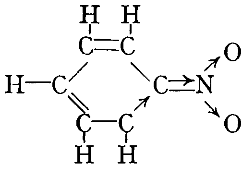
3. *An Investigation of Steric Influences on the Phenomenon of Mesomerism.*

By R. H. Birtles and G. C. Hampson.

The first physical evidence for the existence of permanent " electromeric " or " mesomeric " effects in unsaturated compounds came from the work of Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668), in which he correlated the differences between the electric moments of aromatic and tertiary aliphatic compounds with the directive influences of the respective groups in aromatic substitution. As regards physical interpretation, it was later suggested that this phenomenon arose as a result of wave-mechanical resonance between different structures (Sutton, *Trans. Faraday Soc.*, 1934, **30**, 789; Ingold, *Chem. Reviews*, 1934, **15**, 225; Kumler and Porter, *J. Amer. Chem. Soc.*, 1934, **56**, 2549). For example, each molecule of nitrobenzene is considered to be a resonance hybrid between the normal molecule and structures of the type



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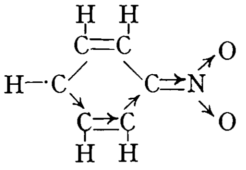
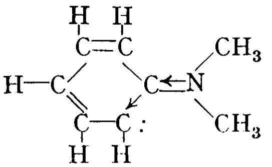


Opposite mesomeric effects occur with *o*, *p*-directing groups such as the dimethylamino-group :



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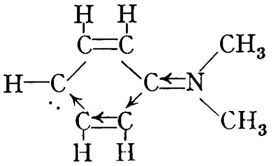
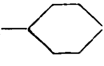
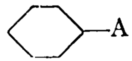
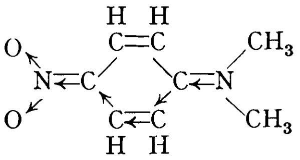


In *p*-disubstituted benzene derivatives the mesomeric effects of the two para-groups may reinforce or oppose each other. This is revealed by the fact that the electric moment of a *p*-disubstituted benzene compound A——B is not always the vector sum of the moments of the two monosubstituted derivatives A and B. The degree of deviation varies with the nature of the groups A and B, two groups of opposite type showing the greatest deviation (see Marsden and Sutton, J., 1936, 599, and references therein). An extreme case is *p*-nitrodimethylaniline, where the mutual reinforcement of the mesomerism is so great that the moment, 6·87, of the compound is very much greater than the sum of the moments of nitrobenzene, 3·95, and dimethylaniline, 1·58 (all moments in this paper are given in Debye units), even although these two component moments are not collinear (*idem, ibid.*).



If the above type of structure is really important there should be two further consequences : (1) The bond joining the group to the benzene ring should be shorter than the normal single-bond distance (Pauling, *Proc. Nat. Acad. Sci.*, 1932, **18**, 293, 498; Brockway, *ibid.*, 1933, **19**, 303, 868; Brockway and Pauling, *ibid.*, p. 860). (2) With groups such as NO_2, NH_2, NMe_2 or OMe there should be a tendency for the oxygen, hydrogen and methyl groups respectively to be brought into, and held in, the plane of the benzene ring. This follows from simple ideas of stereochemistry, based on tetrahedral atomic models.

If now we consider an aromatic compound in which two methyl groups have been substituted in the *o*, *o*′-positions to the polar group, the establishment of conditions (1) and (2) will be impeded for steric reasons. Hence the introduction of the *o*-methyl groups should reduce the probability of the quinonoid type of structure, and consequently the " mesomeric moment " should be diminished.

To test the theory we have measured the electric moments of a number of mono- and di-substituted derivatives of durene, and the results are shown in Table I together with those for the corresponding derivatives of benzene. The latter were taken from the " Table of Dipole Moments " by Sidgwick and collaborators (*Trans. Faraday Soc.*, 1934, **30**, Appendix).

TABLE I.

