483. *The Dipole Moments of Some Aromatic Nitro-compounds in relation to the Steric Inhibition of the Mesomeric Effect of the Nitro-group.*

By A. C. LITTLEJOHN and J. W. SMITH.

The dipole moments of some derivatives of nitrobenzene, *m*-dinitrobenzene, and 1 : 3 : 5-trinitrobenzene have been determined from measurements on benzene solutions. After inductive effects have been taken into account, the results, in conjunction with other data, indicate that an *ortho*-chlorine atom, -bromine atom, or -*tert.*-butyl group reduces considerably the effective group moment of a nitro-group. A methyl group has a much smaller effect. However, only when substituents occupy both positions *ortho* to the nitro-group, or when one substituent in such a position has also another substituent adjacent to it, is the group moment reduced almost to that of a nitro-group in a saturated aliphatic compound. It is shown that appreciable out-of-plane deflection of the groups in these compounds is improbable, and the results are interpreted in terms of slight in-plane deflection of the bonds between the substituents and the benzene nucleus together with a reduction in the effective moment of the nitro-group arising from steric inhibition of its mesomeric effect.

IT has been shown [1,2] that the use of the classical laws of induction assists in interpreting the dipole moments of a number of monosubstituted diphenyls and 2 : 2′- and 3 : 3′-disubstituted diphenyls, the most self-consistent results being obtained when the effective centres of the dipoles of the substituents are assumed to lie near to their polarisable centres. An attempt has been made, therefore, to use this method to assist in interpreting the dipole moments of polysubstituted benzenes, especially those for which the values appear to be anomalous. These include molecules with large balanced dipoles, and nitro-compounds in which the mesomeric effects of the nitro-groups may be partially or completely inhibited through steric factors.

To augment the data available for comparison, the dipole moments of *m*-dinitrobenzene and of various derivatives of nitrobenzene, *m*-dinitrobenzene, and 1 : 3 : 5-trinitrobenzene 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 concentration, and the other symbols have their usual significance. In calculating the dipole moment values it has been assumed that ${}_{\mu}P_2 = P_{2\infty} - [R_D]_2$. For trinitro- and tribromo-compounds, however, where atom polarisation may contribute appreciably to the value of $P_{2\infty}$ the moments have also been calculated by making further allowances for atom polarisation equal to the $P - [R_D]$ differences for 1 : 3 : 5-trinitrobenzene [3] (9·6 c.c.) and 1 : 3 : 5-tribromobenzene [4] (2·1 c.c.), respectively. The values of the dipole moments, in benzene solution, so deduced are shown in parentheses in Table 1 : they are regarded as the more probable values and are used in the subsequent discussion.

The measurements on *m*-dinitrobenzene, *p*-chloronitrobenzene, and *p*-bromonitrobenzene, repeated on account of the variations in the recorded values, agree closely with those of Le Fevre and Le Fèvre [3] and of Tiganik.[4] Tiganik's results, when recalculated with modern values of the universal constants, lead to dipole moment values almost identical with ours.

It has been confirmed that the dipole moment of *m*-dinitrobenzene is appreciably smaller than that of nitrobenzene, although on simple vector theory the values should be equal. The dipole moments of the *m*-dihalogenobenzenes are also smaller than those of the corresponding monohalogenobenzenes. The classical laws of induction can be used to calculate the moment induced in each substituent by the presence of the other, and hence

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[1] Littlejohn and Smith, *J.*, 1953, 2456.

[2] *Idem, J.*, 1954, 2552.

[3] Le Fèvre and Le Fèvre, *J.*, 1950, 1829.

[4] Tiganik, *Z. phys. Chem.*, 1931, **13**, *B*, 425.

to derive " theoretical " values of the moments of the disubstituted benzenes. For this purpose the dipoles have been assumed to be effectively located at the polarisable centres of the substituent groups : for the nitro-group this is 1·95 Å from the nucleus of the carbon atom to which it is linked, whilst for the halogen substituents it is at the nucleus of the halogen atom. By using the same polarisability values as in the previous work,[2] it is found that such mutual induction can account for only a small fraction of the differences observed between the moments of mono- and *m*-di-substituted benzenes (Table 2). Further, as the distances between the substituents are relatively large in these compounds, the calculated effect of mutual induction is comparatively insensitive to the exact locations assumed for the dipoles.

