209. *An Investigation of Steric Influences on the Phenomenon of Resonance.* Part II.*

By C. E. INGHAM and G. C. HAMPSON.

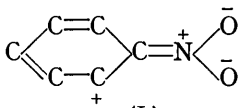
The discrepancy between the dipole moments, calculated by vector addition, and the observed moments of compounds such as *p*-nitroaniline and *p*-nitrophenol has been ascribed to resonance in which one of the contributing structures has a quinonoid form. The moments of durene compounds containing substituents such as NO_2, NR_2, or OR are lower than those of their benzene analogues, and as calculation shows that this cannot be due to induction effects in the methyl groups of the durene radical, the conclusion is drawn that the lowering of moment is due to a damping of the resonance, arising from steric factors. The *o*-methyl groups prevent the assumption of the planar configuration necessary for the quinonoid form. The substituted mesitylenes show the same behaviour, the differences between their moments and those of their benzene analogues being in the direction of the corresponding aliphatic compounds. Substitution of a more bulky alkyl group for the hydrogen in an amino- or a hydroxyl group results in a much greater suppression of the resonance. A comparison of the moment of 2-nitro-*m*-5-xylidine, in which only the nitro-group is blocked by methyl groups, with those of *p*-nitroaniline and nitroaminodurene shows that the steric effect of the *o*-methyl groups on the large oxygen atoms of the nitro-group is more important than that on the hydrogen atoms of the amino-group.

An explanation is offered of the anomalous nitration of *m*-2-xylidine.

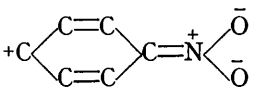
The moments of mesidine, dimethylmesidine, durenol, nitrodimethylaminodurene, nitrodurenol, nitroethoxydurene, and 2-nitro-*m*-5-xylidine have been measured in benzene solution at 25°; they are 1·40, 1·03, 1·68, 4·11, 4·08, 3·69, and 5·04 respectively.

IN a previous paper (Birtles and Hampson, J., 1937, 10) were given the results of the dipole-moment measurements of some substituted durene compounds. It was pointed out that, if the permanent "electromeric" or "mesomeric" effect in a conjugated system is to be ascribed to resonance between the normal classical structure and one or more "excited" structures in which an electronic rearrangement has taken place, then in the case of a substituted benzene compound, such as nitrobenzene, the molecule should have some of the properties of a quinonoid structure and the bond linking the nitro-group to the benzene ring should be a hybrid of single- and double-bonded forms. Owing to the stabilising influence of the resonance, the properties of this linking bond, such as its length and its force constant, are closer to those of the more stable double bond (Pauling, *Proc. Nat. Acad. Sci.*, 1932, **18**, 293, 498; Brockway, *ibid.*, 1933, **19**, 868; Brockway and Pauling, *ibid.*, p. 860; Pauling and Huggins, *Z. Krist.*, 1934, **87**, 205; Badger, *J. Chem. Physics*, 1935, **3**, 710).

In a resonating molecule there is no tautomeric movement of the atomic nuclei, the position taken up by the atoms being that which is most nearly common to the various contributing structures. In the case of nitrobenzene, the stable configuration will be when the oxygen atoms of the nitro-group are in the plane of the benzene ring, for although the excited structures (I) and (II) contribute only slightly to the resonance (the mesomeric



(I.)



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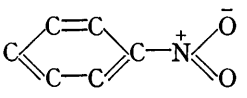


(III.)

moment is only of the order of one-tenth of the difference between the moments of the normal structure and of the more polar excited structures), the double bond linking the nitro-group to the benzene ring in (I) and (II) will impose a planar configuration on the molecule. Rotation of the nitro-group will involve an activation process, only those

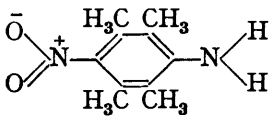
* In accordance with common practice, the word "resonance" has been substituted for "mesomerism."

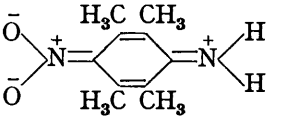
molecules which have acquired sufficient energy of activation to overcome the resonance energy being capable of rotation.