				Diff.
Nitrodurene	3·39	Nitrobenzene	3·95	0·56
Aminodurene	1·39	Aniline	1·53	0·14
Bromodurene	1·55	Bromobenzene	1·52	0·03
Nitroaminodurene	4·98	*p*-Nitroaniline	6·10	1·12
Bromoaminodurene	2·75	*p*-Bromoaniline	2·93	0·18
Bromonitrodurene	2·36	*p*-Bromonitrobenzene	2·65	0·29
Pentamethylaniline	1·10	*p*-Toluidine	1·36	0·26
Dinitrodurene	0·60	*p*-Dinitrobenzene	0·60	0·00

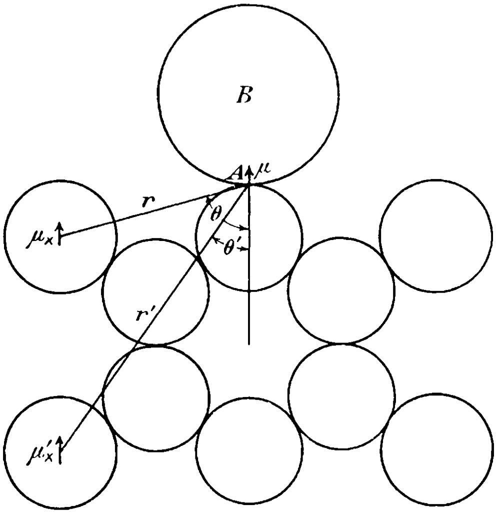
We will consider first the three monosubstituted derivatives. The moments of nitrodurene and aminodurene differ considerably from those of nitrobenzene and aniline, whereas the moments of bromodurene and bromobenzene are essentially the same. The differences between the moments of the durene compounds and those of the corresponding benzene compounds may be due to one or both of two causes; either the mesomeric effect in the durene compounds is reduced as predicted by the above theory, or the polar group sets up induced moments in the methyl groups of the durene molecule. The changes in moment are in the sense required by the former explanation, for the moments of the nitro- and the amino-durenes are intermediate between those of the corresponding benzene and aliphatic compounds (aliphatic nitro-compounds have moments of *ca.* 3·1, Hunter and Partington, J., 1933, 309; and methylamine one of 1·23, Steiger, *Helv. Physica Acta*, 1930, **3**, 161; *Physikal. Z.*, 1931, **32**, 425). If the induction effect were the sole explanation, it is difficult to see why the effects in the cases of aminodurene and bromodurene should be of opposite kinds.

An attempt has been made to estimate the inducing influence of the polar group by the method used by Hampson and Weissberger in the case of the chloronaphthalenes (J., 1936, 393). In these calculations a number of approximations and assumptions have to be made. For example, in addition to the difficulty of locating the position of the inducing dipole, the expression $\mu' = \frac{\varepsilon + 2}{3} \cdot \frac{\alpha c \mu}{\varepsilon r^3}$ only holds for values of r greater than about 3·5 A., *i.e.*, values for which the finite length of the dipole can be neglected.*

For the purposes of the calculation, the dipole has usually been located at the point of contact of the two component atoms of the polar bond (Smallwood and Herzfeld, *J. Amer. Chem. Soc.*, 1930, **52**, 1919; Hampson and Weissberger, *loc. cit.*), but since in the durene compounds it is found that the induced moments are very sensitive to the exact location of the inducing dipole, values have been worked out for various positions.

We will first consider the case of bromodurene, with the dipole located at the point of contact A of the carbon and bromine atoms (see figure).

The induced moment μ_x parallel to the inducing dipole is given by the expression $\mu_x = [(\varepsilon + 2)/3]\alpha\mu(3\cos^2\theta - 1)/\varepsilon r^3$. Using as standard data throughout, $\varepsilon = 2{\cdot}27$, $\mu = 1{\cdot}52 \times 10^{-18}$, $\alpha = 1{\cdot}82 \times 10^{-24}$, $C_{ar.}$–$C_{ar.}$ = 1·40 A., and $C_{ar.}$–$C_{al.}$ = 1·47 A., we obtain results shown in the top row of Table II. Hence on this hypothesis the moment of bromodurene should be 1·52 + 2(0·02 — 0·08) = 1·40.



