89. *The Magnitude of the Solvent Effect in Dipole-moment Measurements. Part VI. Induced and Mesomeric Moments of the Alkyl Halides and the Halogenobenzenes.*

By ARNOLD AUDSLEY and FRANK R. GOSS.

The influence on the primary moment (μ_P) of alkyl radicals, known as the radical effect, is due to moments (μ_I) induced in the alkyl chains which, unlike the actual inductive effects, are not proportional to μ_P. This is due to a spatial effect arising from the disposal of the polarisable matter about the dipole axis which varies independently of the ratio μ_I/μ_P but can be determined simultaneously with the dipole moment by making use of the solvent-effect equation developed earlier in this series. In Part V (this vol., p. 358) we found that the radical effect consists of three parts, and it is now shown that the influence of the spatial effect on each of these parts varies through a series of alkyl halides in the order AlkF > AlkCl > AlkBr > AlkI. The spatial effect is negligible for the alkyl iodides, whence it is shown that the true μ_I/μ_P ratio for the tertiary halides is 0·410, and that this can be applied to analogous halogen compounds; hence we have calculated the mesomeric moments (μ_M) for the aromatic series. These values of μ_M for the halogens can be expressed as a linear function of the atomic number (Z) in the formula $\mu_M = 1{\cdot}15 - 0{\cdot}012Z$, and consequently they follow the known order for the mesomeric effect F > Cl > Br > I. They are in good agreement with those obtained by Groves and Sugden (J., 1937, 1992) by quite a different method of approach. The corrected moments for the halogenobenzenes follow the sequence PhI > PhBr > PhCl > PhF, earlier values for iodobenzene being too low owing to neglect of the solvent effect, which follows the sequence PhI $\ggg$ PhBr > PhCl > PhF.

THE total dipole moment of the simpler organic compounds can be expressed as the sum of a primary moment μ, arising in the bond C—X where X is the polar group, an induced moment μ_I, which is the vectorial component of the inductive effects in the carbon chain, and a mesomeric moment μ_M, if there is any mesomeric effect associated with the molecule. This conception was stated by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668; cf. Ingold, *Chem. Reviews*, 1934, **15**, 254), who expressed the total moment as an algebraic sum $\mu = \mu_P + \mu_I + \mu_M$. He made the comparison between *tert.*-butyl and phenyl compounds because the relevant components of the moments induced in the C—C bonds of the benzene ring by the primary moment could be assumed to correspond with, and for practical purposes be equal to, those of the *tert.*-butyl radical. The difference between these values was then taken as equal to the mesomeric moment. This procedure may lead to fallacious results for two reasons: (i) the moments used for both the aliphatic and the aromatic compounds have been those measured in dilute solution, and have lacked a correction for the solvent effect; (ii) no account has been taken of the effect of the shape of the radical on the induced moments. Calculations dealing with this spatial effect were made by Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171).

It is not practicable, in order to overcome the first difficulty, to measure all the required moments in the vapour state, because, as Groves and Sugden (J., 1937, 158) have shown, the vapours of some of the *tert.*-butyl halides decompose too rapidly. We now obviate this difficulty by correcting solution values by means of the solvent-effect equation as described in earlier parts of this series (see Part V, *loc. cit.*); this solvent correction is particularly large for iodobenzene, which has a solvent-effect constant [K] of 2·28, the largest yet determined. The radical effect of the induced moments has, in the case of the alkyl iodides, been shown (*ibid.*) to consist of three parts: (*a*) a large induced moment for the sequence Me, Et, Pr$^\beta$, Bu$^\gamma$; (*b*) a small series induced moment not noticeable beyond the butyl compounds; and (*c*) a series decrement which appears to continue right along the alkyl chains. These three parts of the radical effect were interpreted on the basis of Frank's calculation that the induced moments only augment the primary moment if the bulk of the polarisable matter is introduced along, or near to, the axis of the dipole.

In order to overcome the second difficulty, the investigation of the spatial effect on these three parts of the radical effect has now been extended to alkyl fluorides, chlorides, and bromides. For the purpose of following changes in the spatial effect it is fortunate that, by measuring the polarisation of suitable liquid mixtures and applying the solvent-effect equation, we can obtain (see Table I), not only the corrected dipole moments, but also the solvent-effect constants [K] which, as explained in Part V, give a measure of the proportion of the polarisable matter of the molecule which is disposed in the line of the dipole. These constants decrease in the order in which the halogen atoms affect the length of the polar axis, I > Br > Cl > F, and if plotted against the atomic numbers of the appropriate halogens, they lie on smooth equidistant curves, which are moreover of considerable value in checking the accuracy of the experimental data. The value of [K] for *tert.*-butyl chloride is of special interest, for although the molecule has a large moment [$\mu = 2{\cdot}04$ D.; Wiswall and Smyth

TABLE I.

