Electric Dipole Moments of Polyhalogenoaromatic Compounds. Part 1. Inductive Effects in Polychlorobenzenes and Polychlorotoluenes

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The electric dipole moments of 20 polychloro-benzenes and -toluenes have been determined in dilute solution in benzene at 298 K. The departures from additivity in the moments are explained in terms of inductive effects between *ortho*-substituted (and to a lesser extent *meta*-substituted chlorine atoms) which lessen the apparent C–Cl bond moment, and similar induction between *ortho*- or *meta*-substituted chlorine atoms and methyl groups which enhances the apparent methyl group moment. It has previously been suggested that these departures from additivity are caused by variation in atom polarisation, changing mesomeric effects, or by steric distortion: no evidence is found for these explanations. The possible effects of these electron shifts in the ground state on rates of electrophilic or nucleophilic attack on these molecules are discussed.

THE dipole moments of several polychloroaromatic compounds have been discussed in detail by Smyth and Lewis [1] who interpreted their results in terms of inductive and resonance effects, pointing out that only the former was required to explain the variations in moment where polysubstitution into the benzene ring by methyl groups and chlorine atoms is concerned. Also the reductions in the moments of *o*- and *m*-dihalogenobenzenes compared to the values expected by vectorial addition have been shown by Smallwood and Herzfeld [2] to be of the order expected if caused by mutual induction. Littlejohn and Smith [3] have attempted to calculate the reduction in moment due to induction in both *ortho*- and *meta*-di-substituted halogenobenzenes but found that their calculated reductions were smaller than those observed by a factor of three. They concluded that although the total displacement of the electrons in the ring brought about by the inductive effect of the substituents is greater in the *meta*-di-substituted benzenes than in the monosubstituted benzenes, the effect attributable to each substituent is less in the former than the latter. On the other hand Huang [4] has interpreted the dipole moments of various polyfluorinated benzenes and toluenes in terms of an enhanced $+M$ (hyperconjugative effect) for the methyl group in tetra- and penta-fluorotoluenes, arguing that induced moments must be negligible since the moments of chloromesitylene, chlorodurene, and chlorobenzene are indistinguishable, as are those of the bromoarene analogues.

In view of these somewhat contradictory interpretations of the data we have investigated the dipole moments of several polychlorinated benzenes and toluenes in dilute solution in benzene.

DISCUSSION

Our results for the polychlorobenzenes, together with some literature values for polyfluoro- and polybromobenzenes are given in Table 1. The most striking effect is the gradual decrease in apparent group moment of the chlorine atom on further substitution by chlorine in the ring. Thus the moment of *m*-dichlorobenzene is 0.1 D lower than that expected by vectorial addition of two chlorobenzene moments at an angle of 120°, while the moments of 1,2,3,5-tetrachlorobenzene and pentachlorobenzene are almost 0.6 D lower. Examination of these polychlorobenzene moments shows that they may be calculated with reasonable accuracy by assigning the following empirical values to the C–Cl moment in various environments: with one *ortho*-chlorine atom, 1.31 D; with two *ortho*-chlorine atoms, 1.13 D; and otherwise 1.48 D. Bond angles of 60, 120, and 180° are used as appropriate. Thus the calculated moment of 1,2,4-trichlorobenzene is obtained by combining two vectors, magnitude 1.48 and 2.27 D, at an angle of 150°.

There are several possible explanations for this marked change in moment on further substitution. First the

TABLE 1

Measured, expected, and empirically calculated dipole moments of some polyhalogenobenzenes in benzene at 298 K