When two groups of opposite type, an *op*-directing group and a *m*-directing group, are substituted para to one another in the benzene nucleus, each reinforces the type of resonance characteristic of the other, there being a mutual stabilisation of the excited form, the combination of these secondary effects causing an abnormally large variation in the moment (Marsden and Sutton, J., 1936, 599).

If the presence of a mesomeric or resonance effect in a substituted benzene molecule tends to impose a coplanar arrangement of the atoms in a substituent group such as a nitro- or a dimethylamino-group, then conversely we might expect that anything which tends to prevent such coplanarity, as, *e.g.*, the steric effect of an *o*-alkyl group, would reduce the resonance. This was tested (Birtles and Hampson, *loc. cit.*) by measuring the dipole moments of a number of substituted durene compounds, and it was shown that in all cases where there was a "branched" substituent the steric effect of the methyl groups reduced the mesomeric moment, the measured moment of the compound being found to lie between the moments of the corresponding benzene and alkyl derivatives. Rough calculations showed that the change in moment could not be due to induced effects in the methyl groups, and this was further confirmed by the fact that, when the substituent was a single atom, such as a bromine atom, where no steric influences would be involved, the moment of the durene compound was the same as that of the corresponding benzene compound. The work has now been extended to a number of other derivatives of durene and mesitylene, and the results are all found to agree with this hypothesis.

It was shown in the previous communication that the moment of nitroaminodurene, although lower than that of *p*-nitroaniline, was still greater than the sum of the moments of mononitrodurene and monoaminodurene, indicating that the resonance between (IV)

(IV.) 

 (V.)

and (V) had not been completely suppressed. If now the amino-group be methylated, the increased steric effect, due to the replacement of the amino-hydrogen atoms by the more bulky methyl groups, should result in a still greater decrease in the mesomeric moment, as compared with *p*-nitrodimethylaniline. One object of this research, therefore, was the investigation of the dimethylamino-derivatives. In addition, it was required to determine whether the same damping of resonance occurs in nitrodurenol and whether the effect is increased by alkylation of the hydroxyl group. Finally, the importance of induction effects in the methyl groups attached to the nucleus was investigated by comparing the moments of some mesitylene and durene derivatives.

These new results are given in the following table, together with the moments of the corresponding derivatives of benzene.

Substance.	μ, D.	Substance.	μ, D.	Diff.
Mesidine	1·40	Aniline	1·53	− 0·13
Dimethylmesidine	1·03	Dimethylaniline	1·58	− 0·55
Durenol	1·68	Phenol	1·61	+ 0·07
Nitrodimethylaminodurene	4·11	*p*-Nitrodimethylaniline	6·87	− 2·76
Nitrodurenol	4·08	*p*-Nitrophenol	5·04	− 0·96
Nitroethoxydurene	3·69	*p*-Nitroanisole	4·76	− 1·07
2-Nitro-*m*-5-xylidine	5·04	*p*-Nitroaniline	6·10	

It will be observed that the moments of mesidine and aminodurene (1·39; Birtles and Hampson, *loc. cit.*) are identical within experimental error. In both these compounds the amino-group is adjacent to two *o*-methyl groups, and the identity of moment indicates that it is the steric effect rather than the induction effect which is important, in agreement with the conclusion drawn from the result for bromodurene. The moments lie between that of aniline (1·53) and that of a primary alkylamine (μ for methylamine = 1·23; Steiger, *Physikal. Z.*, 1931, **32**, 425), as would be expected if the effect of the *o*-methyl

