are less certain :

α-Phenylpropaldehyde	2·79	Acraldehyde	2·88
β-Phenylpropaldehyde	2·31 (2·34 in hexane)		

Aliphatic and Substituted Aliphatic Aldehydes.—The only published values of the moments of aldehydes in the vapour state are 2·68 (Zahn, *Physikal. Z.*, 1932, **33**, 686) and 2·72 (calculated by Højendahl, Thesis, Copenhagen, 1928, 128, from the measurements of Pohrt, *Ann. Physik*, 1913, **42**, 569) for acetaldehyde. No value for the moment of formaldehyde derived either from solution or from vapour measurements has been published.

The moment of acetaldehyde in benzene is 2·49, that of propaldehyde, 2·54, is slightly greater, and the moments of the higher members attain a practically constant value (2·57). *iso*Butaldehyde and *iso*valeraldehyde have very slightly higher moments than the corresponding straight-chain compounds. This is a general result in an aliphatic series, although the difference in this case is of the same order as the experimental error.

The difference between the moments of acetaldehyde and the constant value attained by the higher members of the series represents the moment induced in the chain by the primary dipole. This difference is considerably less than in many other series, *e.g.*, the acid chlorides and the nitriles. The reason is probably to be sought in the smaller angle between the C_1–C_2 axis of the carbon chain and the axis of the —CHO dipole, which must lie coincident with, or at a small angle to, the C=O direction. In the acid chlorides this angle is 164° (Part XVI, *loc. cit.*), and in the aldehydes it is approximately 125° if the angles are assumed to be tetrahedral. This angle will be discussed later. The magnitude of the induction effect in a series is, however, probably affected by a number of factors, including the polarisability of the groups forming the principal dipole (Cowley and Partington, *Nature*, 1937, **140**, 1100; this vol., p. 977).

The moment of chloral, 1·58, can be composed of those of acetaldehyde and ααα-trichloroethane; the moment of the latter is 1·57 (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 669). The angle between the resultant aldehyde moment and the C_1–C_2 axis is found from a vector diagram (Fig. 1) to be 142°. This angle is considerably greater than the theoretical tetrahedral angle between a double and a single bond attached to carbon (125° 16′), but in the calculation no allowance has been made for the effect of the C=O moment on the very polarisable —CCl_3 group. The calculation of the latter effect is complicated by the difficulty of locating the point at which the polarisability of the C—Cl_3 group can be assumed to act, and consequently by the uncertainty of the small distances involved.

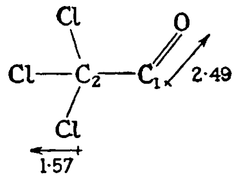

Fig. 1.

Bromal has a higher moment (1·69) than chloral (1·58), which would be expected since the —CBr_3 moment is lower than the —CCl_3 moment.

Phenylacetaldehyde has a moment of 2·48, which is about the same as that of acetaldehyde (2·49) but considerably less than that of benzaldehyde (2·96, present measurements). In the series of acid chlorides, nitriles, and alkyl chlorides, the values of the moments of the benzyl compounds lie between those of the methyl and ethyl compounds, and in the series now studied the results are analogous (Part XVII, *loc. cit.*).

Acraldehyde has a moment of 2·88. A value of 3·54 has been obtained for crotonaldehyde in carbon tetrachloride solution (Bentley, *Trans. Faraday Soc.*, 1934, **30**, " Table of Dipole Moments "). The latter aldehyde would be expected to have a higher moment than the former since in it a methyl group has been substituted for a hydrogen atom attached to the unsaturated CH:CH·CHO group. It is possible that the moment of acraldehyde is lowered by polymerisation in solution.

Benzaldehyde and Substituted Benzaldehydes.—The moment of benzaldehyde (2·96) found is considerably higher than those previously reported. The material first used was purified from a commercial specimen, and the results obtained with this were identical with those found for a specimen obtained from Kahlbaum (" for scientific purposes ").

Williams (*loc. cit.*) obtained for the moment of benzaldehyde a value of 2·75, and Goebel and Wenzke (*loc. cit.*) a value of 2·77. The latter authors at the same time report a value of 2·77 for the moment of acetophenone. Other values for acetophenone are 2·97 (Hassel and Uhl, *Z. physikal. Chem.*, 1930, *B*, **8**, 187), 2·93 (Donle and Fuchs, *ibid.*, 1933, *B*, **22**, 1), and 3·00 in the vapour state (Groves and Sugden, J. 1935, 974). Since the presence of benzoic acid as an impurity would lower the apparent moment (*i.e.*, 16% of benzoic acid would lower the moment by 0·2 unit), it is considered that the higher value now reported for the moment of benzaldehyde is probably more correct than previous results.