TABLE 1. *Summary of polarisation data for benzene solutions.*

	100α	$-10^3\beta$	$10^3\gamma$	$P_{2\infty}$ (c.c.)	$[R_D]_2$ (c.c.)	μ (D)	Previous values (D)
m-Dinitrobenzene	957	468	132	336·7	37·6	3·83	3·81,[5] 3·78,[4] 3·81,[4] * 3·96,[6] 3·86[3]
2 : 4-Dinitrodiphenyl	859	426	254	446·9	63·3	4·34	
2 : 4 : 6-Trinitrodiphenyl	118	484	267	121·1	70·7	1·57 (1·41)	
p-Chloronitrobenzene	475	419	143	174·8	37·8	2·59	2·36,[7] 2·34,[8] 2·57,[4] 2·59,[4] * 3·12[9]
p-Bromonitrobenzene	402	566	179	187·7	41·2	2·68	2·45,[8] 2·65,[4] 2·67[4] *
1-Chloro-2 : 4-dinitrobenzene	607	520	169	262·5	42·5	3·28	3·29,[10] 3·00,[11] 3·24[3]
1-Bromo-2 : 4-dinitrobenzene	522	625	173	280·4	45·8	3·39	3·1 [11]
1 : 3 : 5-Tribromo-2-nitrobenzene	312	729	155	255·8	54·5	3·14 (3·12)	
1 : 3 : 5-Tribromo-2 : 4-dinitro-benzene	276	742	155	258·8	59·8	3·12 (3·10)	
1-*tert*.-Butyl-2 : 4-dinitrobenzene...	1000	335	79	475·8	56·6	4·53	

* Recalculated.

TABLE 2. *Parameters assumed for substituent groups and the observed and calculated dipole moments of* m-*disubstituted benzenes.*

Group X	Polarisability (10^{-25} c.c.)	Distance from ring carbon atom of dipole and polarisable centre	Dipole moments (D)		
				m-$C_6H_4X_2$	
			PhX	obs.	calc.
Nitro	2·24	1·95	4·01	3·83 †	3·98
Chloro	1·91	1·69	1·58 [1]	1·49 *	1·57
Bromo	3·05	1·88	1·56 [1]	1·47 *	1·55
Iodo	5·07	2·00	1·40 [1]	1·28 *	1·39

* Recalc. from Tiganik's results.[4] † Present work.

The effect is still more pronounced in *ortho*-disubstituted benzenes, for which, on simple vector theory, the dipole moments should be 1·732 times the values for the corresponding mono-substituted benzenes. Although for these compounds the calculated inductive effects of the substituents upon one another depend rather critically upon the location assumed for the dipole, such effects can account for only about one-third of the apparent reduction in the group moments. Mutual repulsion of the groups may be responsible in part for the reduction in the moments of the *ortho*-compounds, but in *meta*-disubstituted benzenes it is much too feeble to cause an increase of about 2½° in the angle between the dipoles which would be necessary to account for the observed values of the dipole moments. It also seems improbable that the results are due to solvent effects, as these are likely to be relatively smaller for the disubstituted than for the monosubstituted benzenes. A reduction in the mesomeric effect of each group in the presence of the other

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[5] Williams and Schwingel, *J. Amer. Chem. Soc.*, 1928, **50**, 362.
[6] Higasi, *Bull. Inst. Phys. Chem. Res. Japan*, 1941, **20**, 218.
[7] Walden and Werner, *Z. phys. Chem.*, 1929, **2**, *B*, 10.
[8] Lütgert, *ibid.*, 1931, **14**, *B*, 350.
[9] Jagielski and Weslowski, *Bull. Acad. polon. Sci.*, 1935, *A*, 260.
[10] Hassel and Naeshagen, *Z. phys. Chem.*, 1931, **18**, *B*, 79.
[11] Lütgert, *Z. phys. Chem.*, 1932, **17**, *B*, 460.

would account for the lower moment of *m*-dinitrobenzene than of nitrobenzene, but would be expected to cause the moments of the *m*-dihalogenobenzenes to be greater than those of the corresponding monohalogenobenzenes. The most probable explanation, therefore, is that although the total displacement of the electrons of the ring brought about by the inductive effect of the substituents is greater in the *meta*-disubstituted benzenes than in the monosubstituted benzenes, the effect attributable to each substituent is less in the former than in the latter. Hence in calculating "theoretical" values of the dipole moments of derivatives of *m*-dinitro- or *m*-dihalogeno-benzenes it seems most logical to assume the effective group moments to be equal to the moment of this disubstituted compound.