groups was to suppress the resonance. Methylation of the amino-group produces a very much greater effect, the moment of dimethylmesidine being lower than that of mesidine and very much lower than that of dimethylaniline (1·58; Fogelberg and Williams, *ibid.*, p. 27; Marsden and Sutton, *loc. cit.*). The steric effect of the *o*-methyl groups on the bulky dimethylamino-group must almost completely suppress the resonance. The most striking case of all, however, is when a dimethylamino-group is para to a nitro-group. In *p*-nitrodimethylaniline, the moment 6·87 (Marsden and Sutton, *loc. cit.*) is very much larger than the sum of the moments of nitrobenzene (3·95) and dimethylaniline (1·58), indicating a pronounced stabilisation of the quinonoid form. When the same two groups are introduced into durene, the moment of the nitrodimethylaminodurene is only 4·11. The difference of 2·76 between this and the moment of *p*-nitrodimethylaniline is certainly much too large to be ascribed to any induction effects, and must represent a large inhibition of the resonance. A similar effect was observed in nitroaminodurene (Birtles and Hampson, *loc. cit.*), but here the difference in moment between the durene compound (4·98) and *p*-nitroaniline (6·10) was only 1·12. These results clearly show the greatly enhanced steric effect of the *o*-methyl groups on the large dimethylamino-group in preventing conjugation of the group with the benzene ring. The effect, in fact, is so great that it actually reverses the direction of the change in moment due to dimethylation of the amino-group. The moment of *p*-nitrodimethylaniline is greater than that of *p*-nitroaniline, whereas in the durene compounds the methylated compound has the lower moment. The much smaller interaction between the two groups in the durene compound is shown by the fact that the value of 4·11 is now less than the sum of the moments of the two monosubstituted derivatives,* as would be expected if little or no interaction occurs, since the moments of the two groups are not coaxial. In 2-nitro-*m*-5-xylidine only the nitro-group is subject to the steric effect of the *o*-methyl groups, the amino-group being unrestricted. For comparison with *p*-nitroaniline and nitroaminodurene the moment of 5·04 must of course be corrected for the moment of the methyl groups; we then see that the main moment of the molecule, due to the nitro- and the amino-group and any interaction between them, is of the order of 5·4. This value lies between 4·98 for nitroaminodurene, where both the amino- and the nitro-group are restricted, and 6·10 for *p*-nitroaniline, where both the groups are free from any steric effect. The fact that it lies closer to the value for the durene compound indicates, as would be expected, that the blocking of the nitro-group is the main cause of the reduction of the mesomeric moment, as the steric effect on the large oxygen atoms of the nitro-group must be larger than the effect on the smaller hydrogen atoms of the amino-group. It would be interesting to determine the moment of 5-nitro-*m*-2-xylidine, in which the amino-group is blocked and the nitro-group is free, but so far this compound has not been prepared. Preparation by nitration of the acetyl derivative of *m*-2-xylidine is not possible, for Noelting and his collaborators (Noelting and Stöcklin, *Ber.*, 1891, **24**, 568; Noelting, Braun, and Thesmar, *Ber.*, 1901, **34**, 2259; Noelting and Thesmar, *Ber.*, 1902, **35**, 629) showed that the 5-position is not attacked and that nitration occurs in the 4- and the 6-position. This result is at first sight surprising, but it affords interesting chemical support for the hypothesis which this research was designed to test. The steric effect of the *o*-methyl groups reduces the resonance, and hence the directing power of the amino-group, to such an extent that the methyl groups become the main directive influences.

Of the hydroxy-compounds, it will be observed that the moment of durenol is higher than that of phenol and is nearer to that of an alcohol (μ for ethyl alcohol is 1·70, for *cyclo*hexanol 1·69, for benzyl alcohol 1·70; Sidgwick *et al.*, "Table of Dipole Moments," *Trans. Faraday Soc.*, 1934, **30**, Appendix), again indicating that in the durene compound the mesomeric moment into the ring has been reduced by the steric effect. The moment of

* There is some uncertainty in the value of 3·39 previously reported for the moment of mononitrodurene, owing to the difficulty of preparing the compound in a pure state and the very small quantity of material which was available for the measurement. The value of 3·64 given by Brown, de Bruyne, and Gross (*J. Amer. Chem. Soc.*, 1934, **56**, 1291) for nitromesitylene agrees well with 3·67 found by Hammick, New, and Williams (J., 1934, 29) for the same compound, and would indicate that the above value for mononitrodurene is too low. Further attempts to prepare a purer sample of this compound have so far failed.

p-nitrophenetole has not been determined, and hence the value for *p*-nitroanisole, which should be close to it, has been used for comparison with that of nitroethoxydurene. As with the nitroamino- and nitrodimethylamino-compounds, both nitrodurenol and nitroethoxydurene have lower moments than the corresponding benzene compounds, the difference being greater in the case of the ethoxy- than in that of the hydroxy-derivatives. Owing to the weaker directive power of the hydroxy- and ethoxy-groups, such large differences as are found in the amino- and dimethylamino-derivatives are not to be expected.