The values for the moment of benzophenone in benzene solution reported vary between 2·95 and 3·03. Müller (*Physikal. Z.*, 1933, **34**, 689) obtained a polarisation corresponding with 2·97, which we have confirmed. It thus appears that in benzene solution the moments of benzaldehyde, acetophenone, and benzophenone are all approximately the same, *viz.*, 2·93—2·97.

The moment of benzaldehyde may be derived from the following components (Fig. 2) : (1) The C=O moment : this is taken as 2·25 since the moment of acetaldehyde is 2·5 and that of acetone 2·75 (average of several values in the supplementary list to the Discussion on Dipole Moments, *Trans. Faraday Soc.*, 1934, **30**) ; it agrees well with the vapour value calculated as 2·28 (Groves and Sugden, J., 1937, 1999). (2) The moments m_x and m_y induced by the C=O group in the polarisable atoms forming the benzene ring : m_x is in the C=O direction and m_y is at right angles to it. (3) An electromeric moment m_1 acting across the ring. (4) The C–H moment is formally neglected but is really included in that of C=O.

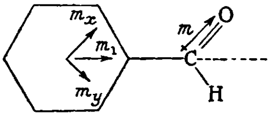

Fig. 2.

The induced moments m_x and m_y are calculated by the method of Smallwood and Herzfeld (*J. Amer. Chem. Soc.*, 1930, **52**, 1919) for various possible values of θ, the angle between the C=O direction and the projection of the C_1–C_4 axis of the ring (Fig. 2). The polarisability of the benzene ring is assumed to act at the centre and an average value of 1×10^{-23} cm.^{3} is used. The C–C distance in the ring is taken as 1·40 A. and the $C_{\text{aliphatic}}$–C_{aromatic} distance as 1·50 A. These values are derived from electron diffractions (see *Ann. Reports*, 1937, **34**, 197). The C=O moment is assumed to act at the point of contact of the carbon and oxygen atoms, *i.e.*, at 0·70 A. from the carbon nucleus. The moments induced in a vacuum are multiplied by the factor $(\varepsilon + 2)/3\varepsilon$ to allow for the presence of the medium (Frank, *Proc. Roy. Soc.*, 1935, *A*, **152**, 171).

For a particular value of θ, the electromeric moment in the ring, m_1, is derived from a vector diagram with the use of the values of m_x and m_y determined above and the total moment of benzaldehyde (2·96). With this particular model the moments of *p*-chloro- and *p*-nitro-benzaldehydes and of *p*-tolualdehyde are calculated with the use of the moments 0·4 for toluene, 1·55 for chlorobenzene, and 3·97 for nitrobenzene (average values in the literature). These calculations are made for various values of θ and the calculated results are given in Table II, together with the experimental values for the *p*-substituted benzaldehydes.

When a second substituent enters the para-position to the first in a benzene compound, the resultant dipole moment is not exactly the value which would be obtained by vector addition, even when the moments of both groups lie in the plane of the benzene ring. An interaction moment arises. Tiganik (*Z. physikal. Chem.*, 1931, *B*, **13**, 425) obtained values of 1·56, 3·97, and 2·57 for the moments of chloro-, nitro-, and *p*-chloronitro-benzene respectively. The moment of the last compound, calculated by vector addition from those of the two monosubstituted compounds, is 2·41, and the difference between this and the experimental value gives an interaction moment of 0·16. Similarly with *p*-bromonitrobenzene an interaction moment of 0·21 is obtained from the results of Tiganik. An interaction moment of 0·16 also exists in *p*-chlorophenyl *iso*cyanate (Sidgwick, Sutton, and Thomas, J., 1933, 409).

The figures given in parentheses are the interaction moments, or the moments which are added vectorially to the C_6H_5X group moment (where X = CH_3–, Cl–, or –NO_2) in order that the calculated moment of the *p*-substituted benzaldehydes shall be equal to the observed values. These interaction moments are taken as negative when they act across the ring towards the aldehydo-group.

TABLE II.