Compound	Moment (D)	Expected value *	Empirically calculated value †
Chlorobenzene	1.58, 1.58 [c]	1.58	
o-Dichlorobenzene	2.25, 2.27 [c]	2.73	2.27
m-Dichlorobenzene	1.48, 1.48 [c]	1.58	1.48
1,2,3-Trichlorobenzene	2.44, 2.33 [d]	3.16	2.44
1,2,4-Trichlorobenzene	1.25	1.58	1.24
1,2,3,4-Tetrachlorobenzene	1.87, 1.92 [1]	2.73	1.95
1,2,3,5-Tetrachlorobenzene	0.97, 0.65 [e]	1.58	0.96
Pentachlorobenzene	1.05 [a]	1.58	0.95
Fluorobenzene	1.43 [c]	1.43	
o-Difluorobenzene	2.40 [f]	2.48	
m-Difluorobenzene	1.38 [b,g]	1.43	
Pentafluorobenzene	1.43,[g] 1.38 [4]	1.43	
2,4,6-Trichlorofluorobenzene	1.29	1.43	
2,3,5,6-Tetrachlorofluorobenzene	1.27	1.43	
Bromobenzene	1.56 [a]	1.56	
o-Dibromobenzene	2.13,[5] 1.82 [h]	2.70	
m-Dibromobenzene	1.47,[5] 1.24 [h]	1.56	
1,2,3,5-Tetrabromobenzene	0.70	1.56	

* Calculated on the basis of additivity of the moments of the monosubstituted compounds. † See text.

[a] Ref. 1 gives 1.01 D (after recalculation, using dilute solutions only); note *d* gives 0.88 D. [b] Gas-phase value, corrected to benzene solution. [c] A. L. McClellan, 'Tables of Experimental Dipole Moments', Freeman, San Francisco, 1963. [d] J. A. A. Ketelaar, *Rec. Trav. chim.*, 1940, **59**, 757. [e] O. Hassel, *Z. Phys. Chem.*, 1932, **B12**, 79. [f] E. Bergmann, L. Engel, and S. Sandor, *Ber.*, 1930, **B63**, 2572. [g] E. M. Moore and M. E. Hobbs, *J. Amer. Chem. Soc.*, 1949, **71**, 411. [h] A. Mansingh and D. B. McClay, *J. Chem. Phys.*, 1971, **54**, 5322.

magnitude of the atom polarisation in these compounds must be considered; however this would be expected to increase throughout this series being especially large for molecules with balanced dipoles. One would therefore expect anomalously high, rather than low, values of the moments of the more completely substituted compounds, resulting from an increasing underestimation of this parameter. Further, Tiganik [5] and Smyth [1] have shown that the value of $(P_{2\infty} - R_D)$ approximates to zero in the cases of *sym*-trichloro- and *sym*-tribromobenzene, trichloromesitylene, and dichlorodurene. Also, the empirically calculated values of the C–Cl moments apply equally well to the di-, tri-, tetra-, and pentachlorobenzenes.

Another possible reason for the variation is a gradually increasing steric distortion, in line with the angular deviations suggested by Bastiansen and Hassel.[6] This does not seem possible in view of other, some more recent, structural determinations,[7-9] although bond angles for a compound in the solid state may not necessarily be the same as those for the compound in solution. It has also been pointed out [3,10] that angular deviations of the magnitude reported [6] would result in atom polarisations for molecules such as trichloromesitylene in solution which are an order of magnitude higher than those observed.

Thirdly we must consider the possibility that the $-I$ effect of one chlorine atom enhances the $+M$ effect of a second, thereby reducing the overall moment of both chlorine atoms. This requires that the two electronic effects are not considered in isolation as is usual,[3] but that they are interdependent. However, examination of the dipole moments of 1,2-dichlorocyclohexanes [11] suggests that this is not a major contribution since a similar reduction is seen in this saturated system. The relative constancy of the moments of the polyfluorobenzenes may be used to reject Littlejohn and Smith's [3] explanation of the observed effect, since decreasing polarisability of the benzene ring on polysubstitution should apply equally to the polyfluorobenzenes as to the polychlorobenzenes.