This has been done when deriving the calculated moments given in Table 3. Here the figures shown under μ (calc.) (*a*) are the values obtained by vector addition, assuming no distortion of the valency angles and without correction for inductive effects of one group upon another. The figures under μ (calc.) (*b*), on the other hand, include corrections for these inductive effects: in deriving these it has been assumed that the polarisabilities of the methyl and the *tert.*-butyl group are 1·91 and 7·42 c.c., respectively, that their group moments are —0·37 and —0·53 D, respectively, and that their polarisable centres are located 1·55 Å and 2·07 Å, respectively, from the nucleus of the ring carbon atom to which they are bonded. For other groups the data shown in Table 2 were used. In calculating the theoretical moments of derivatives of 1 : 3 : 5-trinitrobenzene or 1 : 3 : 5-tribromobenzene the effective group moments of the nitro-group and bromine atom have been taken as equal to the dipole moments of the *m*-disubstituted compounds, although a slightly lower figure might be more correct. As these arise only in calculating the inductive effects in other substituents, however, the error arising from this cause cannot be very great.

TABLE 3. *Observed and calculated dipole moments of nitro-compounds.*

	μ (obs.) (D)	μ (calc.) (D)		Effective moment of *o*-nitro-group (D)
		(*a*) neglecting induction	(*b*) with allowance for induction	
4-Nitrodiphenyl	4·36	4·01	4·18	—
2 : 4-Dinitrodiphenyl	4·33	3·83	4·13	—
2 : 4 : 6-Trinitrodiphenyl	1·57 (1·41)	0·0	1·32	—
p-Nitrotoluene	4·44 [4]	4·38	4·42	—
o-Nitrotoluene	3·72 [4]	3·83	3·86	3·87
2 : 4 : 6-Trinitrotoluene	1·37 (1·19) [3]	0·37	0·75	3·33
Nitromesitylene	3·67 [3]	4·01	4·10	3·58
p-*tert.*-Butylnitrobenzene	4·64 [12]	4·54	4·65	—
1-*tert.*-Butyl-2 : 4-dinitrobenzene	4·53	4·09	4·70	3·54
p-Chloronitrobenzene	2·57	2·43	2·45	—
o-Chloronitrobenzene	4·36 [4]	4·99	4·86	3·57
1-Chloro-2 : 4-dinitrobenzene	3·32	3·33	3·39	3·65
2-Chloro-1 : 3 : 5-trinitrobenzene	1·13 (0·90) [3]	1·53	1·42	3·30
2 : 4-Dichloro-1-nitrobenzene	2·66 [13]	3·51	3·38	3·62
2 : 5-Dichloro-1-nitrobenzene	3·48 [3]	4·01	3·99	3·50
1 : 3-Dichloro-5-nitrobenzene	2·66 [13]	2·52	2·54	—
p-Bromonitrobenzene	2·65	2·45	2·49	—
o-Bromonitrobenzene	4·23 [4]	4·97	4·86	3·47
1-Bromo-2 : 4-dinitrobenzene	3·39	3·34	3·46	3·63
1 : 3 : 5-Tribromo-2-nitrobenzene	3·14 (3·12)	4·01	3·81	3·31
1 : 3 : 5-Tribromo-2 : 4-dinitrobenzene	3·12 (3·10)	3·83	3·79	3·31

In addition to the compounds the dipole moments of which have been determined in the present work, Table 3 includes a number of related compounds for which comparable data are available. Where necessary the original experimental results have been reassessed, using modern methods of extrapolation of the data and modern values of the universal constants.

On the simple vector addition theory the dipole moment of 2 : 4 : 6-trinitrodiphenyl

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[12] Le Fèvre, Le Fèvre, and Robertson, *J.*, 1935, 480.