θ.	m_x.	m_y.	m_1.	Calculated moments.		
				p-$Cl{\cdot}C_6H_4{\cdot}CHO$.	*p*-$Me{\cdot}C_6H_4{\cdot}CHO$.	*p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$.
50°	0·26	0·52	0·47	1·85 (–0·32)	3·28	2·18 (+0·30)
53	0·22	0·54	0·52	1·87 (–0·27)	—	2·27 (+0·20)
55	0·19	0·55	0·57	1·90 (–0·25)	—	2·30 (+0·16)
57	0·15	0·56	0·63	1·94 (–0·20)	—	2·33 (+0·08)
60	0·11	0·56	0·71	1·96 (–0·15)	3·29	2·37 (+0·05)
				Experimental values.		
				2·03	3·30	2·41

This is illustrated in Fig. 3 for the case where θ is 55°. μ is the resultant benzaldehyde moment (including m_x, m_y, and m_1), μ_{Cl} and μ_{NO_2} are the chlorobenzene and the nitrobenzene moment, respectively, while μ_E and μ_{E_1} are the corresponding interaction moments. μ_R and μ_{R_1} are the resultant moments of *p*-chloro- and *p*-nitro-benzaldehyde, respectively, when the interaction moments μ_E and μ_{E_1} are not included, while μ_R' and μ_{R_1}' are the corresponding values when allowance is made for μ_E and μ_{E_1}.

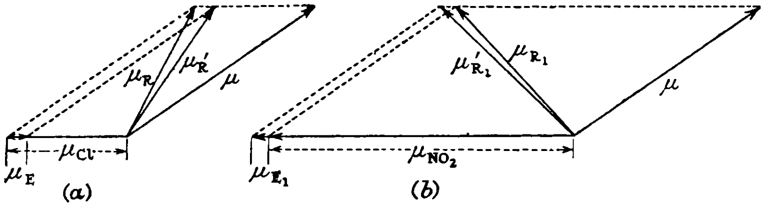

FIG. 3.

If the interaction moments are neglected the angle is found to exceed 60°. This is improbable, since the theoretical angle on the classical ideas of tetrahedral carbon is 55°.

The interaction moments of the *p*-substituted benzoyl chlorides have been found (Part XVII, *loc. cit.*); the values are given in Table III together with the interaction moments taken from Table II for $\theta = 55°$. In the calculations in Part XVII the angle between the resultant —COCl moment and the C–C axis was only 16° and was found independently.

TABLE III.

Interaction moments.

p-Chlorobenzoyl chloride	$-0{\cdot}18$	*p*-Chlorobenzaldehyde	$-0{\cdot}25$
p-Nitrobenzoyl chloride	$+0{\cdot}15$	*p*-Nitrobenzaldehyde	$+0{\cdot}16$
p-Methylbenzoyl chloride	$-0{\cdot}09$	*p*-Methylbenzaldehyde	$-0{\cdot}05$

The electromeric effect of the $—CH_2Cl$ group has a small value of an order comparable with that of the $—CH_3$ moment (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 686). In view of this result it seems reasonable to suppose that the —CHO and the —COCl group have similar electromeric effects, and that the interaction moments in analogous compounds are approximately of the same order.

The value 55—58° for θ, the angle between the C=O direction and the axis of the benzene ring, appears to agree quite well with the results for the *p*-substituted benzaldehydes when a reasonable allowance is made for the interaction moments. In subsequent calculations the values of m_1 corresponding to $\theta = 55°$ in Table II are used.

No electron-diffraction measurement with benzaldehyde appears in the literature. A value of 122° ± 5° has been obtained for the C—C=O angle in acetaldehyde (Ackermann and Mayer, *J. Chem. Physics*, 1936, **4**, 377), which gives a value of 58° for θ.

p-*Phthalaldehyde.*—From the results for benzaldehyde, the moment of *p*-phthalaldehyde can be calculated by assuming free rotation of the two —CHO groups (Fig. 4). With the assumption of an angle of 55° between the C–C axis of the ring and each of the C=O groups, the use of the component moments 2·25, m_1, m_x, and m_y corresponding to this angle (see Table II) leads to the result that the resultant moments reduce to two of magnitude 1·69 at right angles to the axis of the ring and capable of rotating about it if there is no interference (Fig. 5).

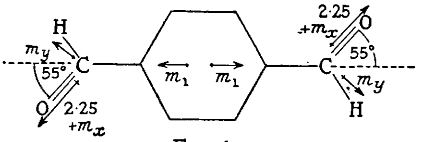

FIG. 4.