One is therefore left with the original explanation [1,2] that the decrease is due almost entirely to mutual induction between the substituent groups. This is completely consistent with the empirical values for the C–Cl moments observed, the reduction being three times as great for an *ortho*- than for a *meta*-substituent. This decrease of reduction in moment with increasing distance apart of the dipoles concerned favours an inductive mechanism. A second *ortho*-chlorine substituent gives rise to only two-thirds of the reduction caused by the first; presumably since the effective polarisability of the original chlorine atom will have been decreased by the first polarisation. The much smaller deviations in the polyfluorobenzenes are also explicable on this hypothesis since the C–F bond is much less polarisable than the C–Cl bond (R_D values 1.44 and 6.51 cm^3 respectively). The moment reductions in 2,4,6-tri- and 2,3,5,6-tetra-chlorofluorobenzenes are less than those in the corresponding 1,2,3,5-tetra- and pentachlorobenzenes, again as expected, while the reductions in the polybromobenzenes are greater (R_D for C–Br 9.39 cm^3) although the accuracy of these literature values appears to be suspect. Such an inductive effect may of course act directly through space or through the bonds within the molecule; in either case a reduction in moment will result, and the lack of success in the accurate calculation of this inductive effect,[1,3] would seem to make it unprofitable to speculate which mechanism would give a better description.

In Table 2 we report the dipole moments of some polychlorotoluenes, together with some relevant literature values. Apparent moments of the methyl group are calculated on the basis that the total moment of the chlorine substituents is equal in magnitude and direction to that of the corresponding polychlorobenzene compound. This assumption may be justified on the grounds that the small methyl group moment seems unlikely to change significantly the chlorine substituent moments and that in practice it leads to consistent values.

TABLE 2

Dipole moments of some polychlorotoluenes in benzene at 298 K

Compound	Moment (D)	Apparent moment of methyl group
Toluene	0.35, 0.37 [5]	0.35
p-Chlorotoluene	1.93, 1.95 [5]	0.35
m-Chlorotoluene	1.82, 1.78 [5]	0.43
3,4-Dichlorotoluene	2.65, 2.95 [a]	0.43
3,5-Dichlorotoluene	1.90 [b]	0.42
o-Chlorotoluene	1.40, 1.40 [c]	0.49
2,4-Dichlorotoluene	1.83, 1.95 [a]	0.53
2,5-Dichlorotoluene	0.55	0.55
2,4,5-Trichlorotoluene	1.75	0.53
2,6-Dichlorotoluene	0.97, 1.11 [a]	0.51
2,4,6-Trichlorotoluene	0.54 [1]	0.54
Pentachlorotoluene	1.62, 1.55 [1]	0.57
2,3,5,6-Tetrafluorotoluene	0.66 [4]	0.66
Pentafluorotoluene	1.94 [4]	0.56

[a] D. V. G. L. N. Rao, *Indian J. Phys.*, 1956, **30**, 1. [b] A. A. Maryott, M. E. Hobbs, and P. M. Gross, *J. Amer. Chem. Soc.*, 1940, **62**, 2320. [c] P. Walden and O. Werner, *Z. Phys. Chem.*, 1929, **B2**, 10.

The methyl group moment in toluene is essentially unchanged by substitution of a *para*-chlorine atom. However there appears to be a clear enhancement of 0.08 D in the moment on substitution of either one or two *meta*-chlorine atoms. Interestingly the second *meta*-substituent appears to make no further difference, but this conclusion is based on the single literature figure for 3,5-dichlorotoluene. *ortho*-Substitution results in a greater increase in methyl group moment than does *meta*-substitution: a value of 0.20 D seems generally applicable. Again a saturation effect is noticeable; the enhancement for two *ortho*-chlorine substituents is not significantly greater than for one. It will be observed that the apparent moment for the methyl group in *ortho*-chlorotoluene is rather lower than the others; this may not in fact be significant since the error in this value is ±0.08 D, compared with ±0.02 D generally. This greater error is caused by the magnitude of the angle (78°) between the unknown methyl group moment and the resultant moment of the whole molecule. The error in the derived moment is a minimum when its direction coincides (either 0 or 180°) with that of the resultant.

The magnitudes of these enhancements, and their constancy with increasing substitution of the ring are clearly consistent with a short-range inductive effect, and not through an enhancement of the hyperconjugative effect of the methyl group by the increasing total $-I$ effect of the halogens.[4] Huang's argument that mutual inductive effects are negligible since the moments of chloromesitylene, chlorodurene, and chlorobenzene are indistinguishable from each other is not valid since in these molecules the moment induced by the single chlorine atom in each of the two *o*-methyl groups could well be almost cancelled by the small moments induced in the chlorine atom in the opposite direction by each of the methyl groups. In 2,6-dichlorotoluene the situation is reversed, there being two larger induced moments in the central methyl group, opposed by only one of smaller magnitude in each of the C–Cl bonds, these latter two being 120° apart. For this reason the apparent moments of the methyl groups in the *ortho*-substituted toluenes may be slightly underestimated; it cannot be a large effect since the enhancement is reasonably independent of the direction of the resultant moment of the molecule.