[13] Thomson, *J.*, 1944, 404.

should be zero. The greatest contribution to the substantial moment which is observed must come from the inductive effect, and hence it is satisfactory that, in spite of the somewhat arbitrary assumptions which have to be made, especially regarding the dielectric constant of the intervening medium between the polarisable groups and the polar groups, and the locations of the dipoles, the calculated moment is relatively near to the observed value, the difference being actually less than for 4-nitrodiphenyl. The moments of *p*-nitrotoluene and *p-tert.*-butylnitrobenzene are within experimental error of the calculated values, but those of *p*-chloro- and *p*-bromo-nitrobenzene exceed the calculated values by 0·12 and 0·16 D, respectively. Such differences have usually been ascribed to the mutual enhancement of the mesomeric effects of *op*- and *m*-directing groups when they occupy positions *para* to one another. It is significant, however, that the dipole moment of 1 : 3-dichloro-5-nitrobenzene also exceeds the calculated value by 0·12 D, although in this compound the mesomeric effects of the nitro-group and of the chlorine atoms cannot mutually enhance one another. It seems possible, therefore, that the increase in the moments of these compounds over the calculated values may be due rather to the withdrawal of electron density from the ring through the strong inductive and mesomeric effects of the nitro-group. This will cause the displacement of the ring electrons by the inductive effects of the halogen atoms to be much less than in the halogenobenzenes, so that the effective " group " moments of the chlorine and bromine atoms are reduced to about 1·46 and 1·40 D, respectively. In support of this argument it may be added that, in spite of the fact that the mesomeric effect of the fluorine atom is greater than that of other halogen atoms, the observed moment of *p*-fluoronitrobenzene [14] (2·64 D) is only 0·11 D in excess of the calculated value.

So far as the other compounds listed in Table 3 are concerned, however, there is another factor which must come into play. The mesomeric contribution to the dipole moment of nitrobenzene depends upon the overlap of the π-orbitals of the nitro-group with the π-orbitals of the benzene ring. This in turn demands that the three atoms of the nitro-group can come into or near to the plane of the ring. When such coplanarity is inhibited through steric causes, as in nitromesitylene and nitrodurene,[15] the overlap is decreased and hence the effective moment of the nitro-group is reduced. In the limit, if such overlap were prevented completely, the moment of the nitro-group would be expected to be reduced to the value which it has in saturated aliphatic compounds, *i.e.*, about 3·25 D. Some such restriction must be expected in all compounds which contain a nitro-group in a position *ortho* to other substituents. The observed moments of the various nitro-compounds have therefore been used in calculating the values of the group moments of the nitro-groups in positions *ortho* to other substituents. In these calculations it has been assumed that any other nitro-groups present in the molecule retain an effective value of 3·83 D, as in *m*-dinitrobenzene, and that the effective group moments of chlorine and bromine are 1·46 and 1·40 D, respectively. The values so deduced are shown in the last column of Table 3.

In spite of the evidence obtained by Bastiansen and Hassel [16] from electron-diffraction measurements that the C–Cl bonds in such compounds as *o*-dichlorobenzene and hexachlorobenzene are deflected at least 12° out of the plane of the ring, dielectric polarisation evidence is against such a state of affairs for 1 : 3 : 5-trihalogeno-2 : 4 : 6-trinitrobenzene and the trihalogeno- and trinitro-mesitylenes. Tiganik's values [4] for the $P_{2\infty} - [R_D]_2$ differences for *sym*-trichloro-, -tribromo-, and -trinitro-benzene and mesitylene are 2·1, 2·1, 10·7, and 0·5 c.c., respectively. These are of the order to be expected for the atom polarisations of molecules with balanced dipoles of the magnitudes present in the respective compounds. For 1 : 3 : 5-trichloro- and 1 : 3 : 5-tribromo-2 : 4 : 6-trinitrobenzene, however, the corresponding differences are only 9·0 and 9·5 c.c., respectively. As would be

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[14] Leonard and Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1565.

[15] Kofod, Sutton, de Jong, Verkade, and Wepster, *Rec. Trav. chim.*, 1952, **71**, 521.

[16] Bastiansen and Hassel, *Acta Chem. Scand.*, 1947, **1**, 489.

