

## A NEW INTERPRETATION OF DIPOLE MOMENTS OF ALIPHATIC AND AROMATIC NITRO COMPOUNDS\* \*\*

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The concept of mesomeric dipole moments has been revised both experimentally and theoretically on the example of nitro compounds. While the dipole moments of aliphatic nitro compounds increase steadily with the size of the hydrocarbon residue (up to 3.55 D for 1-nitroadamantane), those of 2,4,6-trisubstituted benzenes decrease with the size (polarizability) of the substituent (up to 3.40 D for 2,4,6-triphenylnitrobenzene). Hence, neither the difference between nitrobenzene and an aliphatic derivative, nor between nitrobenzene and 2,4,6-trimethylnitrobenzene can be taken as a quantitative measure of the mesomeric interaction between the nitro group and the aromatic nucleus. Simple calculation of induced dipole moments, however, without using the simplification of the point dipole accords with the experimental results in a semi-quantitative manner. It follows that the mesomeric effect of the nitro group must be very small and it is not manifested clearly in the dipole moment values.

Sutton's concept of mesomeric dipole moments<sup>1,2</sup> is based on comparison of similar conjugated and non-conjugated molecules. The simple algebraic difference or, if appropriate, the vector difference of the corresponding dipole moments is considered to be the quantitative measure of the mesomeric effect and is explained in terms of mesomeric formulae. Thus the results together with this interpretation have represented an important support of the theory of resonance or mesomerism. The proper experimental background consists in the following facts:

1. Dipole moments of unsaturated or aromatic monofunctional derivatives differ from those of corresponding saturated aliphatic derivatives<sup>2</sup>; with donor substituents they are lower, *e.g.* chlorobenzene (*I*) as compared with alkyl chlorides, with acceptor substituents higher, *e.g.* nitrobenzene (*II*) as compared with nitro alkanes. By prolonging the conjugated system the effect increases<sup>3-5</sup>.

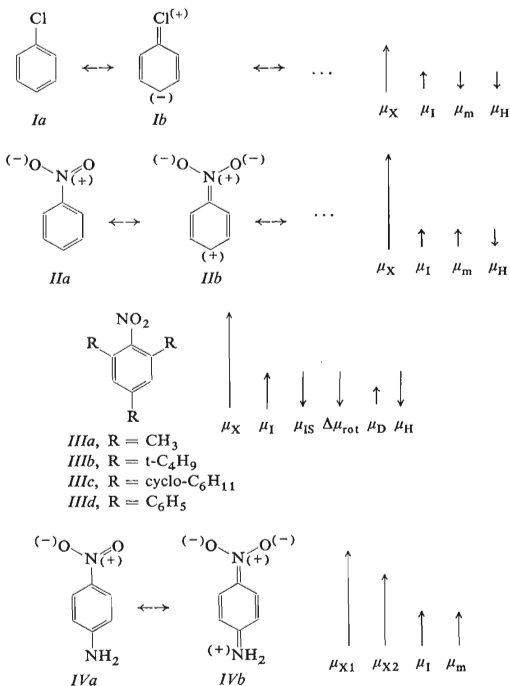
2. Moments of aromatic nitro compounds are reduced by steric hindrance which twists the nitro group out of the ring plane; *e.g.* the moments of 2,4,6-trimethylnitro-

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benzene and 2,3,5,6-tetramethylnitrobenzene are lower than that of nitrobenzene<sup>6,7</sup> although the contributions of the methyl groups should cancel.

3. Dipole moments of conjugated bisderivatives with one donor and one acceptor group (e.g. 4-nitro-N,N-dimethylaniline) exceed the sum obtained from the two pertinent monoderivatives<sup>2,3,5</sup>. They are reduced by the steric hindrance<sup>8,9</sup> as ad 2.