Polarisation constants of carbon tetrachloride solutions at 20°.

	Calculated values.*			Exptl. value.	Derived poln. coeffs.			Solvent-effect constant,	Corr. dipole moment,
	P_{E+A}.	P_E.	P_A.	P_∞.	Z.	Y.	P_0.	$[K]$.	μ, D.
Methyl fluoride	12·1	6·5	5·6	vapour values [1]					1·76
Ethyl fluoride	16·6	11·0	5·6						1·84
n-Amyl fluoride	30·2	24·6	5·6	70·2	117·5	87·6	35·6	0·87	1·30
tert.-Butyl fluoride	calculated (see text)								[1·72]
tert.-*Amyl fluoride*	30·7	25·1	5·6	88·6	132·0	127·4	49·9	0·75	1·54
Methyl chloride	15·4	11·3	4·1	vapour values [2]					1·84
Ethyl chloride	19·9	15·8	4·1						2·01
n-Butyl chloride	29·0	24·9	4·1	106·3	88·4	171·6	76·1	1·13	1·90
tert.-Butyl chloride	see Part IV (J., 1941, 864)							0·99	2·04
Methyl bromide	19·1	14·1	5·0	vapour value [1]					1·72
Ethyl bromide	see Part IV								1·99
n-Butyl bromide	32·7	27·7	5·0	107·2	78·8	165·5	79·7	1·36	1·95
tert.-Butyl bromide	33·3	28·3	5·0	131·1	92·9	217·4	99·4	1·22	2·17
Methyl iodide	see Part IV (*loc. cit.*)							1·72	1·56
Ethyl iodide								1·62	1·89
n-Butyl iodide	see Part V (*loc. cit.*)							1·49	1·93
tert.-Butyl iodide								1·36	2·20
Fluorobenzene	see Part IV (*loc. cit.*)							1·44	1·44
Chlorobenzene								1·61	1·64
Bromobenzene								1·88	1·68
Iodobenzene	41·4	38·3	3·1	77·8	23·2	81·1	60·0	2·28	1·69

* Calculated from the contributory values for P_E and $P^{\text{liq.}}_{E+A}$ recorded in J., 1941, 864, Table II. Using these additive P_{E+A} values, moments have been recalculated from the vapour data of:

[1] Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499.

[2] Fuchs, *Z. Physik*, 1930, **63**, 824.

(*J. Chem. Physics*, **1941**, **9**, **356**) record **2·13**, but this value is not corrected for P_{E+A}], it is practically spherical as shown by the similarity in the polarisability of the Cl and Me groups (P_E values are F 0·9, Cl 5·7, Br 8·5, I 13·2, Me 5·6 c.c.). This nearly symmetrical character for the *tert*.-butyl chloride molecule, which has been deduced by Baker and Smyth (*J. Amer. Chem. Soc.*, **1939**, **61**, 2798) from its freedom of rotation in the solid state, is now confirmed by our determination of $[K]$, which is 0·99, or very nearly unity, and this, by definition, is the value for symmetrical compounds.

The moments of the alkyl halides are given in Table I. Values for the volatile compounds are obtained from recorded vapour data, and made comparable with our corrected liquid values by employing throughout additive P_{E+A} coefficients, calculated from the atomic contributions tabulated in Part IV (*loc. cit.*). Our values for *n*-butyl chloride and bromide are lower than those recorded (Smyth and McAlpine, *J. Chem. Physics*, **1935**, **3**, **347**; Groves and Sugden, *loc. cit.*) for the vapours by the same amount as that attributed (see Part V) in the case of *n*-butyl iodide to a different disposition of the alkyl chain in the liquid and the vapour state. The value for *tert*.-butyl fluoride has had to be calculated indirectly, as this compound is both too volatile for accurate determination in the liquid state, and too unstable for vapour measurements (cf. Cooper and Hughes, J., **1937**, **1183**). We have found (see Part V) that tertiary and primary iodides have the same series decrement, so that for the tertiary fluorides has been determined from the difference between the *n*-amyl and the ethyl member (1·84—1·30)/3 = 0·18. This decrement has been applied to the value for *tert*.-amyl fluoride (1·54), giving the calculated moment for *tert*.-butyl fluoride as 1·72 D.