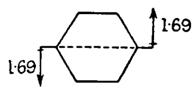

FIG. 5.

Williams's formula (*Z. physikal. Chem.*, 1928, *A*, **138**, 75), *viz.*,

$$\mu^2 = \frac{1}{2\pi}\int_0^{2\pi}\left(2m\sin\theta\,.\cos\frac{\phi}{2}\right)^2 d\phi$$

gives for the calculated moment, on the assumption of completely free rotation, the value $\sqrt{2} \times 1{\cdot}69 = 2{\cdot}38$. This agrees well with the experimental value of 2·35 obtained by Hassel and Naeshagen (Table I). The result supports the assumption that there is free rotation of the —CHO groups about the axis of the ring, and it also suggests that any possible resonance effect in these compounds does not hinder rotation.

Benzophenone and p-*Substituted Benzophenones.*—These results can now be applied to benzophenone. The assumption is made that m_1, the electromeric moment acting along the axis of the benzene ring in benzaldehyde, has the same value in each ring in benzophenone; m_x' and m_y' are the moments induced in the rings by the C=O moment (taken as 2·25 as before) respectively parallel to and perpendicular to its direction. These are calculated as in the case of benzaldehyde, except that in the present case m_y' moments always cancel (Fig. 6). Various values of θ', the angle between the rings, are used. The first value of m_1 in Table IV corresponds to an angle of $\theta = 55°$ in benzaldehyde, and the second to an angle of 60° : the first is considered more probable. The total moment of benzophenone is then equal to

$$\mu = 2{\cdot}25 + 2m_x' + 2m_1 \cos (\theta'/2)$$

The values of μ, the moment of benzophenone, are given in Table IV. The experimental value is 2·97.

TABLE IV.

$m_1 = 0{\cdot}57$	θ'	130°	125°	120°	110°	100°
	μ	2·82	2·92	3·04	3·28	3·50
$m_1 = 0{\cdot}71$	θ'	130°	125°	120°	110°	100°
	μ	2·93	3·05	3·18	3·44	3·68

If account is taken of the interaction moments in the *p*-substituted benzaldehydes, the angle (θ') between the axes of the rings in benzophenone is found to be about 123°. If, however, interaction moments are neglected, the angle θ in benzaldehyde will be greater than 60°, and thence the C—C═O angle will be considerably smaller than the tetrahedral value (125° 16′). When the value of m_1 corresponding to this greater angle of θ is used in the calculation for benzophenone the resulting value of θ' is slightly greater than 130° (Tables II and IV). This may be compared with the value obtained from the dipole moments of the mono- and di-chlorobenzophenones, *viz.*, 131—133° (Sutton and Hampson, *Trans. Faraday Soc.*, 1935, **31**, 945; Bergmann, Engel, and Meyer, *Ber.*, 1932, **65**, 446).

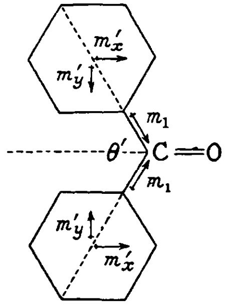

FIG. 6.

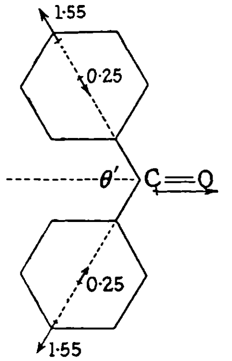

FIG. 7.

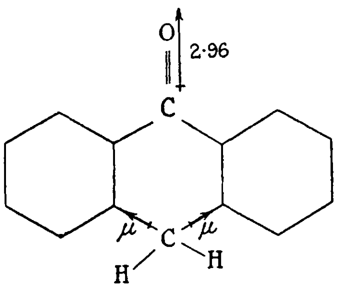

FIG. 8

The calculations of the moment of benzophenone make no allowance for the possibility of the moments m_1, m_x, and m_y in one of the rings having an effect on the other ring. The principal moment acting in each ring is m_1 and a calculation of the effect of the moments m_1 in the other ring shows that the calculated moment of benzophenone will be 0·05 higher, leading to an increase in the angle θ' from 123° to 125°.