If, instead, we locate the dipole at B, the centre of the bromine atom, the results are given in the second row of Table II, leading to a calculated moment in this case of 1·56. These two cases probably represent extreme limits.

In nitrodurene and aminodurene the inducing dipoles are themselves composite, being the resultant of the three bond moments about the nitrogen atom, and the location of this resultant is still more uncertain. Since, however, the moment of the bond between the nitrogen atom and the benzene ring will be less than the other two bond moments, qualitatively, at any rate, we may take as our limits (*a*) the case where the resultant is assumed to be at the centre of the nitrogen atom, (*b*) when it is located on the periphery of the nitrogen atom remote from the benzene ring.

TABLE II.

	r.	r'.	θ.	θ'.	μ_x.	μ'_x.	$\mu_{calc.}$.
Dipole at point of contact of C and Br atoms	2·57	4·32	75°	35°	—0·08	+0·02	1·40
Dipole at centre of Br atom	3·10	5·33	53° 24′	27° 48′	+0·004	+0·015	1·56

The calculations then show that for case (*a*) the moments of nitrodurene and aminodurene should be the same as those of nitrobenzene and aniline, while for case (*b*) they should be considerably larger. Since, however, the moments of the durene compounds are *smaller* than those of the corresponding benzene compounds, it follows that these differences cannot be due solely to induced effects in the methyl groups, and that some other influence

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* μ' is the induced dipole; ϵ is the dielectric constant across the part of the material in which the induction occurs; this is taken as the same as the dielectric constant of the material in bulk. α is the polarisability and may be deduced from the electronic polarisation term corresponding to that part of the molecule (assumed to be spherically symmetrical) in which the effect is being calculated, using the Debye equation $\alpha = 3P_E/4\pi N$; μ is the moment of the inducing dipole, r is the distance from this dipole to the polarisable centre, and c is an orientation factor (Frank, *Proc. Roy. Soc.*, 1935, *A*, **152**, 171).

is operative. This, as we have seen, must be a damping of the resonance due to the steric effect of the methyl groups.

With bromodurene no such effect is observed, nor is it to be expected, since here the ortho-methyl groups will only exert a steric influence by virtue of condition (1) (p. 11), and this would be but a feeble influence in comparison with condition (2).

Turning now to the disubstituted derivatives, we again observe (Table I) that the durene compounds have lower moments than the corresponding benzene compounds. This is especially marked in the case of the nitroamino-derivatives where the difference between the moments of the benzene and the durene compounds is 1·12. The moment of the amino-group is not, of course, coaxial with the benzene ring and hence, assuming vector addition, we should expect the moment of nitroaminodurene to be less than the algebraic sum of the moments of nitrodurene and aminodurene. The observed moment (4·98) in fact exceeds this sum (3·39 + 1·39) by an amount 0·20, but not by so much as the moment of *p*-nitroaniline exceeds the sum of the moments of nitrobenzene and aniline, *viz.*, 6·1 — (3·95 + 1·53) = 0·62. It is clear, therefore, that even in the durene compounds there is some interaction between the para-groups. In other words, the conclusion seems to be that in the monosubstituted durenes the mesomerism is reduced by the steric effect of the methyl groups, but that in the disubstituted durenes the two para-groups can bring about a mutual stabilisation of the quinonoid form though not to such a large extent as in the benzene compounds.