expected if the in-plane vibrations are more restricted than in the *sym*-trisubstituted benzenes, these values are appreciably less than the sums of the differences for the parent compounds. If the C–halogen and C–N bonds were each deflected 12° alternately on each side of the plane of the ring, as visualised by Bastiansen and Hassel for hexachlorobenzene, the trihalogenotrinitrobenzenes should have dipole moments of the order of 1·5 D, corresponding with an orientation polarisation at 20° of about 47 c.c. In these compounds there is a chance that the relative deflections of the chlorine and nitrogen atoms may be such that all moment contributions cancel out, but such could not be the case for mesitylene derivatives. The $P_{2\infty} - [R_D]_2$ differences for trichloro-, tribromo-, and trinitro-mesitylene are 3·2, 2·8, and 13·6 c.c., respectively. These values are very little greater than the sums of the corresponding differences for the parent compounds, whereas if the groups were deflected 12° out of the plane of the ring, so that all three methyl groups were on one side and the other substituents on the opposite side, orientation polarisations of 31 c.c. for the trihalogenomesitylenes and 140 c.c. for trinitromesitylene would be expected. Even if the molecules were distributed between various structures with out-of-plane deflections of the groups such that adjacent groups are not always on opposite sides of the plane of the ring, the mean orientation polarisation would still be expected to be quite appreciable. The evidence suggests, therefore, that when nitro-groups and halogen atoms or methyl groups alternate round the ring the out-of-plane deflection of the C–N and C–X bonds can only be very slight. Similar conclusions were reached by Kofod, Kumar, and Sutton [17] with regard to the groups in trichloromesitylene. It seems most logical to assume, therefore, that in all the compounds discussed here any bond deflection occurs in the plane of the ring and not at right angles to it.

An in-plane deflection of the groups in positions *ortho* to one another will modify the dipole moment of the molecule, and hence will lead to errors in the calculated value of the moment of the nitro-group. The sense of the error, however, depends on the nature of the substituents, and hence each compound must be considered separately. Thus an increase in the angle between the C–N and C–Me bond axes in *o*-nitrotoluene above the value of 60° assumed in deriving the calculated moments given in Table 3 would increase the dipole moment of the molecule: hence the figure of 3·87 D derived for the effective moment of the nitro-group is a maximum value. For *o*-chloro- and *o*-bromo-nitrobenzene, on the other hand, an increase in the angle between the axes of the C–N and C–halogen bonds would decrease the dipole moment of the molecule, so the calculated values of the nitro-group moment (3·57 and 3·47 D, respectively) are minimum figures. Amonst the trisubstituted benzenes studied, in-plane deflection of the groups *ortho* to one another would decrease the dipole moments of 2 : 4- and 2 : 5-dichloro-1-nitrobenzene, so the calculculated nitro-group moments (3·62 and 3·50 D, respectively) are minimum values. Similar deflection, however, would have only a slight effect on the moments of 2 : 4-dinitro-1-halogenobenzenes, so the moments of the *o*-nitro-groups in these molecules are probably very near to the calculated values (3·65 and 3·63 D, respectively). For 1-*tert.*-butyl-2 : 4-dinitrobenzene a deflection would increase the dipole moment, and the calculated group moment must be interpreted as a maximum value.

Comparison of the figures for the various compounds studied suggests, therefore, that the effective moment of a nitro-group with one substituent in a position *ortho* to it varies with the nature of this group; for Bu^t, Br, Cl, and Me it is about 3·5, 3·63, 3·65, and 3·8 D, respectively. On this evidence the steric effects of these groups upon the mesomerism of the nitro-group follow the expected order, but, excepting perhaps for the *tert.*-butyl group, one *ortho*-group is insufficient to reduce the effective moment of a nitro-group to the value it shows in a saturated aliphatic compound.

In the 2 : 4 : 6-trisubstituted nitrobenzenes the nitro-group will not undergo in-plane displacement, so it is to be expected that the C–Me bonds in nitromesitylene, for instance, may undergo greater deflection than the C–Me bond in *o*-nitrotoluene, but the angle

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[17] Kofod, Kumar, and Sutton, *J.*, 1951, 1790.

between the C–N and C–Me bond axes will be less than in the latter compound. Hence the steric obstruction to coplanarity of the nitro-group with the ring may be expected to be greater in trisubstituted nitrobenzenes than in *o*-monosubstituted nitrobenzene. Similar conditions should prevail in the *sym*-trinitro-compounds, where only the nitro-groups *ortho* to the other substituent can undergo permanent in-plane deflection. Again the angle between the C–N and C–X bond axes will be less than in the corresponding *o*-nitro-compound, and since it seems probable that a nitro-group may tend to suffer less in-plane deflection than other groups, the steric obstruction to mesomerism of the *o*-nitro-groups in 2 : 4 : 6-trinitrotoluene would be expected to be greater than in nitromesitylene.

