DIPOLE MOMENT AND ELECTRON DISTRIBUTION OF THE AMIDE GROUP*

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Dipole moments of five substituted N,N-dimethylbenzamides *Ia—Ie* were measured in benzene and dioxan solutions. The group moment of 12·7 . 10^{-30} C m (at an angle of 80° to the $C_{(1)}$—C bond) was resolved into components and a mesomeric moment of 4·7 . 10^{-30} C m (in the direction from N to C) was derived, accounting for the conjugation within the dimethylamide group. A smaller mesomeric moment in the same direction was found for the unsubstituted amide group. The results are but roughly consistent with an interpretation in terms of the mesomeric formulae *A* ↔ *B*.

The concept of mesomeric dipole moments[1] was originally connected with the classic theory of resonance and interpreted the differences between observed and expected dipole moments in terms of contributing mesomeric structures. However, some pertinent experimental facts retain their validity irrespective of the theoretical interpretation. Accordingly, the mesomeric moment can be either viewed as a theoretically important quantity giving evidence about the electronic structure of the molecule, or merely as an empirical correction necessary to match the experimental values[2]. Ast he most important phenomena in this field we may quote: *a*) The difference in dipole moments of an aromatic and the corresponding aliphatic derivative is accounted for by a mesomeric moment[1-3] which is believed to express the degree of conjugation with the benzene nucleus. *b*) The conjugation of one donor and one acceptor group through the benzene nucleus, as in 4-nitro-N,N-dimethylaniline, requires an additional mesomeric moment[2-4]. *c*) In some functional group a double bond is conjugated with a lone electron pair (amides, thioamides, amidines). A mesomeric moment can be detected if the experimental moment is compared to calculations based on model compounds or on bond moments[5,6]. *d*) The dipole moments of some long conjugated systems (polymethine dyes) are so high that the charge separation is evident without any calculations[4].

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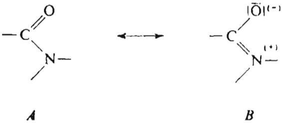
The case (*a*) has been given most attention and it seems proven that conjugation is not the only reason of the effects observed[7,8]. In addition these effects are rather small. On the other hand, there are no doubts about a significant conjugation and effective charge separation in good examples ad (*b*) and (*d*). All these cases have in common that they are based essentially on observed facts. On the contrary, a comparison of experiments with calculation is inevitable in the case (*c*) and the result may be rather sensitive to the assumptions made. Then the significance of the mesomeric moment as a mere empirical correction comes forward.



A typical example of this situation is the amide group. There are no principal doubts that charge separation occurs and that the C—N bond order is enhanced and C=O reduced. However, a simple description in terms of two mesomeric structures *A* and *B* does clearly not account for all details of the structure[9,10]. An evidence from dipole moments is rather difficult to obtain for several reasons. In addition to technical and theoretical problems with association of amides in non-polar solutions[11-13], it is mainly the calculation from bond moments which is not completely reliable and all its errors are accumulated in the value of the mesomeric moment. For this reason several values (even zero) have been used in the literature[5,6,11,14-16]. In order to obtain more reliable values, it is in our opinion necessary to avoid association and to introduce polar substituents with known direction of their dipole moments. In this communication we report the results obtained on *para*-substituted N,N-dimethylbenzamides *Ia*–*Ie* (Table I). This simple approach has not yet been used for this familiar functional group.

EXPERIMENTAL

Materials. Substituted N,N-dimethylbenzamides *Ia*—*Ie* were prepared from acid chlorides and dimethylamine in anhydrous ether. The melting points (Table I) agreed mostly well with those reported recently[17], with the exception of 4-methyl-N,N-dimethylbenzamide (*Ib*), m.p. 37°C (hexane), which was described previously as a liquid[17,18].

Measurements. The dipole moments were determined by the Guggenheim–Smith method[19]; experimental details were described previously[20], the concentration range was shifted to $4 . 10^{-3}$ to $5 . 10^{-2}$M. When evaluating the dipole moment we preferred the correct equation[19]

$$\mu^2 = \frac{27kTM_2}{4\pi N d_1}\left(\frac{\alpha}{(\varepsilon_1 + 2)^2} - \frac{\gamma}{(n_1^2 + 2)^2}\right)$$

to the simplified version assuming n_1^2 equal to ε_1. There is no need for such simplification although the error introduced would be completely negligible in benzene solution and only just perceivable in dioxan.