All these facts are commonly explained by the mesomeric electron displacement, as visualized e.g. by the formulae **Ib** and **IIb**. The mesomeric dipole moments have been obtained as the difference between the benzene derivative on the one hand, and either an aliphatic reference compound or a sterically hindered derivative **III** on the other hand. The calculated values<sup>1,10</sup> conform approximately to other quantities expressing the mesomeric effect and have been included with this interpretation

into many textbooks<sup>10,11</sup>. However, the gross difference between an aromatic and an aliphatic compound can include at least two additional components<sup>3,8</sup>. The hybridisation moment due to different state of the  $C_{(1)}$  atom, and the moment induced in the highly polarizable  $\pi$ -electron system. To account for the latter, Sutton proposed tert-butyl compounds as the aliphatic standard<sup>1</sup> although the polarizabilities of the tert-butyl and phenyl groups are certainly not exactly equal. All the components are schematically pictured at the formulae *I–IV*. The induced moment ( $\mu_i$ ) is always of the same direction as the intrinsic moment of the functional group ( $\mu_x$ ) while the hybridisation moment ( $\mu_H$ ) is opposite; the direction of the mesomeric moment ( $\mu_m$ ) varies with the character of the functional group. Considering mainly the hybridisation moment as the possible complication, Staab infers<sup>11</sup> that the existence of a mesomeric moment is more safely experimentally proved in the case of acceptor (*II*) than of donor (*I*) groups. In our opinion, however, the hybridisation moment may not be important since in the experimental values only the difference of the bond moments  $C_{sp^2}-X$  and  $C_{sp^2}-H$ , or  $C_{sp^3}-X$  and  $C_{sp^3}-H$ , respectively, are reflected, so that the effect of carbon hybridisation must largely cancel. It is merely the induced moment which has been underestimated in the case of acceptor groups. For similar reasons, Kofod and coworkers<sup>7</sup> prefer the difference between the compound *IIIa* and *II* to estimate the pure contribution of the mesomeric moment of the nitro group.

Our doubts about the above interpretation originated in arguments from quite remote areas, indicating that the mesomeric effect of acceptor groups should be much weaker than that of donor groups. Particularly the dissociation constants of substituted benzoic acids revealed<sup>12</sup> that conjugation of nitro, cyano, and sulphonyl groups with the benzene nucleus alone is negligible as far as a donor group is not present in the *para* or *ortho* position. The same result has been obtained recently from ESCA chemical shifts of the nitro group<sup>13</sup>. Trotter pointed out that the C—N bond in nitrobenzene<sup>14</sup> is not appreciably shortened when compared to nitromethane or to 2,4,6-trimethylnitrobenzene<sup>15</sup>. Neither is any conjugation in nitromethane anion.<sup>16</sup> We explained<sup>12</sup> the diverse behaviour of donor and acceptor groups in terms of the Mulliken's theory<sup>17</sup> which predicts that the "isovalent" conjugation  $Ia \leftrightarrow Ib$ , or,  $IVa \leftrightarrow IVb$ , characterized by the same number of  $\pi$ -bonds in the two limiting formulae, is much more significant than the "sacrificial" conjugation  $Ila \leftrightarrow I Ib$  (one bond less in *I Ib*).

The intention of the present study is to reveal the difference between donor and acceptor groups even in the field of dipole moments. We have centered our attention to the nitro group which is sensitive to steric hindrance of conjugation and to which most of the arguments have been applied. An experimental and a theoretical approach has been used. Experimentally we have reinvestigated the dipole moments of one series of aliphatic nitro compounds with different size of the hydrocarbon residue, and one series of sterically hindered nitrobenzene derivatives *III* with different groups R. Although many of these compounds have been already studied<sup>18–22</sup> we have felt that measurements under the same conditions are necessary for a more detailed comparison. In a theoretical approach we have tried to compute very approximately the induced moments, particularly in the sterically hindered derivatives *III*.

The experimental results are listed in Table I. Considering the estimated error of 0.05 D (in addition to the uncertainty arising from the atomic polarization) the agreement with previous results is very good in most cases. Nevertheless one discrepancy<sup>21</sup> points out the danger in comparing dipole moments from different laboratories. The moments of aliphatic nitro compounds increase steadily with the size of the hydrocarbon rest up to 1-nitroadamantane, giving thus no possibility to settle any standard value.