From our definition of the solvent-effect constant (see Part V) and Frank's calculation of the influence of the spatial effect on the radical effect, the apparent direction of the induced moments (*a*) in the sequence Me, Et, Pr^{β}, Bu^{γ} should be opposed to their true direction, when the value of $[K]$ falls below unity. This prediction is precisely borne out by our results, particularly those for *tert*.-butyl fluoride. The radical effect (*a*) is undoubtedly reversed for the fluorides; further, the data show that all three parts of the radical effect exhibit a decrease with the falling values of $[K]$ in the series $I > Br > Cl > F$, the small series inductive effect (*b*) observed for the lower iodides tending to disappear at the lower values of $[K]$, whilst the series decrement (*c*) along the alkyl chains becomes more prominent, being 0·01, 0·04, and 0·07 for the iodides, bromides, and chlorides, until for the fluorides it reaches the large value of 0·18 D. already noted.

These relationships between $[K]$ and μ enable us to conclude that the true induced moments in the alkyl halides are successively masked in passing down the series I, Br, Cl, F by changes in the disposal of the polarisable matter about the C—X bond arising from the decreasing radius of the halogen atoms. If we could imagine an alkyl series where such spatial considerations did not affect the induced moments, the observed moments for a lengthening chain might be expected (cf. Smyth and Rogers, *J. Amer. Chem. Soc.*, **1930**, **52**, **2237**) to reach a constant value. This is very nearly the case for the iodides, which with their small series decrement of 0·01 D. must suffer little or no spatial effect. We are therefore justified in concluding that for the iodides the spatial effect can be neglected in comparison with the other manifestations of the radical effect, which means that the radical effect for the Me, Et, Pr^{β}, Bu^{γ} sequence can, in the case of the iodides, be taken to represent the true induced moments of these groups.

Following Groves and Sugden (*loc. cit.*), we assume that the primary moment is identified with the moment of the methyl halide, and any error so introduced has only a negligible effect on our subsequent calculations. The order of μ_P for the C—X bonds, Cl > F > Br > I, is not precisely the same as that of the inductive ($-I$) effect, F > Cl > Br > I, but as Ingold (*loc. cit.*, p. 240) says, this order must be partly upset for dipole moments by the apparent size of the halogen atoms, which are in the reverse order F < Cl < Br < I. Now, we have shown in the previous paragraph that the moment of *tert.*-butyl iodide should give us the true inductive ratio μ_I/μ_P for the tertiary halides, free from spatial effect. This ratio is 0·64/1·56, or 0·410, which should therefore give, not only the true induced moment in all the tertiary halides as recorded in Table II, but also the observed induced moments in analogous halogen compounds, for which the spatial effect is negligible and $[K]$ is therefore large. It is accordingly the appropriate ratio for the halogenobenzenes, as these all have $[K]$ greater than any of the *tert.*-alkyl halides, and it is also in good agreement with the value of 0·433 calculated by Groves and Sugden (*loc. cit.*). The mesomeric moments recorded in this paper (Table II) and calculated from the relation $\mu = \mu_P + \mu_I + \mu_M$ are therefore of the same order of magnitude as those obtained by Groves and Sugden, although there are small deviations due to the employment by them of only partly corrected solution data for fluoro- and iodo-benzene. These values of μ_M for the halogens can be expressed as a linear function of the atomic number (Z) in accordance with the equation $\mu = 1{\cdot}15 - 0{\cdot}012Z$, and are therefore in the order F > Cl > Br > I established by Baddeley and Bennett (J., 1933, 261; cf. Bird and Ingold, J., 1938, 918) for the mesomeric effect.

New polarisation data are presented in Table I for the polar liquids in mixtures with carbon tetrachloride dealt with in this paper. From these data the dipole moments and solvent-effect constants have been calculated by the usual solvent-effect method. Moments recalculated from previously recorded vapour data, by making use of the additive P_{E+A} values tabulated in Part IV, are also included.

TABLE II.

Primary, induced, and mesomeric moments of tert.*-halides and halogenobenzenes.**

	MeX (μ_P).	μ_I ($0{\cdot}64\,\mu_P/1{\cdot}56$).	$\mu_P + \mu_I$.	PhX ($\mu_P + \mu_I + \mu_M$).	μ_M.
F	1·76	−0·72	−2·48	−1·44	+1·04
Cl	1·84	−0·75	−2·59	−1·64	+0·95
Br	1·72	−0·70	−2·42	−1·68	+0·74
I	1·56	−0·64	−2·20	−1·69	+0·51

* Values in the last four columns have been assigned their appropriate algebraic signs.