No attempt has been made to make a more quantitative calculation of the mesomeric moment in any of these compounds, as has been done by Sutton and his collaborators (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668; Sutton and Hampson, *Trans. Faraday Soc.*, 1935, **31**, 945; Marsden and Sutton, J., 1936, 599), owing to the fact that dipole-moment data are not available for the *p*-methyl derivatives, and because of the uncertainty of the allowance to be made for induction effects. An attempt to overcome the latter difficulty has recently been made by Groves and Sugden (J., 1937, 1992), but the results cannot be regarded as more than qualitative. There can be no doubt, however, that the dipole-moment measurements herein described clearly indicate the steric effect of *o*-methyl groups in preventing the adoption of the stereochemical configuration necessary for the resonance; a more quantitative discussion is hardly justified at this stage.

Experimental.

Preparation and Purification of Materials.—Mesidine. 15 G. of recrystallised nitromesitylene (prepared according to " Organic Syntheses," Vol. 14, p. 68) were added to 60 g. of stannous chloride and 100 c.c. of concentrated hydrochloric acid, sufficient alcohol being added to bring all into solution at the boiling point. A little granulated tin assisted the ebullition, and the mixture was boiled under reflux for about 3 days, fresh tin and acid being added from time to time. Alcohol and unchanged nitro-compound were removed by steam-distillation, and the residue, after being made alkaline with a large excess of sodium hydroxide, was again steam-distilled. The distillate was extracted with ether, the ethereal solution dried (sodium sulphate), the ether removed, and the residue distilled and collected between 225° and 230°. Redistillation gave a product, b. p. 227° (Ladenburg, *Annalen*, 1875, **179**, 172, gave 229—230°, and Biedermann and Ledoux, *Ber.*, 1875, **8**, 58, b. p. 227°).

Dimethylmesidine. 60 G. of methyl sulphate were heated to 150° on an oil-bath and 25 g. of mesidine added at such a rate (8—10 mins.) that this temperature was maintained without further external heating; after being kept at this temperature for a further 20 mins., the mixture was cooled in ice, made alkaline with sodium hydroxide, and extracted with ether. The red-brown oil remaining after removal of ether was heated with 35 g. of acetic anhydride for 2 hours, excess anhydride decomposed by water and excess sodium hydroxide, and the mixture extracted with ether. The dimethyl derivative was separated from the extract by shaking with dilute hydrochloric acid, and precipitated from the acid layer with ammonia. Further extraction with ether and drying with anhydrous sodium sulphate gave a product of b. p. 213° (Hofmann, *Ber.*, 1872, **5**, 718, gives b. p. 213—214°).

Nitroaminodurene. The following procedure gave a much better yield (80%) than that of Birtles and Hampson (*loc. cit.*). 20 G. of dinitrodurene and 500 c.c. of alcohol were boiled under reflux, and a solution of sodium disulphide (prepared by warming a solution of 70 g. of $Na_2S,9H_2O$ in about 200 c.c. of water with 9 g. of flowers of sulphur) was added slowly with stirring, the mixture being stirred at its b. p. for 6—7 hours. The separation and purification were then carried out as before.

Nitrodimethylaminodurene. Two methods were tried, the second being the better. (i) 25 G. of methyl sulphate were heated to 150° on an oil-bath and 10 g. of nitroaminodurene slowly added, the same procedure then being employed as in the preparation of dimethylmesidine. On addition of sodium hydroxide to the acetic anhydride solution, however, a red oil was formed which was very difficult to purify. Extraction with ether was not very efficient, but on shaking the ethereal extract with dilute hydrochloric acid and adding ammonia to the acid solution, a light red oil separated which eventually solidified. Crystallisation from alcohol gave yellow crystals contaminated with red tar, but repeated recrystallisation from alcohol and ligroin eventually gave a pure product (*ca.* 1 g.), m. p. 90°. (ii) 4·7 G. of nitroaminodurene, 17 g. of methyl iodide, 4 g. of sodium hydroxide, and about 20 c.c. of methyl alcohol were heated in a sealed tube to 150° for 8 hours. On cooling, a mass of yellow crystals