The moment of nitrobenzene, appreciably higher, is reduced in 2,4,6-trimethylnitrobenzene to a value comparable to aliphatic derivatives, but it is reduced still further in derivatives with larger and more polarizable groups, reaching finally for 2,4,6-triphenylnitrobenzene (*III d*) the value 3.40 D, *i.e.* lower than for 1-nitroadamantane. These facts are not explicable in terms of mesomerism and its steric inhibition: Assuming that the twisting angle  $\varphi$  in 2,4,6-trimethylnitrobenzene<sup>15</sup> is 66.4° and that the degree of conjugation is proportional to  $\cos^2 \varphi$ , the conjugation should be reduced to some 16%. This corresponds to the dipole moment difference of 0.32 D between *II* and *III a*. Any bulkier *ortho* substituents, twisting the nitro group almost by 90°, should not produce a further reduction of the dipole moment by more than 0.06 D. Experimentally the effects up to 0.25 D are found. Neither can any hindrance of mesomerism explain why the dipole moment of a crowded aromatic derivative is less than of an aliphatic one.

TABLE I  
Experimental Dipole Moments of Nitro Compounds (benzene, 25°C)

Compound	$\mu$ (0%) <sup>a</sup>	$\mu$ (10%) <sup>a</sup>	Literature values (ref.)
Nitromethane	3.17	3.16	3.13 <sup>b</sup> (18)
Nitroethane	3.22	3.21	3.22 (19)
1-Nitropropane	3.29	3.27	—
2-Nitropropane	3.33	3.31	—
2-Nitro-2-methylpropane	3.44	3.42	—
Nitrocyclohexane	3.55	3.53	3.6 (20)
1-Nitroadamantane	3.58	3.55	3.82 (21)
Nitrobenzene ( <i>II</i> )	3.99	3.97	3.93 <sup>b</sup> (18)
2,4,6-Trimethylnitrobenzene <i>III a</i>	3.68	3.65	3.70 (6,7)
2,4,6-Triisopropylnitrobenzene	—	—	3.59 (22)
2,4,6-Tri-tert-butylnitrobenzene <i>III b</i>	3.51	3.45	3.48 (22)
2,4,6-Tricyclohexylnitrobenzene <i>III c</i>	3.53	3.46	—
2,4,6-Triphenylnitrobenzene <i>III d</i>	3.48	3.40	—

<sup>a</sup> Average values from several determinations, see Table III. Correction for the atomic polarization 0% or 10% of the molar refraction, respectively. <sup>b</sup> Average values from several sources.

We conclude that neither the difference between nitrobenzene and any aliphatic nitro compound, nor between nitrobenzene and 2,4,6-trimethylnitrobenzene can be taken as a measure of the mesomeric interaction. On the other hand the whole pattern in Table I is compatible with the explanation by induction. In order to support this hypothesis semi-quantitatively, we have made a simple calculation of the induced moments in the framework of classical electrostatics<sup>23</sup>. The calculations were based on actual molecular geometry whenever available<sup>15,24</sup> and on Le Fèvre's group polarizabilities<sup>25</sup>; they differed from most previous attempts<sup>8,26</sup> mainly by the fact that the point dipole approximation has not been used. In fact this approximation, neglecting the dipole length in comparison with its distance, is far from realistic in molecular dimensions, particularly for the non-linear nitro group, and in addition is completely unnecessary. Hence, we preferred to represent the nitro group as a system of three charges on the two oxygen and one nitrogen atoms. The main inaccuracy inherent in the whole model is thus the symbolic representation of the polarized group ( $\text{CH}_3$ ,  $t\text{-C}_4\text{H}_9$ ,  $\text{C}_6\text{H}_5$ ) by one point.

The calculation proceeds as follows: The unknown intrinsic dipole moment of the  $\text{NO}_2$  group is designated by  $\mu_X$  and the charges on O and N atoms are calculated from the known geometry and expressed as functions of  $\mu_X$ . The moments induced in the methyl group of nitromethane are calculated separately for each charge and vectorially added. The resulting  $\mu_1$  is added to  $\mu_X$  and the sum compared with the experimental moment of nitromethane; from the comparison the value of  $\mu_X = 2.8$  D has been obtained and the charges on individual atoms computed. With these values the dipole moment of nitrobenzene may now be calculated by the same procedure yielding 3.88 D. In all calculations the macroscopic dielectric constant of benzene was introduced, which is essentially identical with the microscopic constant of the solute molecule.

