802. *The Steric Inhibition of Mesomerism in Aromatic Compounds.*

By J. W. SMITH.

The dipole moments of 2 : 4 : 6-tribromobenzaldehyde, *o*-methylacetophenone, and 2 : 4 : 6-tribromoacetophenone in benzene solution are 2·53, 2·60, and 2·58 D, respectively. Dipole-moment evidence regarding the relative steric effects of *o*-methyl groups and *o*-bromine atoms in inhibiting the mesomerism of various groups linked to a benzene nucleus is reviewed. The mesomerism of an amino- or hydroxyl group is decreased by methyl groups but not by bromine atoms, whilst that of an aldehyde is decreased by bromine atoms but not by methyl groups. Both substituents diminish the mesomerism of a nitro-group, but bromine atoms have the greater effect. The mesomeric effect of the dimethylamino-group seems to be repressed almost completely by either substituent: that of the acetyl group is also repressed strongly by bromine atoms, but methyl groups have a similar effect only when they occupy both *ortho*-positions. It is inferred that factors other than the " size " of the obstructing groups are involved, and it is suggested that interactions between a hydrogen atom of a methyl, aldehyde, amino-, or hydroxyl group and a bromine atom have a less strongly repulsive character than the interactions at equal internuclear distances between oxygen and bromine atoms, or between a hydrogen atom and a methyl group. Models based on a fixed scale of atomic radii may therefore give misleading impressions of the possibilities of steric interference between groups.

THE mesomeric effect of a group substituted in an aromatic nucleus is conditioned by the overlap of an orbital of the substituent group, or of the atom adjacent to the aromatic ring, with the π-electron system of the ring. For the nitro-, formyl, acetyl, hydroxyl, alkoxyl, amino-, and substituted amino-groups maximum overlap is attained when the plane of the substituent comes as near as possible to the plane of the aromatic ring. Hence any factors which tend to inhibit attainment of this conformation will reduce the mesomeric effect of the substituent. Since the mesomeric effect in a benzene derivative is reflected in the vector difference between its dipole moment and that of its aliphatic analogue,[1] changes in this " mesomeric moment " on introducing potentially obstructive *ortho*-groups have frequently been used as evidence of steric inhibition of mesomerism. The most convincing examples have involved comparisons of the dipole moments of nitromesitylene [2] (3·67 D) and nitrodurene [3] (3·62 D) with that of nitrobenzene * (4·01 D) and of the moments of dimethylmesitylene [4] (1·03 D) and of 2 : 4 : 6-tribromo-*NN*-dimethylaniline [5] (1·02 D) with that of *NN*-dimethylaniline (1·58 D). The fact that the moments of the two trisubstituted dimethylanilines are almost equal, and not much higher than the moment of trimethylamine (0·86 D), suggests that in these compounds the mesomeric effect of the dimethylamino-group is almost wholly suppressed. Mesomerism appears to be strongly inhibited also in methylmesidine, the dipole moment [6] of which (1·22 D) is much lower than that of *N*-methylaniline [7] (1·61 D) and nearer to that of dimethylamine [8] (1·17 D).

---

* Dipole-moment values quoted without reference are mean values from the literature, recalculated when necessary by using modern values of the universal constants.

[1] Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668.
[2] Hammick, New, and Williams, *J.*, 1934, 29.
[3] Kofod, Sutton, de Jong, Verkade, and Wepster, *Rec. Trav. chim.*, 1952, **71**, 521.
[4] Birtles and Hampson, *J.*, 1937, 10.
[5] Few and Smith, *J.*, 1949, 2663.
[6] Smith, *J.*, 1953, 109.
[7] Few and Smith, *J.*, 1949, 753.
[8] Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374.

