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THE CONCEPT OF MESOMERIC DIPOLE MOMENTS

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The classical concept of mesomeric dipole moments represents one of the important experimental supports of the theories of resonance or mesomerism. It is essentially based on the following experimental facts[1]:

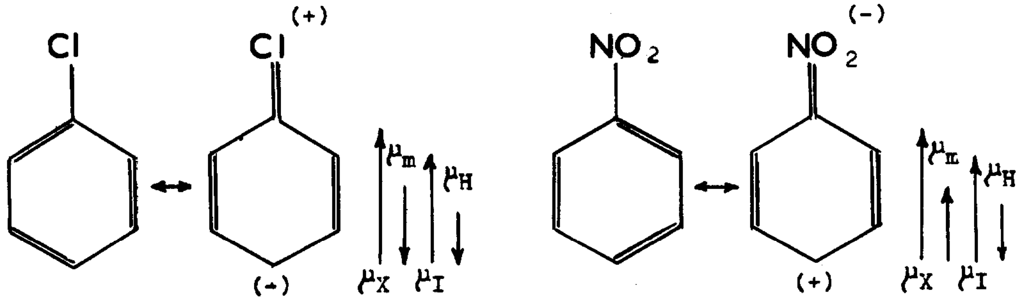
(i) Dipole moments of unsaturated compounds with a donor substituent (e.g. chlorobenzene I) are lower, with an acceptor group (e.g. nitrobenzene II) higher than those of corresponding saturated derivatives (methyl chloride and nitromethane, respectively). The difference increases with the length of the conjugated system.

(ii) The moments of nitromesitylene or nitrodurene are reduced in comparison with nitrobenzene.

(iii) Moments of conjugated bisderivatives (e.g. 4-nitro-N,N-dimethylaniline) are higher than the sum of the corresponding monoderivatives and can be also reduced by steric hindrance.

All these findings are explained[1] by the mesomeric formulae as Ib for chlorbenzene, or IIb for nitrobenzene. The additional effects have been taken into account : a small constant contribution (μ_H) of different hybridisation in aliphatic and aromatic compounds and polarization of π-electrons (μ_I)by substituent dipole (μ_X). The μ_I component is of the opposite direction than the mesomeric moments (μ_m) in I, but of the same direction in II. To correct for this effect Sutton takes the more polarizable tert-butyl compounds as a standard of aliphatic derivatives[1]: with the refinement - or even without it - the concept of mesomeric moments is quite generally accepted and explained in many textbooks.

Our analysis of reactivity data[2], in agreement with some other findings[3] concerning bond lengths and molecular configuration ,threw some doubts on this. concept and pointed out that the situation may be different in the two types of substituents. In II only the sacrificial conjugation in Mulliken's terminology[4] is present which we expected (according to the results quoted[2,3] and in spite of some other meanings[5]) to be much weaker than the isovalent[4] conjugation in I. Therefore we reinvestigated the problem by an experimental and a theoretical



Ia Ib IIa IIb

approach with particular attention to nitro compounds. The dipole moments of aliphatic nitro derivatives (Table I), measured under comparable conditions in our laboratory, increase steadily, i.e. above the value of tert-nitrobutane, up to 1-nitroadamantane, but do not reach that of nitrobenzene.

Table I

Experimetal dipole moments of nitroalkanes and 2,4,6-trialkyl-nitro-benzenes (benzene, 25°, 10% correction for P_A)

$R-NO_2$

R	μ,D
CH_3	3.16
C_2H_5	3.20
C_3H_7	3.27
i-C_3H_7	3.31
t-C_4H_9	3.43
cyclo-C_6H_{11}	3.52
1-adamantyl	3.55
C_6H_5	3.98

$2,4,6-R_3C_6H_2NO_2$

R	μ,D
CH_3	3.66
i-C_3H_7(cf.[6])	3.59
t-C_4H_9	3.45
cyclo-C_6H_{11}	3.51
C_6H_5	3.40

This could be explained by the theory of mesomerism as well as the larger polarizability of the π-electrons. In second series, including sterically hindered 2,4,6-trialkyl nitrobenzenes, the dipole moments drop with the size (and/or polarizability) of the alkyls, being finally lower than the highest values of the first series. This fact is not understandable in terms of the mesomerism, neither are the differences within the second series, since already in nitromesitylene the mesomerism should be reduced to ca.16%, corresponding to the dihedral angle[3b] of 67°.

In our theoretical approach we calculated the induced moments on the basis of the classical electrostatic model and of the estimated group and bond polarizabilities[7] but we did not use the common approximation of point dipole[8]; in addition the real molecular geometry was introduced and the anisotropic polarizability of the benzene nucleus[7] as well as the moments induced in the alkyl group were accounted for.

Table II

Changes of dipole moments due to 2,4,6,-trialkyl substitution in aromatic compounds

Source of difference	$\mu(Me_3C_6H_2NO_2) - \mu(C_6H_5NO_2)$	$\mu(t\text{-}Bu_3C_6H_2NO_2) - \mu(C_6H_5NO_2)$	$\mu(Me_3C_6H_2CN) - \mu(C_6H_5CN)$
Valence deflection	+0.02	+0.02	0.00
Moments induced in the ortho alkyls	-0.22	-0.33	+0.03
Moments induced in the para alkyl	$+0.00_2$	+0.01	$+0.00_2$
Difference in phenyl polarizability	-0.01	-0.01	0
Σ	-0.21	-0.31	+0.03
Experimental difference	-0.32	-0.52	+0.16(cf.[9])

The important results are listed in Table II. They reflect qualitatively the effect of ortho-substitution and the different behaviour of nitromesitylene and mesitoic nitrile. The reduced moment of the former seems thus to be due essentially to the moments induced in the methyl groups, closely situated to the oxygen atoms, and only to a negligible extent also to the lowered polarizability of the benzene nucleus in the perpendicular direction. The former effect is also responsible for the difference between nitromesitylene and 2,4,6-tri-tert-butyl-nitrobenzene. In mesitoic nitrile the first factor is reversed due to different geometry, the second is absent. Another possible source of difference in dipole moments - valence deflection of the ortho methyl groups[3a] - seems to be much less importance and moreover it is of opposite direction.

The calculations could be certainly improved by adjusting some parameters to yield a better agreement with the experiment. However we feel that the calculations are sufficiently precise for our purpose with respect to the combined error of the experimental method (± 0.1D). Hence we are satisfied with a qualitative picture, showing that other explanations than the mesomerism are at least possible.

Our results may be summarized that the mesomeric moments can certainly not explain all experimental results, although we cannot decide with certainty whether such an explanation is possible on the basis of induced moments alone. At any rate the mesomeric moments of the nitro group (and probably of the other acceptors too) in monofunctional derivatives are much smaller than it has been commonly assumed, as far as they exist at all. This finding should be respected in all discussions of mesomerism or resonance theory and of its experimental supports, even in textbooks.

On the contrary there are no doubts about the existence of mesomeric moments in the case of donor groups and of bisderivatives of donor-acceptor type. These latter compounds give still a nice example of steric inhibition of mesomerism (e.g. 3,5-dimethyl-4-nitroaniline) and should replace the usually quoted nitromesitylene in pertinent discussions. Furthermore the change of conception does not impair the usefulness of so-called mesomeric moments in approximate computation of dipole moment by the vector addition of bond moments ; these values are purely formal in character and are used essentially as empirical corrections.

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