These conclusions are supported by the calculated values of the effective moments of the *o*-nitro-groups in these compounds. A small increase in the angle between the C–Me and C–N bond axes will increase the moment of nitromesitylene very slightly but that of 2 : 4 : 6-trinitrotoluene much more, so, bearing in mind the directions of the dipoles in the two compounds, it can be inferred that the calculated nitro-group moments (3·58 and 3·33 D) are maximum and minimum values, respectively, although the value for nitromesitylene is probably nearly correct. By analogous arguments the group moments calculated from the dipole moments of 2-chloro-1 : 3 : 5-trinitrobenzene, 1 : 3 : 5-tribromo-2-nitrobenzene, and 1 : 3 : 5-tribromo-2 : 4-dinitrobenzene, 3·30, 3·31, and 3·31 D respectively, are all minimum values. The fact that they are almost equal could be accounted for by assuming that the angle of deflection of the C–N bonds in the trinitro-compound is about two-fifths of the deflection of the C–Br bonds in the tribromo-compounds, but it seems most likely that the effective moments of the *o*-nitro-groups in these compounds are not much more than 3·30 D, which is little above the nitro-group moment in a saturated aliphatic compound (about 3·25 D). Further, since it is improbable that the deflection of the C–N bonds in 2 : 4 : 6-trinitrotoluene is greater than in 1-bromo-2 : 4 : 6-trinitrobenzene, the effective moments of the *o*-nitro-groups in 2 : 4 : 6-trinitrotoluene must be lower than that of the nitro-group in nitromesitylene, as is to be expected if the mesomeric effect of the nitro-groups is more restricted sterically in the former than in the latter.

The evidence suggests, therefore, that in 2-chloro-1 : 3 : 5-trinitrobenzene, 1 : 3 : 5-tribromo-2-nitrobenzene, and 1 : 3 : 5-tribromo-2 : 4-dinitrobenzene the mesomeric effects of the nitro-groups *ortho* to a halogen atom are almost wholly suppressed. The effect may be less fully suppressed, however, in 2 : 4 : 6-trinitrotoluene, and is only partially suppressed in nitromesitylene. As for the trisubstituted nitrobenzenes, halogen atoms in positions *ortho* to the nitro-group are more effective in inhibiting its mesomeric effect than are methyl groups, but in each case the influence of the substituent group is more pronounced in the trinitro-compounds than in trisubstituted nitrobenzenes. This is attributable to a " buttressing " action, resulting in a reduced in-plane deflection of groups which have other groups in the two positions *ortho* to them. In this connection it may be pertinent that, although the dipole moment of nitrodurene might be expected to be equal to or, if inductive effects are taken into account, slightly greater than, that of nitromesitylene, the experimental value [15] (3·62 D) seems to be significantly lower. This may be attributable to a decreased deflection of the methyl groups *ortho* to the nitro-group, and the consequent decrease in the mesomeric effect of the latter, through the presence of the methyl groups in the *meta*-positions.

EXPERIMENTAL

Materials.—Benzene was purified, dried as previously described,[1] and redistilled under anhydrous conditions immediately before use.

Commercial samples of pure *m*-dinitrobenzene, *p*-chloronitrobenzene, *p*-bromonitrobenzene, 1-chloro-2 : 4-dinitrobenzene, and 1-bromo-2 : 4-dinitrobenzene were recrystallised from alcohol and had m. p. 91°, 83°, 127°, 51°, and 75°, respectively. 2 : 4-Dinitrodiphenyl and 2 : 4 : 6-trinitrodiphenyl, prepared by Ullmann's method [18] from iodobenzene and 1-chloro-2 : 4-dinitrobenzene or 2-chloro-1 : 3 : 5-trinitrobenzene, and recrystallised from alcohol and light petroleum,

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[18] Gull and Turner, *J.*, 1929, 496.

respectively, had m. p. 111° and 131°, respectively. 1 : 3 : 5-Tribromo-2-nitrobenzene was prepared by Loudon's method [19] from 1 : 3 : 5-tribromobenzene, and crystallised repeatedly from chloroform : it had m. p. 125°. 1 : 3 : 5-Tribromo-2 : 4-dinitrobenzene and 1-*tert.*-butyl-2 : 4-dinitrobenzene, kindly lent by Professor E. E. Turner and Dr. M. S. Lesslie, respectively, were recrystallised from alcohol and had m. p. 192° and 62°, respectively.

Methods.—Dielectric constants, specific volumes, and refractive indices were measured at 25° by the method used previously, excepting that the dielectric constant of pure benzene was assumed to be 2·2741.[20] The results are shown in Table 4. The $P_{2\infty}$ and $[R_D]_2$ values were derived both from the parameters α, β, and γ and from the specific polarisations of the individual solutions, the results for the two methods being in satisfactory agreement.