It has been shown,[9] however, that repression of the mesomeric effect is only partial in nitromesitylene and nitrodurene, but is probably almost complete in 1 : 3 : 5-tribromo-2-nitrobenzene. The moments of these and related compounds suggest that bromine atoms have a greater effect than methyl groups in obstructing the co-planarity of a nitro-group with the aromatic ring. The dipole moments [6] of mesidine and aminodurene (1·45 D), however, are lower than that of aniline (1·53 D), whilst that of 2 : 4 : 6-tribromoaniline (1·73 D) is higher. The moments induced in each substituent in these compounds by the dipoles of the others, calculated by using the classical laws of induction, indicate that, whatever conformation the amino-group may assume, the direct inductive effect cannot alter the moment of the molecule by more than 0·02 D. Hence, the values of the moments cannot be explained on the grounds of inductive effects alone: this inference is supported by the fact that dimethylmesidine and 2 : 4 : 6-tribromo-*NN*-dimethylaniline, in which the inductive effects should be very similar to those in mesidine and 2 : 4 : 6-tribromoaniline, respectively, have almost equal moments. The mesomeric moments in mesidine and aminodurene must therefore be less, whilst that in tribromoaniline is greater, than in aniline. The probable reason for the latter circumstance is that the strong inductive effect of the bromine atoms decreases the electron density in the ring and so causes an increase in the mesomeric effect of the amino-group. Since for aminobromodurene, in which similar effects should operate, the moment [4] (2·75 D) is less than the vector sum of the moments of aniline and bromodurene (2·81 D), it must be inferred that *ortho*-methyl groups exert a greater restriction upon the mesomerism of the amino-group than do *ortho*-bromine atoms. A similar position may exist with phenols, since the dipole moments of mesitol [10] (1·36 D) and 2 : 4 : 6-tribromophenol [11] (1·56 D) are, respectively, less and greater than that of phenol [12] (1·45 D), but the uncertainty in the calculation of the direction of the dipole in the phenol molecule makes the position less clearly defined.

In view of these apparent differences in the relative steric effects of *ortho*-bromine atoms and methyl groups it is of interest to compare their effects upon the mesomeric moments of other groups, and the formyl and acetyl groups naturally suggest themselves. To complete the data necessary for comparison, the dipole moments of 2 : 4 : 6-tribromobenzaldehyde, 2 : 4 : 6-tribromoacetophenone, and *o*-methylacetophenone have been determined from measurements on benzene solutions. The results are recorded in Table 1, where α, β, and γ are the limiting values of $d\varepsilon/dw$, dv/dw, and dn^2/dw, respectively, at zero

TABLE 1. *Polarisation data for benzene solutions.*

$100w$	ε	v	n_D	P_2	$[R_D]_2$	$100w$	ε	v	n_D	P_2	$[R_D]_2$
2 : 4 : 6-*Tribromobenzaldehyde*											
0·0000	2·2741	1·14460	1·4980	—	—	3·0946	2·3428	1·12223	1·5000	181·2	54·9
1·2058	2·3009	1·13596	1·4987	185·2	54·5	4·5860	2·3770	1·11133	1·5010	179·9	54·6
2·1983	2·3228	1·12882	1·4994	182·8	55·0	5·4775	2·3977	1·10466	1·5016	178·9	54·3
$\alpha = 2{\cdot}192$; $\beta = -0{\cdot}713$; $\gamma = 0{\cdot}185$; $P_{2\infty} = 185{\cdot}4$ c.c.; $[R_D]_2 = 54{\cdot}7$ c.c.; $\mu = 2{\cdot}53$ D.											
o-*Methylacetophenone*											
0·0000	2·2741	1·14459	1·4980	—	—	2·9958	2·4441	1·13979	1·4988	176·5	40·7
0·9615	2·3273	1·14305	1·4982	177·1	40·4	3·7254	2·4863	1·13860	1·4990	175·5	40·7
1·7467	2·3720	1·14179	1·4985	177·2	40·9						
$\alpha = 5{\cdot}53$; $\beta = -0{\cdot}1603$; $\gamma = 0{\cdot}080$; $P_{2\infty} = 178{\cdot}9$ c.c.; $[R_D]_2 = 40{\cdot}8$ c.c.; $\mu = 2{\cdot}60$ D.											
2 : 4 : 6-*Tribromoacetophenone*											
0·0000	2·2741	1·14460	1·4980	—	—	3·4935	2·3517	1·12063	1·4999	192·0	58·8
1·1012	2·2982	1·13706	1·4986	194·0	59·3	4·1614	2·3677	1·11600	1·5003	192·6	58·8
2·2147	2·3229	1·12943	1·4992	193·1	59·0	4·5277	2·3765	1·11357	1·5005	192·3	59·0
$\alpha = 2{\cdot}175$; $\beta = -0{\cdot}686$; $\gamma = 0{\cdot}166$; $P_{2\infty} = 194{\cdot}8$ c.c.; $[R_D]_2 = 58{\cdot}9$ c.c.; $\mu = 2{\cdot}58$ D.											