Another disubstituted durene compound which might be considered is that in which only one of the substituents is sterically influenced by the methyl groups; such a case is bromonitrodurene. Here the difference between observed (2·36) and calculated (3·39 — 1·55 = 1·84) moments is 0·52 and is greater than the corresponding difference (0·22) for *p*-bromonitrobenzene. A possible explanation is as follows :

In nitrodurene the mesomerism is reduced by a steric effect, but the introduction of a bromine atom, with its donating power into the ring, may partially overcome the steric effect and increase the importance of the quinonoid form. This interaction between the para-groups will cause the moment to be greater than the vector sum of the moments of nitrodurene and bromodurene. In nitrobenzene there is no such steric effect, and though the introduction of a para-bromine atom appears to bring about a further stabilisation of the quinonoid form, the interaction moment may not be so large as with the durene compound.

The moment (0·60) of dinitrodurene is in complete agreement with the small moments found for other symmetrical polynitro-compounds (H. O. Jenkins, J., 1936, 862).

EXPERIMENTAL.

Preparation and Purification of Materials.—Durene. Some of the durene was supplied by the Eastman Kodak Co. of Rochester, N.Y.; the rest was prepared from crude xylene by the Friedel–Crafts reaction with aluminium chloride and methyl chloride according to Smith's method (" Organic Syntheses," 1930, **10**, 32). The crude mixture of xylenes and tri-, tetra-, penta-, and hexa-methylbenzenes which is obtained was twice fractionated, and the durene was isolated from the fraction of range 180—205° by freezing it out in an ice–calcium chloride mixture and filtering it off. Finally it was recrystallised from alcohol; m.p. 79—80° (Smith, *loc. cit.*, 79—80°).

Dinitrodurene. Smith's method (*op. cit.*, p. 40) was used. A solution of 13·4 g. of durene in 150 c.c. of chloroform was added to 75 c.c. of concentrated sulphuric acid, the mixture cooled, and slowly nitrated with 6 g. of fuming nitric acid (*d* 1·5) with stirring, the temperature being kept below 50°. The acid layer was removed, and the chloroform layer washed with sodium carbonate solution and dried. Most of the chloroform was then distilled off, and the dinitrodurene obtained as white crystals by pouring into 250 c.c. of warm alcohol. Recrystallisation from alcohol gave a product, m. p. 207·5° (Smith, *loc. cit.*, 207—208°).

Nitroaminodurene. 3 G. of dinitrodurene were dissolved in 180 c.c. of boiling alcohol and to this solution, which was kept boiling and mechanically stirred, was added gradually an aqueous solution of 1·5 g. of sodium disulphide (prepared by dissolving 3·2 g. of $Na_2S,9H_2O$ in about 20 c.c. of water and warming with 0·45 g. of flowers of sulphur). After this addition the solution was stirred at its b. p. for a further 2 hours, excess alcohol evaporated off, and the remaining solution poured into cold water. The yellow precipitate was filtered off, washed with water, and heated with a large amount of dilute hydrochloric acid. The mixture was then filtered, to remove any sulphur or unchanged dinitrodurene, and ammonia added to the filtrate. The orange precipitate was filtered off and dried; m. p. 156—158°; yield about 0·5 g., but about 2 g. of unchanged dinitrodurene, contaminated with sulphur, were recovered. The experiment was repeated with different amounts of sodium disulphide but no increase in yield was found. It was finally decided to treat the recovered dinitrodurene with more sodium disulphide solution and repeat the experiment several times in this way. Thus 15 g. of dinitrodurene gave 8 g. of nitroaminodurene together with 3·3 g. of unchanged dinitrodurene; recrystallised from alcohol, it had m. p. 161—162° (Cain, *Ber.*, 1895, **28**, 968, gives m. p. 158—159°). *Nitrodurene.* This was prepared according to Cain (P., 1909, 260). 4·5 G. of nitroaminodurene were dissolved in alcohol, 4—5 g. of concentrated sulphuric acid added with shaking and cooling, and the mixture diazotised with 2—3 g. of sodium nitrite. The mixture was then heated on a water-bath to remove nitrogen, most of the alcohol evaporated off, a little water added, and the mixture steam-distilled. At first alcohol came over, and then a whitish oil which solidified in the receiver. This was filtered off and dried. Recrystallisation from alcohol gave a pale yellow solid, m. p. 68·8—69·8° (Cain, *loc. cit.*, gives m. p. 70°).