was obtained. The mixture was boiled for 3 hours under reflux with 20 g. of acetic anhydride, excess anhydride then being decomposed with water, and the solution made alkaline with dilute sodium hydroxide solution. Extraction with ether and treatment with dilute hydrochloric acid and ammonia as before gave 2 g. of crude product, which was purified by crystallisation from alcohol and ligroin; yellow needles, m. p. 90° (Found: C, 64·6; H, 8·0; N, 12·8. Calc. for $C_{12}H_{18}O_2N_2$: C, 64·9; H, 8·1; N, 12·6%).

Nitroethoxydurene and nitrodurenol. 18 G. of nitroaminodurene were dissolved in about 700 c.c. of alcohol, 18 g. of concentrated sulphuric acid added with stirring and cooling, and the mixture diazotised with 12 g. of sodium nitrite. The mixture was then warmed on a water-bath to expel nitrogen, most of the alcohol evaporated off, and the residue steam-distilled. A yellow oil, consisting of a mixture of mononitrodurene (cf. Birtles and Hampson, *loc. cit.*) and nitroethoxydurene, first came over. After 2—3 g. had collected, a white oil distilled which was collected separately. This was fairly pure nitroethoxydurene (yield 6 g.). Recrystallisation from alcohol gave a white solid, m. p. 75·5° (Found: C, 64·7; H, 7·4; N, 6·4. Calc. for $C_{12}H_{17}O_3N$: C, 64·6; H, 7·6; N, 6·3%).

The residue in the flask after the steam-distillation showed phenolic properties and proved to be nitrodurenol. The yellow solid was filtered off, dissolved in sodium hydroxide (forming a deep red-brown solution), reprecipitated by hydrochloric acid, and the pale yellow solid recrystallised from alcohol; the m. p. could not be raised above 123—124° (Jacobsen and Schnapauff, *Ber.*, 1885, **18**, 2844, give m. p. 130°) (Found: N, 7·2. Calc. for $C_{10}H_{13}O_3N$: N, 7·2%).

Durenol. A solution of 5 g. of aminodurene in 7 g. of concentrated sulphuric acid and 100 c.c. of water was cooled, and diazotised with 2·5 g. of sodium nitrite. The mixture was then warmed on a water-bath until evolution of nitrogen ceased, and the resulting pale yellow solid was purified as for the above nitrodurenol, being finally recrystallised twice from ligroin; yield 2 g., m. p. 117° (Jacobsen and Schnapauff, *loc. cit.*, give 117°).

2-*Nitro*-m-5-*xylidine*. 28 G. of nitromesitylene, 70 g. of sodium dichromate, and 150 c.c. of water were mixed and stirred mechanically while 92 c.c. of concentrated sulphuric acid were slowly added, the temperature being kept below the b. p. The mixture was then boiled under a reflux for an hour, cooled, and 200 c.c. of water added. A sticky green solid separated, which was filtered off, washed, and digested with 5% sulphuric acid for some time to remove chromic salts. After cooling, the solid was filtered off, dissolved in warm 5% sodium hydroxide solution, and the cooled solution filtered from unchanged nitromesitylene and chromic hydroxide. Excess of dilute sulphuric acid reprecipitated the nitromesitylenic acid which was filtered off, washed, dried, and recrystallised from alcohol. This is the symmetrical acid (see Emerson, *Amer. Chem. J.*, 1886, **8**, 269). 25 G. of it were converted into the acid chloride with 20 g.