---

[9] Littlejohn and Smith, *J.*, 1957, 2476.

[10] Brown, de Bruyne, and Gross, *J. Amer. Chem. Soc.*, 1934, **56**, 1291.

[11] Hassel and Naeshagen, *Z. phys. Chem.*, 1931, **12**, *B*, 79.

[12] Boud, Cleverdon, Collins, and Smith, *J.*, 1955, 3793.

concentration, and the other symbols have their usual significance. The values of the dipole moments shown are calculated on the assumption that $P_{E+A} = [R_D]$. The alternative assumption that $P_{E+A} = 1{\cdot}05[R_D]$ leads to values 0·02 D lower.

The observed moments in benzene solution of benzaldehyde, acetophenone, and their derivatives are shown in Table 2, where comparison is made with the moments of some aliphatic compounds. The dipoles of both benzaldehyde and acetophenone must reside principally in the carbonyl group, and hence the mesomeric moment, which is in the sense of a displacement of electrons away from the ring, will augment the primary moment. As a result the observed moments are appreciably higher than those of aliphatic aldehydes and ketones.

TABLE 2. *Dipole moments in benzene solution.*

	μ (D)		μ (D)
Benzaldehyde	2·92	Acetophenone	2·96 [14]
Mesitaldehyde	2·96 [13]	Acetylmesitylene	2·81 [14]
		2 : 5-Dimethylacetophenone	2·85 [14]
		o-Methylacetophenone	2·60
2 : 4 : 6-Tribromobenzaldehyde	2·53	2 : 4 : 6-Tribromoacetophenone	2·58
n-Valeraldehyde	2·57	*n*-Butyl methyl ketone	2·67
n-Heptaldehyde	2·56	Hexyl methyl ketone	2·70

Since the moment of mesitaldehyde is slightly higher than that of benzaldehyde, whilst the moment of acetylmesitylene is less than that of acetophenone, *ortho*-methyl groups seem to have no appreciable effect in inhibiting the mesomerism of the formyl group, but decrease that of the acetyl group. This is in accordance with studies of the Raman C=O stretching frequency [15] and ultraviolet absorption intensities,[16] which indicate that steric interference is only slight in mesitaldehyde but strong in acetylmesitylene. Hence, in the latter, the obstruction to co-planarity seems to be caused principally by the repulsion between the *ortho*-methyl groups and the acetyl methyl groups. Therefore, as was foreseen by Bentley, Everard, Marsden, and Sutton,[14] when only one *ortho*-methyl group is present the molecule should be able to pass much more readily through the coplanar configuration with the oxygen atom near to the *ortho*-methyl group than through that in which the methyl groups approach one another. Hence such a molecule will spend most of its time with the methyl groups remote from one another. This view is supported by the measurements on *o*-methylacetophenone. In the " permitted " co-planar configuration the components to the moment arising from the acetyl group and the *ortho*-methyl group are almost antiparallel, and the calculated moment for this preferred configuration is 2·59 D, much nearer to the observed value (2·60 D) than is that for the " obstructed " coplanar configuration (3·16 D).

In 2 : 4 : 6-tribromobenzaldehyde or 2 : 4 : 6-tribromoacetophenone the mesomeric effect of the formyl or acetyl group should be enhanced by interaction with the mesomeric effects of the bromine atoms, but reduced by the removal of electron density from the ring through their strong inductive effects. Amongst analogous compounds the former effect seems to predominate in *p*-bromonitrobenzene,[9] whilst in 2 : 4 : 6-trichlorobenzonitrile, the moment of which is the same as that of benzonitrile,[11,17] the two effects appear to compensate one another exactly. In view of the behaviour of acetylmesitylene, some steric inhibition of resonance is to be expected in 2 : 4 : 6-tribromoacetophenone. The moments of 2 : 4 : 6-tribromobenzaldehyde and 2 : 4 : 6-tribromoacetophenone, however, are both much lower than, and differ almost equally from, the moments of benzaldehyde and acetophenone, respectively. The amounts by which they differ from the values for aliphatic aldehydes

---

[13] Kadesch and Weller, *J. Amer. Chem. Soc.*, 1941, **63**, 1310.