Bromodurene. This was prepared from durene by the method of Smith and Moyle (*J. Amer. Chem. Soc.*, 1933, **55**, 1676), the crude product being purified by steam-distillation and recrystallisation from alcohol; m. p. 60° (Smith and Moyle, *loc. cit.*, give m. p. 60·5°).

Bromonitrodurene. Bromodurene was nitrated in chloroform solution with a mixture of concentrated sulphuric and fuming nitric acids as described by Smith and Tenenbaum (*J. Amer. Chem. Soc.*, 1935, **57**, 1293). Recrystallisation from alcohol gave white crystals, m. p. 179·2—180·2° (Smith and Tenenbaum give m. p. 179—181°).

Aminodurene. Willstätter (*Ber.*, 1909, **42**, 4159) reduced bromonitrodurene with zinc and acetic acid, but we obtained a better yield (80%) by reducing it with tin and hydrochloric acid in acetic acid solution. 4 G. of bromonitrodurene were dissolved in boiling glacial acetic acid 39 c.c. of concentrated hydrochloric acid added, and then, slowly, 6 g. of granulated tin. The solution was refluxed for several hours, then treated with a large quantity of concentrated sodium hydroxide solution and steam-distilled. A whitish oil solidified to a white solid in the receiver. This was filtered off and dried, and purified by sublimation in a vacuum and recrystallisation from ligroin (b. p. 60—80°); m. p. 72° (Willstätter gives m. p. 75°; Smith and Tenenbaum, *loc. cit.*, m. p. 71—73°).

Bromoaminodurene. 3·5 G. of aminodurene were dissolved in 25 c.c. of glacial acetic acid, and 3·5 g. of bromine in 20 c.c. of glacial acetic acid were slowly added. A white precipitate was immediately formed, which was filtered off, washed with a little acetic acid, and then suspended in water and ammonia added. The base was filtered off, dried, and crystallised from ligroin (b. p. 80—100°); 2·5 g. crystallised (m. p. 137·5—138·5°) and then a further crop of 1 g. (m. p. 135·5—137·5°) was got by cooling the mother-liquor in ice and salt. The latter crop after sublimation in a vacuum had m. p. 138·5—139·5°. Finally the whole was recrystallised from ligroin (b. p. 80—100°); m. p. 138·5—139·5° (Found : C, 53·0; H, 6·1; N, 6·2; Br, 35·1. Calc. for $C_{10}H_{14}NBr$: C, 52·6; H, 6·2; N, 6·1; Br, 35·1%).

Pentamethylaniline. This was prepared by essentially the same method as that described by Dimroth, Leichtlin, and Friedemann (*Ber.*, 1917, **50**, 1543), but aminodurene hydrochloride was used instead of *m*-5-xylidine hydrochloride as the starting material. 12 G. of aminodurene hydrochloride were heated with 2 g. of absolute methyl alcohol in a sealed tube for 8 hours at 250°, and the reaction products worked up in the manner described by Dimroth, Leichtlin, and Friedemann; 3 g. of pentamethylaniline, m. p. 152—153°, were obtained (Dimroth, Leichtlin, and Friedemann give 151—152°).

Measurements.—The data for the determination of dipole moments are in the following tables, where the symbols have their usual significance. All the measurements were carried out in benzene solution at 25·0°.

SUMMARY.