The newly recorded value for the moment of iodobenzene is considerably higher than those already published owing to the unusually large solvent-effect correction associated with the large $[K]$ for this substance (see above). Further, the moments of the halogenobenzenes fall into a regular sequence PhI > PhBr > PhCl > PhF; this order arises from the fact that, although the mesomeric moments decrease in the direction F > Cl > Br > I, the fall in their magnitude is much more rapid than the corresponding fall in the magnitude of the induced moments which are of opposing sign (see Table II). The moments of the *tert.*-butyl halides are also in the reversed order $Bu^{\gamma}I > Bu^{\gamma}Br > Bu^{\gamma}Cl > Bu^{\gamma}F$, but this is due entirely to the operation of the spatial effect dealt with in this paper. Anomalous radical effects noted by Cowley and Partington (J., 1938, 977) and by Groves and Sugden (J., 1937, 158) arise from the same cause.

EXPERIMENTAL.

Density, dielectric constant, and temperature were measured as previously described (Goss, J., 1933, 1343; 1935, 730; 1940, 593).

Preparation and Purification of Materials.—tert.*-Amyl fluoride* is new. It was obtained by distillation of the middle fraction of a Kahlbaum sample of *tert.*-amyl alcohol with excess of 40% hydrofluoric acid. Unsaturated impurities were removed with bromine at 0°, and the fluoride washed with sodium bicarbonate solution and water. After being dried with sodium sulphate it was distilled twice, the lower fraction, b. p. 38°/458 mm., being collected. This fluoride decomposes on distillation at atmospheric pressure and on keeping; as it was not analysed before this occurred and as no further material was available, no better analyses could be obtained (Found: C, 68·2; H, 13·4. $C_5H_{11}F$ requires C, 66·6; H, 12·3%). However, the physical constants now recorded are those of the pure fluoride, measured before decomposition had commenced.

TABLE III.

Criteria of purity.

	Observed.		Previously recorded.			Observed.		Previously recorded.	
	$d_{4°}^{20°}$.	$n_D^{20°}$.	$d_{4°}^{20°}$.	$n_D^{20°}$.		$d_{4°}^{20°}$.	$n_D^{20°}$.	$d_{4°}^{20°}$.	$n_D^{20°}$.
n-Amyl fluoride	0·7885	1·3634	0·7880[1]	1·3580[1]	*n*-Butyl bromide ...	1·2758	1·4399	1·2756[3]	1·4397[3]
tert.-Amyl fluoride ...	0·7780	1·3680	—	—	*tert.*-Butyl bromide	1·2220	1·4283	1·2209[4]	1·4281[4]
n-Butyl chloride ...	0·8846	1·4017	0·8865[2]	1·4024[2]	Iodobenzene	1·8307	1·6206	1·8306[5]	1·6202[5]

[1] Swarts, *Bull. Soc. chim. Belg.*, 1921, **30**, 302. [2] Timmermans and Hennaut-Roland, *J. Chim. physique*, 1930, **27**, 401. [3] Timmermans and Martin, *ibid.*, 1926, **23**, 745. [4] Timmermans and Delcourt, *ibid.*, 1934, **31**, 85. [5] Timmermans and Hennaut-Roland, *ibid.*, 1932, **29**, 529.

n-Amyl fluoride was prepared from the iodide (this vol., p. 366) by the method of Swarts (*loc. cit.*), fluorination being carried out with mercurous fluoride (Henne and Renoll, *J. Amer. Chem. Soc.*, 1938, **60**, 1060). It was twice fractionally distilled, the middle fraction being collected in each case.

tert.-Butyl bromide, prepared by a method similar to that for the chloride (*Organic Syntheses*, 1928, **8**, 50) from recrystallised *tert.*-butyl alcohol (B.D.H.), was washed with ice-cold 1% sodium bicarbonate solution and fractionated (250 mm.), the middle third being collected.

n-Butyl chloride and bromide were prepared from *n*-butyl alcohol (*ibid.*, 1925, **5**, 27; 1921, **1**, 2) and fractionated, the middle third being collected in each case.

TABLE IV.