In their calculations of the angle θ' from the moments of the *p*-chlorobenzophenones, Sutton and Hampson (*loc. cit.*) make no allowance for any interaction moment because, they claim, in a special case (to which the substituted benzophenones belong) the interaction moment in the *p*-mono-derivative and that in the *pp*′-di-derivative are of opposite sign, so that the true value of θ' must lie between two limiting values, for the mono- and the di-derivative, severally.

If, however, in the case of *pp*′-dichlorobenzophenone, allowance is made for the interaction moment produced by chlorine in each ring by assuming that it is the same as it is in benzaldehyde, and a value of 1·55 is taken for the chlorobenzene moment, then an angle of 122½° is obtained for θ' (Fig. 7). It seems probable that the angle between the axes of the rings in benzophenone is 125° ± 3°. From our values of m_1 and the angle 125°, a moment of 1·75 is calculated for the *p*-chlorobenzophenone, which is in good agreement with the experimental value of 1·72 (Bergmann, Engel, and Meyer, *loc. cit.*; Hampson and Sutton, *loc. cit.*).

Anthrone.—The experimental value of the moment of anthrone is 3·66. This moment originates in a C═O moment and its effect in the two rings as in benzophenone, but in addition there are two moments (μ in Fig. 8) each of which may be taken as equal to that of toluene (0·4). The angles θ'' and ϕ are indicated in Fig. 8. If $\theta'' = \phi = 120°$, the total moment of anthrone is calculated as 3·44, which is lower than the experimental value. Probably the moments μ (Fig. 8) are greater than that of toluene. This is indicated by a recent value for the moment of fluorene (0·82; Le Fèvre and Le Fèvre, J., 1937, 203).

EXPERIMENTAL.

The dielectric constants were measured by means of the apparatus described in Parts XII and XIII (J., 1935, 602, 605). Most of the measurements were made with the silvered dielectric cell described in Part XII, but for some of the later ones the platinum plate cell described in Part XX (J., 1936, 1184) was used. For the aliphatic aldehydes and benzaldehyde the measurements were carried out in an atmosphere of nitrogen. The accuracy of the dipole moments is ± 0·02 D., except for acetaldehyde and the phenyl-substituted aliphatic aldehydes and acraldehyde, the properties of which prevented very accurate values from being obtained.

Acetaldehyde, propaldehyde, *n*-butaldehyde, and *iso*butaldehyde, obtained from Kahlbaum, were kept over calcium chloride and fractionated two or three times in an apparatus from which air had been displaced by nitrogen. *n*-Valeraldehyde, from Fraenkel and Landau, and *iso*valeraldehyde, from Kahlbaum, were fractionated twice in nitrogen. Chloral and bromal were obtained from Kahlbaum. The chloral was kept over phosphoric oxide overnight, and fractionated once over fresh phosphoric oxide and twice without it. The bromal was twice fractionated at low pressure. Phenylacetaldehyde and α- and β-phenylpropaldehydes, from Fraenkel and Landau, were purified by twice fractionating them under reduced pressure. Acraldehyde, from Kahlbaum, was fractionated 3 times.

Two specimens of benzaldehyde were used. The first was a commercial specimen purified *via* the bisulphite compound, which was steam-distilled in the presence of sodium carbonate. The distillate was dried over calcium chloride and twice fractionated at low pressure. The second specimen was obtained from Kahlbaum (" for scientific purposes ") and was fractionated once under reduced pressure, only the middle third being used, although the first and the third fraction had identical density and refractive index with the second. The two specimens had identical properties, and the P_2–f_2 points lay on the same line. *p*-Nitrobenzaldehyde, from Kahlbaum (" for scientific purposes "), was recrystallised from alcohol and dried in a vacuum desiccator for a week. *p*-Chlorobenzaldehyde, from Fraenkel and Landau, was fractionated under reduced pressure. It gave a sharper m. p. after this treatment than after recrystallisation.

Anthrone was prepared by partial reduction of anthraquinone with tin and fuming hydrochloric acid (*d* 1·19) in boiling acetic acid solution. It was precipitated by dilution, washed with water, dried, and recrystallised from benzene–light petroleum (3 : 1) (Meyer, *Annalen*, 1911, **379**, 55; " Organic Syntheses," **8**, p. 8).

The benzene was Kahlbaum's " thiophen free " and was purified as before.

The physical constants of the materials used are given in Table V.

TABLE V.