[14] Bentley, Everard, Marsden, and Sutton, *J.*, 1949, 2957.

[15] Murray, Cleveland, and Saunders, *J. Amer. Chem. Soc.*, 1942, **64**, 1181.

[16] Braude and Sondheimer, *J.*, 1955, 3754.

[17] Hassel and Naeshagen, *Z. phys. Chem.*, 1930, **8**, *B*, 357.

and ketones are such as are to be expected from the direct inductive effects between the formyl or acetyl group and the bromine atoms. It appears, therefore, that the mesomeric effects of the formyl and acetyl groups are both repressed almost completely in the tribromo-compounds, whilst even in acetylmesitylene this repression is partial only. The behaviour in 2 : 4 : 6-tribromobenzaldehyde is evidently to be associated with repulsion between the bromine atoms and the aldehydic oxygen atom, so the relative effects of *ortho*-methyl groups and bromine atoms towards coplanarity of the aldehydic oxygen atom with the ring follow the same order as their effects towards the oxygen atoms of a nitro-group.

From the usual conceptions of atomic radii, the bromine atom is larger than a methyl group, so *ortho*-bromine atoms should always exert a greater steric effect upon the mesomerism of a substituent than do *ortho*-methyl groups. In amines, and possibly in phenols, the reverse seems to be the case, so it must be inferred that the characteristics of the groups concerned, as well as their sizes, are significant. Methyl groups appear specifically to repel hydrogen atoms, whilst bromine atoms tend to repel oxygen atoms. There is no evidence of the formation of intermolecular hydrogen bonds by methyl-hydrogen atoms or with bromine atoms as electron donors, but Anzilotti and Curran [18] have postulated the existence of intramolecular O–H · · · Br hydrogen bonds to explain the value of the dipole moment of *o*-bromophenol in carbon tetrachloride. Therefore, it seems reasonable to assume that the interactions between a hydrogen atom of an aldehyde, amino-, or hydroxyl group and a bromine atom in its proximity may not be of such a strongly repulsive character as the interactions between oxygen and bromine atoms or between a hydrogen atom and a methyl group, at the same internuclear distance. Hence the effective " radius " of a bromine atom will be smaller with respect to the approach of a hydrogen atom than of an oxygen atom, whilst the reverse will hold with regard to the effective radius of a methyl group. It follows, therefore, that models based on a fixed scale of atomic radii may give misleading impressions of the distances of closest approach of unbonded atoms and hence of the steric effect of one group on the configurations which can be assumed by another.

EXPERIMENTAL

Materials.—Benzene was purified, dried, and redistilled under anhydrous conditions as previously.[9]

2 : 4 : 6-Tribromobenzaldehyde was prepared from *m*-aminobenzaldehyde by Lock and Schreckeneder's method,[19] but the yield was improved by separating the product after the deamination step by steam distillation: after recrystallisation from alcohol it had m. p. 101° (lit., 98—101°).

2 : 4 : 6-Tribromoacetophenone, prepared by treating 2 : 4 : 6-tribromobenzaldehyde with methyl magnesium iodide and oxidising the carbinol with chromic acid, was recrystallised repeatedly from aqueous alcohol: m. p. 93° (lit., 91·5—93°).

A pure specimen of *o*-methylacetophenone (b. p. 93°/17 mm.), kindly lent by the late Professor E. A. Braude, was used as received.

Methods.—The dielectric constants, specific volumes, and refractive indices of the solutions were measured at 25° by the same methods as previously. The values of P_2 and $[R_D]_2$ derived from the parameters α, β, and γ were in satisfactory agreement with those deduced from the specific polarisations and specific refractions of the individual solutions.

Grateful thanks are tendered to Imperial Chemical Industries Limited for the loan of a precision variable condenser and for a grant for the purchase of materials.

BEDFORD COLLEGE, REGENT'S PARK, LONDON, N.W.1.
[*Received, April 5th,* 1957.]

[18] Anzilotti and Curran, *J. Amer. Chem. Soc.*, 1943, **65**, 609.

[19] Lock and Schreckeneder, *Ber.*, 1939, **72**, 514.