TABLE II

Changes of the Nitrobenzene Dipole Moment Due to 2,4,6- $\text{R}_3$  Substitution

Source of $\Delta\mu$	$\text{R} = \text{CH}_3$	$\text{R} = t\text{-C}_4\text{H}_9$	$\text{R} = \text{C}_6\text{H}_5$	2,4,6- $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CN}^a$
Valence deflection	+0.02	+0.02	0	0
Moments induced in the <i>ortho</i> substituents	-0.22	-0.33	-0.42	+0.03
Moment induced in the <i>para</i> substituent	+0.00 <sub>2</sub>	+0.01	+0.01	+0.00 <sub>2</sub>
Anisotropic polarizability of the benzene ring	-0.08	-0.10	-0.05	0
Total	-0.28	-0.40	-0.46	+0.03
Experimental difference	-0.32	-0.52	-0.57	+0.16 <sup>b</sup>

<sup>a</sup> Related to benzonitrile; <sup>b</sup> ref.<sup>27</sup>.

Although the agreement with the experimental value of nitrobenzene is only fair, the moments of 2,4,6-substituted nitrobenzenes were also calculated with  $\mu_X = 2.8$  D; the results are expressed as differences against nitrobenzene (Table II) which are insensitive to the value of  $\mu_X$ . The moments induced in the central benzene ring were computed taking into account its anisotropic polarizability and the real or estimated molecular geometry (the twisting angle  $\varphi = 66.4^\circ$  or  $90^\circ$  in the case of *IIIa* or *IIIb*, respectively). In addition, the moments induced in the *ortho* and *para* substituents ( $\mu_{IS}$ ) were calculated separately (Fig. 1). In the case of 2,4,6-triphenylnitrobenzene the propeller-like conformation was adopted with twisting angles of  $45^\circ$  for both the nitro group and the phenyls.\* Finally, the term originating in distortion of the substituents valence angles<sup>14</sup> from  $120^\circ$  ( $\mu_D$ ) was evaluated.

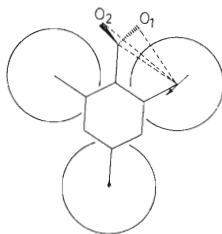


FIG. 1

Schematic Representation of the Moments Induced by the Nitro Group in the *ortho* Substituent

Calculation of the dipole moment only on the basis of induction leads thus to a somewhat low value for nitrobenzene. However, with the many assumptions and at the best semi-quantitative character of the whole procedure it is hardly to decide whether the residual value of 0.09 D may be in fact attributed to the mesomeric interaction. It is only sure that this interaction is much weaker than formerly anticipated, if it is at all manifested appreciably in the dipole moment values. On the other hand, the calculations of induced moments could be easily adjusted to account for the whole observed effect, but with respect to their inherently approximate character we do not feel this to be of much value.

The results for 2,4,6-trisubstituted nitrobenzenes are more definite, showing that the concept of steric inhibition of resonance is unnecessary to account for the experimental results. The most important effect is the induction in the *ortho* substituents ( $\mu_{IS}$ ), somewhat less important is the twisting of the nitro group connected

\* This model is supported by the symmetric  $\text{NO}_2$  frequency of *IIIId* ( $1349\text{ cm}^{-1}$  in chloroform), revealing less steric hindrance than in *IIIa-IIIc* ( $1367$ ,  $1372$ , and  $1377\text{ cm}^{-1}$ , respectively). Assuming the torsion angles of  $90^\circ$ , the agreement with experiment is worse.

with the lower polarizability of the benzene nucleus in the perpendicular direction ( $\mu_{\text{rot}}$ ). Neither of these effect has been hitherto taken into consideration, although they are easily understandable and characteristic for the nitro group. *E.g.* with similar cyano derivatives there is of course no twisting and the induction in the *ortho* groups is not only much smaller but even of the opposite direction (see the last column of Table II). Hence even the difference between nitro and cyano compounds can be qualitatively explained without applying the concept of resonance. The remaining factors seem to be unimportant. The valence deflection ( $\mu_{\text{D}}$ ) was considered by Trotter as an alternative explanation accounting at least for the part of the observed effect<sup>14</sup>. Table II reveals that it is negligible and in addition of the wrong direction. Of course, this effect may become important in derivatives of the type III with the alkyls replaced by halogens<sup>26-28</sup>; a more detailed analysis is, however, difficult in these cases since even the reversed induction (*i.e.* of the nitro group by halogen) comes into consideration.