Compound.	B. p.	$D^{20°}_{4°}$.	$n^{20°}_D$.	$[R_L]_D$.
Acetaldehyde	20·6°/764 mm.	0·8058 ($D^{0°}_{4°}$)	1·3437 ($n^{0°}_D$)	11·56
Propaldehyde	48·2/764	0·8058	1·3639	16·05
n-Butaldehyde	74·5/758	0·8040	1·3807	20·80
*iso*Butaldehyde	63·5/754	0·7904	1·3738	20·82
n-Valeraldehyde	102·5/766	0·8105	1·3947	25·46
*iso*Valeraldehyde	92·5/754	0·8004	1·3904	25·52
Chloral	96·4/749	1·5066	1·4559	26·59
Bromal	66·5/13	2·6748	1·5835	35·10
Phenylacetaldehyde	94·5/23	1·0319	1·5283	35·82
α-Phenylpropaldehyde	98/23	1·014	1·5242	40·41
β-Phenylpropaldehyde	105/15	1·019	1·5266	40·41
Acraldehyde	52·6/766	0·8404	1·3992	16·0
Benzaldehyde (1)	62·2/12	1·0447	1·5455	32·13
Benzaldehyde (2)	78/24	1·0448	1·5455	32·13
p-Chlorobenzaldehyde	102/20	(m. p. 48·5°)		37·0 (calc.)
p-Nitrobenzaldehyde		(m. p. 105·4°)		38·28 (calc.)
Anthrone		(m. p. 154°)		58 (calc.)

Results.—The solvent is benzene (except where otherwise stated), and the temperature 20° in all cases. The symbols are those used in previous papers in this series, and μ is recorded in Debye units (e.s.u. × 10^{-18}).

Acetaldehyde.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8787	2·284	26·64	—
0·03935	0·8764	2·643	30·99	137·2
0·06048	0·8752	2·848	33·10	133·5
0·06482	0·8749	2·901	33·64	134·7
0·09163	0·8732	3·160	35·93	127·8

$P_{2\infty}$ = 143 c.c.; P_{E} = 11·5 c.c.; μ = 2·49.

n-Butaldehyde.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8787	2·276	26·52	—
0·01143	0·8781	2·378	27·97	153·1
0·01629	0·8777	2·421	28·55	151·2
0·02823	0·8771	2·515	29·81	142·9
0·03044	0·8770	2·533	30·04	142·0
0·03704	0·8767	2·578	30·61	136·8

$P_{2\infty}$ = 161 c.c.; P_{E} = 20·8 c.c.; μ = 2·57.

n-Valeraldehyde.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8790	2·281	26·58	—
0·01017	0·8780	2·374	27·96	162·3
0·02066	0·8771	2·468	29·31	158·8
0·02395	0·8770	2·499	29·74	158·6
0·03697	0·8758	2·616	31·33	155·0

$P_{2\infty}$ = 165 c.c.; P_{E} = 25·5 c.c.; μ = 2·57.

Chloral.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8788	2·278	26·54	—
0·01380	0·8884	2·326	27·27	79·08
0·02126	0·8934	2·351	27·65	78·60
0·03421	0·9023	2·396	28·31	78·24
0·04044	0·9066	2·418	28·63	78·17

$P_{2\infty}$ = 79·5 c.c.; P_{E} = 26·5 c.c.; μ = 1·58.

Phenylacetaldehyde.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8789	2·278	26·54	—
0·01239	0·8813	2·389	28·23	163·2
0·02188	0·8832	2·474	29·47	160·4
0·03126	0·8850	2·558	30·67	158·7
0·03765	0·8862	2·616	31·47	157·5

$P_{2\infty}$ = 165·5 c.c.; P_{E} = 35·5 c.c.; μ = 2·48.

β-Phenylpropaldehyde.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8787	2·280	26·57	—
0·01055	0·8808	2·363	27·90	152·2
0·02870	0·8845	2·506	30·10	149·7
0·03697	0·8863	2·570	31·07	148·2

$P_{2\infty}$ = 153·8 c.c.; P_{E} = 40·4 c.c.; μ = 2·31.

p-Nitrobenzaldehyde.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8785	2·281	26·59	—
0·00839	0·8834	2·355	27·70	159·5
0·01197	0·8855	2·385	28·16	158·1
0·01634	0·8878	2·423	28·72	157·0
0·02019	0·8901	2·457	29·21	156·5
0·02345	0·8921	2·484	29·61	155·5

$P_{2\infty}$ = 161·5 c.c.; P_{E} = 38·3 c.c.; μ = 2·41.