As in the case of the polychlorobenzenes, attempts to quantify these arguments by recourse to calculation of inductive effects [1,3] fail because of the extreme sensitivity of the result to the exact position of the contributory dipoles.

Interestingly, the considerable electron shifts observed in the ground states of the polychlorobenzenes are paralleled by an increasing reactivity towards electrophilic substitution; pentachlorobenzene is nitrated *ca.* 250 times more rapidly than expected on the basis of multiplication of the partial rate factors for the nitration of chlorobenzene.[12] A lowering of the $-I$ contribution of the chloro-substituent would be expected to increase the rate of reaction towards electrophiles, if electron shifts in the transition state are similar to those in the ground state. Likewise, it may be predicted that the rate of nucleophilic displacement of say fluorine in polychlorofluorobenzenes will be significantly slower than that expected by multiplication of the substituent rate factors for this displacement in the monochlorofluorobenzenes themselves.

EXPERIMENTAL

B.p.s corrected to 760 mmHg.

Chlorobenzene (commercial material), fractionally distilled, had b.p. 131.5—132 °C; n_D^{20} 1.524 6 (lit.,[13] 132 °C; 1.524 8); *o*-dichlorobenzene (commercial), fractionally distilled, had b.p. 180—180.8 °C; n_D^{20} 1.551 6 (lit.,[13] 180.5 °C; 1.551 5); *m*-dichlorobenzene (commercial), fractionally distilled, had b.p. 172—173 °C; n_D^{20} 1.546 6 (lit.,[13] 173 °C; 1.545 4); 1,2,3-trichlorobenzene (commercial), recrystallised from ethanol, had m.p. 52—53 °C (lit.,[14] 52—53 °C); 1,2,4-trichlorobenzene (commercial), fractionally distilled, had b.p. 213—214 °C, n_D^{20} 1.572 2 (lit.,[13] 213 °C; 1.571 7); 1,2,3,4-tetrachlorobenzene (commercial), recrystallised from ethanol, had m.p. 46—47 °C (lit.,[15] 46—47 °C); 1,2,3,5-tetrachlorobenzene (commercial), recrystallised from ethanol, had m.p. 53—54 °C (lit.,[16] 50—51 °C); pentachlorobenzene (commercial), recrystallised from ethanol, had m.p. 86—87 °C (lit.,[17] 86—87 °C). 2,4,6-Trichlorofluorobenzene was prepared from 2,4,6-trichloroaniline (Balz–Schiemann), recrystallised from ethanol, and had m.p. 11.5—12 °C (lit.,[18] 11.2 °C). 2,3,5,6-Tetrachlorofluorobenzene, prepared by fluoride ion attack on 2,3,5,6-tetrachloronitrobenzene, was recrystallised from ethanol and had m.p. 71.5—72.5 °C (lit.,[19] 71.5—72.5 °C). Toluene (commercial), fractionally distilled, had b.p. 110—111 °C; n_D^{20} 1.497 1 (lit.,[13] 110.6 °C; 1.496 9); *o*-chlorotoluene (commercial), fractionally distilled, had b.p. 159—160 °C; n_D^{20} 1.526 0 (lit.,[13] 159.0 °C; 1.526 8); *m*-chlorotoluene (commercial), fractionally distilled, had b.p. 161—162 °C; n_D^{20} 1.521 9 (lit.,[13] 162 °C; 1.521 4); *p*-chlorotoluene (commercial), fractionally distilled, had b.p. 161—162 °C; n_D^{20} 1.514 6 (lit.,[13] 162 °C; 1.515 0); 2,4-dichlorotoluene (commercial), fractionally distilled, had b.p. 196—197 °C; n_D^{20} 1.550 9 (lit.,[13] 196—197 °C; 1.551 1); 2,5-dichlorotoluene (commercial), fractionally distilled, had b.p. 199—200 °C; n_D^{20} 1.544 8 (lit.,[13] 200 °C; 1.544 9); 2,6-dichlorotoluene (commercial), fractionally distilled, had b.p. 197.5—198 °C; n_D^{20} 1.550 8 (lit.,[13] 198 °C; 1.550 7); 3,4-dichlorotoluene (commercial), fractionally distilled, had b.p. 208—209 °C; n_D^{20} 1.546 8 (lit.,[13] 208.95 °C; 1.547 1); 2,4,5-trichlorotoluene (commercial), recrystallised from ethanol, had m.p. 82—83 °C (lit.,[13] 82.4 °C); pentachlorotoluene (commercial), recrystallised from ethyl acetate, had m.p. 223—225 °C (lit.,[20] 224—225 °C). The liquid solutes were effectively dried by distillation, the solids were dried under vacuum (P_2O_5), with the exception of 2,4,6-