Our statement, considering the little importance of mesomerism in aromatic nitro compounds, may be supported from two sides, either by another experimental approach or on other functional groups. Most relevant are the lengths of C—N bond, confirming Trotter's conclusion<sup>14</sup> by recent results<sup>24,29,30</sup>. In aromatic sterically hindered or non-hindered derivatives the lengths are between 1.466 and 1.486 Å (compare nitromethane 1.470 Å) and do not depend on the twisting angle; in actually conjugated compounds 4-nitrophenol and 4-nitro-N,N-dimethylaniline they are 1.450 and 1.405 Å, respectively. From other acceptor substituents the trifluoromethyl group was particularly studied and possible conjugation was refused<sup>31,32</sup>. In this case there is even no conjugation with the *para* standing amino group, since 3,5-bis-(trifluoromethyl)aniline has an equal dipole moment as 4-trifluoromethylaniline<sup>32</sup>. Dipole moments of aliphatic nitriles and benzonitrile<sup>21,33</sup> are parallel to those of corresponding nitro compounds and seem to be likewise controlled by induction. We believe that the mesomeric dipole moments<sup>2</sup> of all acceptor groups are actually artifacts representing approximately a fraction of their group moments. The rough correlations of these mesomeric moments with other quantities expressing the mesomeric effect, *e.g.* with the  $\sigma_{\text{R}}^+$ ,  $\sigma_{\text{R}}^-$  constants<sup>34</sup>, come into existence due to regular behaviour of the donor groups, the acceptors playing an inferior role in the overall pattern.

We conclude that there is certainly a quantitative, or even qualitative difference between donors and acceptors as to their ability to conjugate with the aromatic nucleus or with similar systems. The mesomeric effect of the acceptor groups has been commonly overestimated; the main problem is that their small, or negligible M-effect is combined with a strong I-effect. In fact the mesomerism is not manifested clearly in the dipole moment values of monofunctional aromatic derivatives and one cannot decide whether it exists at all. This statement is in accord with many observations from various areas<sup>12-17,31-32</sup>. The most important contradictory finding

TABLE III  
Polarization Data of Nitro Compounds (benzene, 25°C)

Compound	$\alpha$	$\beta$	$P_2$	$R_D$	$P_0$	$\mu^a$
Nitromethane	17.63	-0.348	216.9	12.37	204.5	3.16
	17.92	-0.342	220.3	12.37	208.0	3.18
Nitroethane	15.07	-0.281	232.1	17.01	215.1	3.24
	14.82	-0.289	228.4	17.01	211.4	3.21
1-Nitropropane	13.12	-0.160	246.0	21.67	224.3	3.31
	12.82	-0.167	240.8	21.67	219.1	3.27
2-Nitropropane	13.42	-0.182	250.4	21.68	228.7	3.34
	13.49	-0.187	251.5	21.68	229.8	3.35
2-Nitro-2-methylpropane	12.10	-0.130	265.8	26.13	239.7	3.42
	12.31	-0.134	269.8	26.13	243.7	3.45
	12.32	-0.137	269.9	26.13	243.8	3.45
Nitrocyclohexane	10.42	-0.141	291.6	33.41	258.2	3.55
1-Nitroadamantane	7.45	-0.101	310.3	47.57	262.7	3.58
Nitrobenzene (II)	14.24	-0.326	359.7	32.07	327.7	4.00
	14.22	-0.318	359.6	32.07	327.5	4.00
	13.98	-0.335	353.4	32.07	321.3	3.96
2,4,6-Trimethylnitrobenzene (IIIa)	9.18	-0.219	330.7	49.03	281.7	3.71
	9.04	-0.223	326.4	49.03	277.4	3.68
	8.92	-0.218	322.6	49.03	273.6	3.65
2,4,6-Tri-tert-butylnitrobenzene (IIb)	4.65	-0.214	335.7	90.3	245.4	3.46
	4.87	-0.218	347.1	90.3	256.8	3.54
	4.85	-0.212	346.3	90.3	256.0	3.54
2,4,6-Tricyclohexylnitrobenzene (IIIc)	3.79	-0.201	367.3	112.18	255.1	3.52
	3.82	-0.206	368.9	112.18	256.8	3.54
2,4,6-Triphenylnitrobenzene (IIId)	3.90	-0.232	353.3	108.14	245.2	3.46
	3.95	-0.238	355.9	108.14	247.8	3.48
	4.00	-0.240	358.9	108.14	250.8	3.49