It is suggested that if the discrepancies between the observed dipole moments of *p*-disubstituted benzenes and those calculated assuming vector addition are due to resonance involving quinonoid structures, then with substituents such as NO_2, NH_2, NMe_2, and OMe there should be a tendency for the oxygen, hydrogen and methyl groups respectively to be held in the plane of the benzene ring. The introduction of methyl groups in the *o*-positions into these substituents would, on the other hand, exert a steric effect in forcing these three groups out of the plane of the benzene ring.

f_2.	$d_{4°}^{25°}$.	ϵ.	n^2.	P_2.	$_{\text{E}}P_2$.
Nitrodurene.					
0·003706	0·8752	2·3348	2·2588	291·4	55·9
0·003192	0·8750	2·3266	2·2584	294·5	55·0
$_{\text{A+O}}P_2$ = 294·5 — 55·5 = 239 c.c.; μ = 3·39.					
Aminodurene.					
0·012234	0·8757	—	2·2608	—	49·7
0·009543	0·8752	—	2·2598	—	49·5
0·006188	0·8746	2·2904	—	87·9	—
0·003872	0·8742	2·2841	—	89·5	—
0·003247	0·8741	2·2823	—	89·1	—
$_{\text{A+O}}P_2$ = 89·6 — 49·6 = 40 c.c.; μ = 1·39.					
Bromodurene.					
0·016197	0·8857	2·3321	2·2610	103·4	53·1
0·013553	0·8837	2·3222	2·2619	103·1	54·8
0·009479	0·8806	2·3071	2·2590	103·3	53·1
0·004717	0·8771	2·2888	2·2575	100·1	51·9
$_{\text{A+O}}P_2$ = 103·3 — 53·2 = 50·1 c.c.; μ = 1·55.					
Nitroaminodurene.					
0·007850	0·8777	2·5507	2·2608	541·5	56·7
0·007461	0·8775	2·5355	2·2604	540·6	57·1
0·006023	0·8768	2·4853	2·2602	546·1	57·0
0·002912	0·8752	2·3760	2·2589	559·9	58·6
$_{\text{A+O}}P_2$ = 572 — 57 = 515 c.c.; μ = 4·98.					
Bromoaminodurene.					
0·008612	0·8816	2·3693	2·2620	211·8	57·6
0·006308	0·8795	2·3431	2·2607	211·7	57·6
0·004847	0·8782	2·3274	—	213·9	—
$_{\text{A+O}}P_2$ = 214 — 57·6 = 156·4 c.c.; μ = 2·75.					
Bromonitrodurene.					
0·012951	0·8885	2·3806	2·2649	173·2	61·3
0·011839	0·8871	2·3707	2·2644	172·7	61·8
0·006760	0·8812	2·3296	2·2610	175·9	61·9
0·004721	0·8789	2·3125	2·2600	176·0	62·9
$_{\text{A+O}}P_2$ = 178 — 62 = 116 c.c.; μ = 2·36.					
Pentamethylaniline.					
0·010447	0·8758	2·2938	2·2605	79·2	53·9
0·007045	0·8750	2·2866	2·2594	79·0	54·4
$_{\text{A+O}}P_2$ = 79 — 54 = 25 c.c.; μ = 1·10.					
Dinitrodurene.					
0·024643	0·8919	2·2916	2·2639	64·7	57·0
0·022055	0·8899	2·2899	2·2629	64·9	56·8
0·014925	0·8846	2·2841	2·2619	64·2	57·2
0·010945	0·8816	2·2809	2·2602	64·8	57·3
$_{\text{A+O}}P_2$ = 64·6 — 57·1 = 7·5 c.c.; μ = 0·60.					

A number of durene compounds have been made and their electric moments measured. The latter are found to be lower than those of the corresponding benzene compounds, except in the case of bromodurene.

Since calculations show that the results cannot be explained by induced effects in the methyl groups, the conclusion is drawn that the lowering of moment is due to a damping of the resonance by the steric effect of the methyl groups. Bromodurene, on the other hand, has almost the same moment as bromobenzene, and here no steric influence is to be expected.

The moment of dinitrodurene (0·60) is in agreement with the small moments found for other symmetrical polynitro-compounds.

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