f_2.	$d_{4°}^{25°}$.	ϵ.	n^2.	P_2.	$_E P_2$.
		Mesidine.			
0·01976	0·8766	2·3306	—	85·1	—
0·01963	0·8766	2·3304	2·2615	85·0	44·9
0·01120	0·8755	2·3060	2·2597	85·6	45·1
0·00820	0·8752	2·2966	2·2589	84·7	44·5
$_{A+O}P_2$ = 85·3 − 44·8 = 40·5 c.c.; μ = 1·40D.					
		Nitrodimethylaminodurene.			
0·01351	0·8803	2·5875	2·2598	385·2	63·7
0·01064	0·8789	2·5234	2·2594	392·7	64·1
0·00764	0·8776	2·4521	2·2588	395·2	63·9
0·00443	0·8762	2·3786	2·2582	404·9	63·5
$_{A+O}P_2$ = 414·4 − 63·8 = 350·6 c.c.; μ = 4·11D.					
		Durenol.			
0·01215	0·8768	2·3268	—	104·7	—
0·00927	0·8761	2·3140	2·2590	105·2	47·4
0·00835	0·8760	2·3100	2·2587	105·0	46·7
0·00501	0·8753	2·2955	2·2580	106·3	46·4
$_{A+O}P_2$ = 105·5 − 46·8 = 58·7 c.c.; μ = 1·68D.					
		2-Nitro-m-5-xylidine.			
0·00447	0·8767	2·4406	2·2589	570·5	43·8
$_{A+O}P_2$ = 570·5 − 43·9 = 526·6 c.c.; μ = 5·04D.					

f_2.	$d_{4°}^{25°}$.	ϵ.	n^2.	P_2.	$_E P_2$.
		Dimethylmesidine.			
0·03256	0·8758	2·3204	—	76·2	—
0·02976	0·8757	2·3158	2·2579	75·9	54·2
0·01701	0·8751	2·2979	2·2576	76·2	54·2
0·01100	0·8749	2·2886	2·2576	75·4	54·2
$_{A+O}P_2$ = 76·0 − 54·2 = 21·8 c.c.; μ = 1·03D.					
		Nitrodurenol.			
0·01378	0·8820	2·5905	2·2608	367·7	52·6
0·00854	0·8791	2·4716	2·2599	378·0	53·4
0·00640	0·8778	2·4228	2·2596	383·6	49·8
0·00370	0·8763	2·3605	2·2581	391·1	52·6
$_{A+O}P_2$ = 399·0 − 52·9 = 346·1 c.c.; μ = 4·08D.					
		Nitroethoxydurene.			
0·01805	0·8815	2·6223	2·2590	331·2	63·1
0·01339	0·8796	2·5315	2·2585	334·5	63·3
0·00865	0·8776	2·4397	2·2582	338·3	63·6
0·00683	0·8769	2·4049	2·2578	340·2	63·2
$_{A+O}P_2$ = 346·0 − 63·3 = 282·7 c.c.; μ = 3·69D.					
		2-Nitro-m-5-xylidine.			
0·00328	0·8761	2·3938	2·2587	565·4	44·0
$_{A+O}P_2$ = 570·5 − 43·9 = 526·6 c.c.; μ = 5·04D.					

of thionyl chloride. The resulting red liquid was added drop by drop, with stirring, to a mixture of equal vols. of aqueous ammonia (*d* 0·88) and water, cooled in ice, whereupon the acid amide separated as a light brown solid. A paste of 19·5 g. of this amide in water was added with stirring to a solution of sodium hypobromite (NaOH, 20 g.; H_2O, 100 c.c.; Br_2, 16 g.) cooled in ice–salt, and the mixture then removed from the freezing mixture and allowed to warm to room temperature; a further 12 g. of sodium hydroxide were then stirred in, and the mixture warmed to 80° on a water-bath for some time. A yellow solid separated, which was filtered off, washed, and dried. The crude product (10 g.) was dissolved in dilute hydrochloric acid, the solution filtered, and the base reprecipitated by ammonia; orange needles, m. p. 131·6°, were obtained by recrystallisation from alcohol (Found: C, 57·9; H, 6·0; N, 17·0. Calc. for $C_8H_{10}O_2N_2$: C, 57·8; H, 6·0; N, 16·9%).

Dipole-moment Measurements.—The requisite data are on p. 985, where the symbols have their usual significance. All the measurements were carried out in benzene solution at 25·0°.

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