Benzaldehyde.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8788	2·280	26·57	—
0·00496	0·8799	2·344	27·50	215·5
0·00961	0·8809	2·405	28·37	214·0
0·01782	0·8824	2·513	29·85	210·7
0·02140	0·8834	2·560	30·48	209·2

$P_{2\infty}$ = 218 c.c.; P_{E} = 32 c.c.; μ = 2·96.

Propaldehyde.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8788	2·280	26·57	—
0·01162	0·8781	2·385	28·00	150·0
0·02290	0·8775	2·488	29·33	147·2
0·02920	0·8771	2·545	30·03	145·2
0·03960	0·8764	2·642	31·19	143·3
0·04061	0·8765	2·647	31·24	141·6

$P_{2\infty}$ = 153 c.c.; P_{E} = 16·05 c.c.; μ = 2·54.

*iso*Butaldehyde.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8789	2·281	26·58	—
0·01738	0·8773	2·439	28·80	154·7
0·03611	0·8759	2·600	30·92	146·9
0·05318	0·8746	2·737	32·60	139·7

$P_{2\infty}$ = 162 c.c.; P_{E} = 21 c.c.; μ = 2·58.

*iso*Valeraldehyde.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8789	2·280	26·58	—
0·00891	0·8778	2·364	27·82	166·2
0·01840	0·8772	2·451	29·08	162·4
0·02805	0·8763	2·540	30·31	159·6
0·04506	0·8746	2·687	32·28	153·1

$P_{2\infty}$ = 169 c.c.; P_{E} = 25·5 c.c.; μ = 2·60.

Bromal.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8787	2·280	26·57	—
0·00847	0·8970	2·318	27·15	95·3
0·01370	0·9082	2·341	27·51	94·9
0·02005	0·9217	2·371	27·95	95·2
0·03128	0·9455	2·421	28·70	94·6
0·03845	0·9596	2·453	29·20	94·9

$P_{2\infty}$ = 95·5 c.c.; P_{E} = 35·0 c.c.; μ = 1·69.

α-Phenylpropaldehyde.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8787	2·280	26·57	—
0·00716	0·8801	2·362	27·84	202·9
0·02386	0·8835	2·549	30·61	196·1
0·03448	0·8858	2·665	32·24	190·8
0·04439	0·8877	2·779	33·79	189·2

$P_{2\infty}$ = 205 c.c.; P_{E} = 40·5 c.c.; μ = 2·79.

Acraldehyde.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8785	2·281	26·59	—
0·02208	0·8780	2·542	30·01	181·2
0·03368	0·8777	2·680	31·63	176·1
0·05833	0·8771	2·965	34·66	164·8

$P_{2\infty}$ = 191 c.c.; P_{E} = 16 c.c.; μ = 2·88.

p-Chlorobenzaldehyde.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8788	2·280	26·57	—
0·00263	0·8800	2·296	26·82	123·0
0·00438	0·8807	2·306	26·98	119·6
0·00776	0·8823	2·326	27·30	120·3
0·01237	0·8843	2·352	27·71	118·5

$P_{2\infty}$ = 124·0 c.c.; P_{E} = 37·0 c.c.; μ = 2·03.

Anthrone.

f_2.	$D^{20°}_{4°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8791	2·279	26·55	—
0·00331	0·8812	2·346	27·57	335·9
0·00705	0·8833	2·420	28·70	331·6
0·00898	0·8846	2·458	29·26	327·9
0·01165	0·8863	2·511	30·02	324·1
0·01396	0·8875	2·556	30·66	321·1

$P_{2\infty}$ = 341 c.c.; P_{E} = 58 c.c.; μ = 3·66.

β-Phenylpropaldehyde in hexane.

f_2.	$D_{4^\circ}^{20^\circ}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·6776	1·905	28·78	—
0·01308	0·6822	1·972	30·41	154·0
0·02594	0·6870	2·037	31·95	151·1
0·03626	0·6906	2·091	33·19	150·5
0·04542	0·6940	2·138	34·23	148·8

$P_{2\infty} = 156{\cdot}3$ c.c.; $P_E = 40{\cdot}4$ c.c.; $\mu = 2{\cdot}34$.

The authors thank the Chemical Society for a research grant, and one of them (D. I. C.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

Queen Mary College, University of London [*Received, June* 24*th*, 1938.]