TABLE 3

Summary of polarisation data for benzene solutions at 298 K

Compound	α	β	$_\infty P_2$/ cm^3	R_D/ cm^3	μ/D
Chlorobenzene	2.474	−0.244	82.28	31.02	1.58 ± 0.02
o-Dichlorobenzene	3.846	−0.380	139.81	35.85	2.25 ± 0.02
m-Dichlorobenzene	1.716	−0.383	80.80	35.85	1.48 ± 0.02
1,2,3-Trichlorobenzene	3.665	−0.457	162.08	40.68	2.44 ± 0.01
1,2,4-Trichlorobenzene	1.049	−0.456	73.04	40.68	1.25 ± 0.02
1,2,3,4-Tetrachlorobenzene	1.909	−0.530	117.09	45.52	1.87 ± 0.01
1,2,3,5-Tetrachlorobenzene	0.581	−0.506	64.66	45.52	0.97 ± 0.02
Pentachlorobenzene	0.535	−0.500	73.25	50.35	1.05 ± 0.04
2,4,6-Trichlorofluorobenzene	0.948	−0.492	75.08	40.45	1.29 ± 0.08
2,3,5,6-Tetrachlorofluorobenzene	0.814	−0.538	78.74	45.28	1.27 ± 0.07
Toluene	0.083	0.0195	33.38	30.84	0.35 ± 0.02
o-Chlorotoluene	1.718	−0.222	75.74	35.67	1.40 ± 0.03
m-Chlorotoluene	2.840	−0.200	103.24	35.67	1.82 ± 0.03
p-Chlorotoluene	3.221	−0.222	111.48	35.67	1.93 ± 0.02
2,4-Dichlorotoluene	2.325	−0.340	109.02	40.50	1.83 ± 0.08
2,5-Dichlorotoluene	0.274	−0.342	46.79	40.50	0.55 ± 0.02
2,6-Dichlorotoluene	0.709	−0.350	59.62	40.50	0.97 ± 0.02
3,4-Dichlorotoluene	4.831	−0.343	184.78	40.50	2.65 ± 0.02
2,4,5-Trichlorotoluene	1.790	−0.424	107.77	45.33	1.75 ± 0.02
Pentachlorotoluene	1.280	−0.555	108.50	55.01	1.62 ± 0.02

trichlorofluorobenzene (molecular sieve). The purity of all solutes was checked using g.l.c. and ^{1}H n.m.r. and shown to be >99%.

AnalaR benzene was further purified by fractional freezing and had permittivity 2.272 5, and specific volume 1.1446 4. The permittivities of solvent and solutions were measured at 298 K using a Wissenschaftlich-Technische Werkstätten dipolemeter, type DM01. Specific volumes were determined using a Warden's density bottle. Permittivity and specific volume *versus* weight fraction plots were linear within experimental error up to weight fractions of 0.02, and had slopes α and β respectively. Total polarisations were calculated from the values of α and β using the method of Halverstadt and Kumler,[21] and orientation polarisations by subtraction of the appropriate R_D values.[22] Results, together with the standard deviations, are given in Table 3.

Weight fractions, permittivities, and specific volumes of individual solutions are contained in Supplementary Publication No. SUP 22451 (6 pp.).*

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

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