TABLE 4. *Polarisation data for benzene solutions at 25°*

100w	ε	v	n_D
	m-*Dinitrobenzene*		
0·0000	2·2741	1·14462	1·4980
1·1541	2·3851	1·13921	1·4985
1·6037	2·4291	1·13711	1·4987
2·2839	2·4956	1·13396	1·4990
2·6689	2·5337	1·13213	1·4992
3·1343	2·5793	1·12996	1·4994
4·1034	2·6761	1·12542	1·4998
	2 : 4-*Dinitrodiphenyl*		
0·0000	2·2741	1·14462	1·4890
0·4234	2·3104	1·14280	1·4983
0·8419	2·3469	1·14103	1·4987
1·2726	2·3846	1·13922	1·4991
1·6832	2·4208	1·13746	1·4994
2·0686	2·4550	1·13581	1·4998
2·4544	2·4890	1·13418	1·5001
	2 : 4 : 6-*Trinitrodiphenyl*		
0·0000	2·2741	1·14462	1·4980
0·7696	2·2832	1·14094	1·4986
1·3026	2·2896	1·13830	1·4992
1·8233	2·2957	1·13582	1·4996
2·1980	2·3000	1·13399	1·5000
2·7388	2·3064	1·13138	1·5004
2·9797	2·3092	1·13025	1·5007
	p-*Chloronitrobenzene*		
0·0000	2·2741	1·14460	1·4980
0·5268	2·2992	1·14239	1·4982
1·1977	2·3315	1·13958	1·4984
2·1048	2·3754	1·13578	1·4989
2·8501	2·4129	1·13266	1·4993
3·6325	2·4507	1·12931	1·4996
4·5610	2·4970	1·12539	1·5001
5·2193	2·5301	1·12279	1·5005
	p-*Bromonitrobenzene*		
0·0000	2·2741	1·14460	1·4980
0·6691	2·3013	1·14081	1·4984
1·7010	2·3434	1·13497	1·4990
2·7694	2·3876	1·12891	1·4996
3·7271	2·4275	1·12350	1·5002
4·8622	2·4751	1·11709	1·5009
5·8573	2·5214	1·11102	1·5016
	1-*Chloro*-2 : 4-*dinitrobenzene*		
0·0000	2·2741	1·14462	1·4980
1·2290	2·3494	1·13823	1·4988
1·7889	2·3839	1·13531	1·4990
2·3200	2·4173	1·13256	1·4993
2·6489	2·4381	1·13089	1·4994
3·5601	2·4954	1·12610	1·5000
4·4756	2·5546	1·12135	1·5005
	1-*Bromo*-2 : 4-*dinitrobenzene*		
0·0000	2·2741	1·14460	1·4980
1·5173	2·3541	1·13562	1·4988
2·7904	2·4232	1·12715	1·4995
3·4429	2·4590	1·12313	1·4999
4·1361	2·4974	1·11872	1·5005
5·6251	2·5811	1·10949	1·5012
	1 : 3 : 5-*Tribromo-2-nitrobenzene*		
0·0000	2·2741	1·14463	1·4980
1·0851	2·3082	1·13674	1·4985
1·7179	2·3286	1·13206	1·4989
2·1283	2·3418	1·12922	1·4991
2·7229	2·3611	1·12473	1·4994
3·4192	2·3842	1·11969	1·4998
3·6486	2·3916	1·11800	1·4999
	1 : 3 : 5-*Tribromo*-2 : 4-*dinitrobenzene*		
0·0000	2·2741	1·14460	1·4980
1·3596	2·3119	1·13448	1·4987
1·9237	2·3265	1·13033	1·4989
2·9748	2·3586	1·12254	1·4995
5·4337	2·4307	1·10434	1·5008
7·5147	2·4956	1·08881	1·5019
8·5021	2·5264	1·08162	1·5024
	1-tert.-*Butyl*-2 : 4-*dinitrobenzene*		
0·0000	2·2741	1·14458	1·4979
0·7682	2·3516	1·14206	1·4981
1·5262	2·4284	1·13944	1·4983
2·4297	2·5217	1·13641	1·4985
3·1200	2·5935	1·13418	1·4987
4·2742	2·7150	1·13022	1·4991

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BEDFORD COLLEGE, REGENT'S PARK, LONDON, N.W.1.

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