Calculations of theoretical dipole moments. We used the standard bond moments[21] (in 10^{-30} C m): C=O 8·33, C—N 1·50, H—N 4·37, H—C_{al} 1, H—C_{ar} 0, C_{ar}—Cl 5·33, C_{ar}—Br 5·23, C_{ar}—NO_2 13·33. The bond angles used for the dimethylamide group were: C—C=O 119°, C—C—N 118°, C—N—C (*Z*) 121°, C—N—C (*E*) 123°. They are average values from the standard geometrical parameters of the (*Z*) and (*E*)-amide group, respectively[10]. The angles in the unsubstituted amide group were adopted from acetamide[22]: C—C=O 123°, C—C—N 115°, C—N—H (*Z*) 118°, C—N—H (*E*) 120°. The results are not affected by the uncertainty inherent in these values.

DISCUSSION

Considering the data of Table I, the salient feature is the negligible effect of solvent. This suggests that neither association of dimethylamides in benzene nor their solvation in dioxan are of importance under the conditions of measurement. This view is further supported by the observed linear dependence of permittivity on concentration and by the literature data[13] on N,N-dimethylacetamide in the gas phase and

TABLE I

Experimental Dipole Moments of Substituted N,N-Dimethylbenzamides (25°C)

Compound Substituent	M.p., °C	Solvent[a]	α^b	γ^b	μ 10^{-30} C m
Ia	42[c]	Bz	10·73	0·11	12·7[d]
H		Dx	12·70	0·32	12·9
Ib	37[e]	Bz	10·52	0·11	13·2
4-CH_3		Dx	12·30	0·34	13·2
Ic	65[f]	Bz	8·36	0·15	12·4
4-Cl		Dx	10·30	0·41	12·7
Id	72[c]	Bz	7·05	0·14	12·7
4-Br		Dx	7·74	0·34	12·3
Ie	97[c]	Bz	14·52	0·16	16·9
4-NO_2		Dx	17·70	0·35	17·4

[a] Bz benzene, Dx dioxan; [b] slopes of the Guggenheim–Smith plots; $\alpha = d\varepsilon_{12}/dw_2$, $\gamma = dn_{12}^2/dw_2$; [c] in agreement with ref.[17]; [d] ref.[5,28] give 12·7 and 13·1, respectively; [e] described as liquid[17,18]; [f] ref.[17] gives 58—59°C.

in solution. Therefore, we are justified to process the dipole moments in the two solvents together and to consider them as relating to the isolated molecules with a reasonable approximation.

In Fig. 1 the dipole moment of the $CON(CH_3)_2$ group is derived by subtracting vectorially the known moments of the substituents. It means to construe a triangle, given the three sides, for each of the substituents CH_3, Cl, Br, and NO_2 separately. The coincidence of all the results is reasonable, the group moment is determined to 12·7 at an angle of 80° to the $C_{(1)}$—C bond. (All dipole moment values are given in units 10^{-30} C m.) In the next step this value is to be resolved into components.

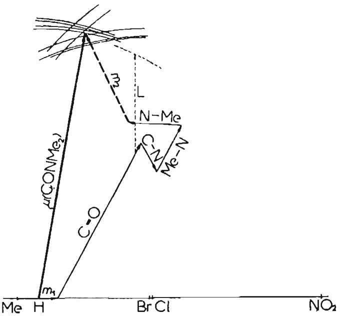


Fig. 1

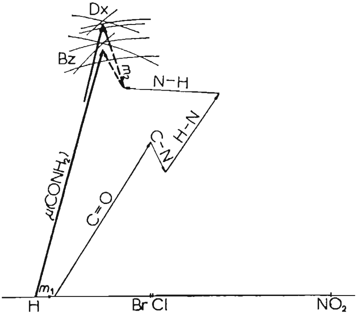
Dipole Moment of the Group $CON(CH_3)_2$ and Its Resolution into Components

Shown are the mesomeric dipole moments expressing the conjugation C_6H_5—CO (m_1) and the conjugation N—CO (m_2), the dotted arrow (L) denoted m_2 as determined by Lumbroso[6].