Polarisations of carbon tetrachloride mixtures at 20°.

c_2.	ϵ.	$d_{4°}^{20°}$.	P_{12}.	P_{S2}.	P_{S1}.	c_2.	ϵ.	$d_{4°}^{20°}$.	P_{12}.	P_{S2}.	P_{S1}.
n-*Amyl fluoride.*											
0·00000	2·2394	1·5940	28·21	70	28·2	0·02397	2·2915	1·5713	29·17	69	28·3
0·00472	2·2503	1·5893	28·41	70	28·2	0·04964	2·3491	1·5480	30·19	69	28·3
0·00649	2·2540	1·5878	28·48	70	28·2	1·00000	4·242	0·7885	59·37	59·4	35
0·01292	2·2686	1·5818	28·74	70	28·2						
tert.-*Amyl fluoride.*											
0·00000	2·2384	1·5942	28·20	89	28·2	0·05508	2·4164	1·5401	31·30	82	28·3
0·00718	2·2629	1·5864	28·64	88	28·2	0·13046	2·6753	1·4723	35·42	80	29
0·01358	2·2845	1·5800	29·02	88	28·2	0·34531	3·420	1·2847	45·82	74	31
0·02652	2·3284	1·5667	29·80	87	28·3	1·00000	5·888	0·7780	71·80	71·8	42
n-*Butyl chloride.*											
0·00000	2·2386	1·5940	28·20	106	28·2	0·17450	3·062	1·4622	39·88	88	30
0·00888	2·2798	1·5871	28·88	105	28·2	0·23031	3·362	1·4211	43·31	85	31
0·01760	2·3213	1·5804	29·55	103	28·2	0·36797	4·056	1·3206	50·17	78	34
0·04055	2·4275	1·5630	31·22	101	28·3	0·43800	4·424	1·2707	53·27	76	36
0·06086	2·5232	1·5475	32·66	98	28·4	0·48141	4·646	1·2400	55·01	75	37
0·10809	2·7495	1·5121	35·86	94	28·9	0·74153	6·028	1·0588	64·12	72	42
0·14211	2·9043	1·4864	37·91	91	29·2	1·00000	7·398	0·8846	71·23	71·2	47
n-*Butyl bromide.*											
0·00000	2·2384	1·5942	28·20	107	28·2	0·09722	2·7001	1·5608	35·27	95	28·8
0·00812	2·2774	1·5914	28·84	106	28·2	0·20833	3·256	1·5232	42·36	86	31
0·01368	2·3025	1·5894	29·26	105	28·2	0·45559	4·478	1·4425	54·41	76	36
0·02483	2·3537	1·5855	30·09	103	28·3	0·76412	5·985	1·3463	65·37	72	42
0·05046	2·4764	1·5767	32·00	100	28·4	1·00000	7·099	1·2758	71·98	72·0	46
tert.-*Butyl bromide.*											
0·00000	2·2384	1·5942	28·20	131	28·2	0·06688	2·6624	1·5643	34·81	121	28·6
0·00437	2·2650	1·5922	28·64	130	28·2	0·13988	3·170	1·5365	41·37	112	30
0·00693	2·2802	1·5911	28·89	130	28·2	0·19850	3·574	1·5075	46·10	106	32
0·00758	2·2850	1·5909	28·97	130	28·2	0·42977	5·385	1·4236	61·15	92	38
0·00898	2·2932	1·5901	29·11	129	28·2	0·60152	6·815	1·3601	69·71	87	43
0·01506	2·3312	1·5873	29·74	128	28·2	0·71839	7·789	1·3179	74·59	85	46
0·03395	2·4491	1·5790	31·61	126	28·3	1·00000	10·248	1·2220	84·66	84·7	53
Iodobenzene.											
0·00000	2·2355	1·5938	28·16	79	28·2	0·14558	2·6332	1·6331	34·78	73	28·5
0·00539	2·2524	1·5953	28·45	79	28·2	0·23074	2·8860	1·6549	38·58	70	28·8
0·01230	2·2711	1·5972	28·78	79	28·2	0·42784	3·414	1·7030	45·90	66	31
0·02447	2·3087	1·6006	29·42	78	28·2	0·63496	3·895	1·7549	51·96	63	33
0·04598	2·3701	1·6064	30·47	77	28·3	1·00000	4·625	1·8306	60·98	61·0	37
0·08908	2·4936	1·6180	32·52	75	28·4						

Iodobenzene, prepared from " AnalaR " aniline (Gattermann, " Laboratory Methods of Organic Chemistry," 1932, p. 278), was washed with sodium thiosulphate solution, dilute sulphuric acid, sodium hydroxide solution, and water, dried with calcium chloride, and twice fractionally distilled at 16 mm.

The criteria of purity for these compounds are recorded in Table III.

Results.—The experimental data and the partial polarisations (P_{S2} for the polar components, P_{S1} for the carbon tetrachloride), obtained as intercepts of the tangents to the P_{12}–c_2 curve at the axes where $c_2 = 0$ and $c_2 = 1$, are all recorded in Table IV.

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