<sup>a</sup> Without correction for the atomic polarization.

concerns the resonance constants determined from the intensity of the  $\nu_{16}$  IR band of benzene monoderivatives<sup>35</sup>. Even here the effect of donors is much stronger than that of acceptors and the possible role of the inductive effect has not been investigated.

On the contrary there are no doubts about the importance of mesomeric moments in monoderivatives with donor substituents and in bisderivatives of the donor-acceptor type.\* These latter compounds are even sensitive to steric inhibition of resonance of the nitro group; e.g. the dipole moment of IV (6.25 D) is reduced<sup>9</sup> in 3,5-di-

\* We do not even exclude the possibility of a perceptible conjugation with larger hydrocarbon residue, e.g. in 4-nitrostilbene<sup>4</sup>.



methyl-4-nitroaniline to 5.04 D. This example should replace the often quoted 2,4,6-trimethylnitrobenzene in textbooks and other discussions. Hence, the general validity of the resonance theory should not be impaired by our arguments, only its range of application should be restricted. Most of the criticism of the resonance theory has been directed toward the representation of a single structure by two formulae. In our opinion it is merely a formal question; more important is the task to estimate the importance of individual mesomeric formulae in different cases and to distinguish, at least semi-quantitatively, the compounds with a strong and weak conjugation.

Finally, it should be mentioned that the so-called mesomeric moments are often used in approximate calculations of dipole moments by vector addition of bond moments (see *e.g.*<sup>36</sup>). These values are purely empirical in character and express simply the difference between an aromatic (or olefinic) and an aliphatic derivative. Their practical usefulness as an empirical correction is thus not impaired by a possible change in their interpretation.

## EXPERIMENTAL

*Materials.* Most of the compounds used were commercial products or prepared by known procedures. 1-Nitroadamantane<sup>37</sup>, m.p. 173–174°C (ref.<sup>37</sup> gives m.p. 173°C). 2,4,6-Tri-tert-butyl-nitrobenzene<sup>38</sup> m.p. 205–206°C (ref.<sup>38</sup> gives m.p. 204–206°C). 2,4,6-Tricyclohexylnitrobenzene was prepared by nitration of 1,3,5-tricyclohexylbenzene (3.3 g) dissolved in 3.5 ml of acetic acid and 2.7 ml of acetic anhydride with 0.8 g of fuming nitric acid ( $k = 1.5$ ) under the same conditions as described for the preceding compound<sup>38</sup>, yield 2.8 g (76%), m.p. 156°C. For  $C_{24}H_{35}NO_2$  (369.5) calculated: 78.00% C, 9.55% H, 3.79% N; found: 77.88% C, 9.43% H, 3.85% N. 2,4,6-Triphenylnitrobenzene<sup>39</sup>, m.p. 144–145°C (ref.<sup>39</sup> gives 145°C).

*Physical measurements.* Dielectric constants and densities of benzene solutions (five concentrations in the range  $2 \cdot 10^{-4}$ – $1 \cdot 10^{-3}$ M) were measured at 25°C, using a 1.5 MHz apparatus (modified bridge method) and Ostwald-Sprengel pycnometer, respectively. Results were evaluated according to Halverstadt and Kumler<sup>40</sup> (Table III).

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