Fig. 2

Dipole Moment of the Group $CONH_2$ and Its Resolution into Components

The same symbols are used as in Fig. 1, experimental data in benzene (Bz) and in dioxan (Dx) according to the literature[11,12,25].



In addition to the C=O, C—N, and H—C bond moments also two mesomeric corrections must be taken into consideration: one (m_1) expressing the conjugation Ar—CO, the other (m_2) the conjugation N—CO. The term m_1 was several times neglected[11,23] or dismissed[5] due to the assumed non-coplanar position of the benzene ring. Nevertheless, it is necessary in our opinion, provided a bond moment system is used with different values for the H—C_{al} and H—C_{ar} bonds. Then the moment m_1 is revealed by simple comparing dipole moments of N,N-dimethylbenzamide and N,N-dimethylacetamide; the latter was measured several times[24] with an average value of 12·7 in benzene. With a value of 0·83 for m_1 as used previously[15], we obtain from Fig. 1 approximately 4·7 for the searched mesomeric moment m_2. Since the two vectors are almost perpendicular, an uncertainty in the former value does not appreciably affect the latter. Noteworthy is the direction of m_2, almost exactly collinear with the N—C bond. Within the framework of the simple mesomeric theory, expressed by the formulae $A \leftrightarrow B$, the calculation from bond moments should give the anticipated dipole moment of A. In the mesomeric moment m_2, the contribution of B is manifested, hence its direction should be approximately from N to O.

Our value of the mesomeric moment m_2 does not differ too much in the absolute value from Lumbroso's[5,6] estimates 3·6, 4·7, and 5·7, respectively. The main difference of the two conceptions is in the use of substituents which enabled us to determine even the direction of the vector m_2. Lumbroso's estimates are based each on one compound only: N,N-dimethylacetamide, or the last number on N,N-dimethylformamide. Their direction had to be simply assumed to be from N to O, in order that its absolute value might be determined (dashed arrow denoted L in Fig. 1). However, this assumption is not warranted in the light of our results.

It is much more difficult to obtain a reliable value of the mesomeric moment m_2 for the unsubstituted amide group since the solution dipole moments cannot by far be related to the isolated molecule. We processed two sets of literature data on substituted benzamides. One was measured in dioxan[11] and the solvent effect was appreciable but not exactly known. The other set was measured in benzene on partly dimerized solutes and the dipole moment of monomeric form was calculated by a rather sophisticated procedure[12]. In addition, the dipole moment of 4-nitrobenzamide was lacking in either set and was extrapolated from measurement in mixed solvents[25]. Considering these circumstances, the coincidence in Fig. 2 is not bad; nevertheless, the two sets differ clearly. The dipole moment of the $CONH_2$ group worked out to 11·7 (at an angle of 74° to the $C_{(1)}$—C bond), or 12·8 (75°) in the two sets, respectively. Accordingly the value of the mesomeric moment m_2 is either 2·0 or 3·1. However, none of these values is quite reliable: those from dioxan solution are clearly enhanced by a specific solvent effect (hydrogen bonds) and the procedure of calculation[12] in benzene solution was not sufficiently verified. The most important finding is thus the direction of the mesomeric dipole moment, approximately along the N—C bond in either case, like in the dimethylamide group.

The following conclusions seem reasonably safe: The mesomeric dipole moment within the amide group (denoted m_2) is perceivable. Even if it can be possibily neglected in some approximate calculations, it makes itself felt on suitable compounds and in more detailed considerations. Its magnitude is certainly not constant but depends on substituents on nitrogen; in particular it is much larger for the dimethylamide than for the amide group. (This behaviour can be qualitatively accounted for by the mesomeric constants[26] σ_R of the groups $N(CH_3)_2$ and NH_2.) The direction of the mesomeric dipole moment, approximately from N to C, cannot be well interpreted in terms of the mesomeric formulae $A \leftrightarrow B$ which yield only a crude picture. Similar conclusions were drawn from other observations[9,10]; in addition we may quote the molar refraction increment of the dimethylamide group[27] which reveals no exaltation, rather a slight depression.

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