625. *Polarisation in Conjugated Systems.   Part IV.   Mesomeric Moments.*

By K. B. EVERARD and L. E. SUTTON.

Mesomeric moments are derived for several 4-substituted derivatives of benzene, diphenyl, stilbene, and 1 : 4-diphenylbutadiene.   When these are plotted against the lengths of the conjugated systems, a series of straight lines are obtained, the slopes of which are characteristic of the substituents. The closeness of the fit is probably accidental, because the mesomeric moments of styrene derivatives do not fall on the lines.

The mesomeric moments of aniline and 4-aminostilbene agree well with those calculated from Coulson and Jacobs's π-electron distribution diagrams (*J.*, 1949, 1983), obtained by molecular-orbital calculations.

FOR the remaining papers in this series it is necessary to derive values of mesomeric moments, since these pertain more closely to the mobile electron distribution in the conjugated systems examined than do the gross dipole moments.   The mesomeric moment (abbreviated to μ_m) of an aromatic compound Ar–X is here defined as the vector difference between its dipole

moment and that of its aliphatic analogue Alk–X (cf. Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668; *Trans. Faraday Soc.*, 1934, **30**, 789; Marsden and Sutton, *J.*, 1936, 599). A discussion of the reason for this definition and its validity will be given in Part V.

For compounds containing angular groups such as NH_2 (or NMe_2) the direction and magnitude of the σ-bond moment are needed. The former would be available if the nitrogen valency angle in aniline and related compounds were known. No reliable value seems to exist, however, so it is necessary to derive one. For this purpose, the dipole moments of *p*-phenylenediamine and benzidine, and of their *NNN'N'*-tetramethyl derivatives were measured (Part I). It was then assumed (i) that the N–H and N–Me bond moments, the nitrogen valency angle, and the rotational orientation of one group are not affected by the presence of the other group, (ii) that the N–H and N–Me σ-bond moments are the same as in ammonia and trimethylamine (1·31 and 0·86), and (iii) that one-third of the lone-pair dipole can be reckoned as part of each bond moment. It follows that the component of the amino-group moment resolved at right angles to the 1 : 4 diagonal of the ring is $1/\sqrt{2}$ times the moment of *p*-phenylenediamine or benzidine (a general proof of this is given by Everard and Sutton, *J.*, 1951, 16). This component is wholly due to the effective moments of the two N–H bonds. Knowing these, the angles between each of the bonds, and between one of the bonds and the 1 : 4 diagonal, can be calculated vectorially. The same treatment can be applied to the tetramethyl compounds. The value obtained for the nitrogen valency angle is 108—111°, *i.e.*, approximately tetrahedral; but it is rather sensitive to the assumptions made.

It will further be assumed that the bond angles and the σ-bond moments are constant, no matter what is joined to the amino-group. Though these assumptions are crude, they are unlikely to invalidate the conclusions that we shall draw later.

Derivation of the mesomeric moment also requires a knowledge of the direction of the gross moment in the compounds with angular substituents. One way of obtaining this in the specific case of dimethylaniline has been described by Marsden and Sutton (*loc. cit.*): it involved measuring the moment of dimethyl-*p*-toluidine. Owing to the small value of the methyl-substitution moment, this method is rather sensitive to error. Nevertheless, the value that we have recalculated agrees well with that obtained from the moments of the amine and the corresponding *p*-diamine by Hertel and Dumont's method (*Z. physikal. Chem.*, 1935, *B*, **30**, 139) based on the vectorial property that the total moment of each amino-group must be the resultant of those perpendicular to and parallel to the axis of rotation. The former component is found as above (1·13 for NH_2; 0·79 for NMe_2). The latter, and hence the direction of the total moment, then follows.

Similar considerations apply to the acetyl group. The direction of the moment of acetophenone was given as 130° ± 1° to the Ph–Ac bond by Bentley, Everard, Marsden, and Sutton (*J.*, 1949, 2957); this value was obtained from the moments of some *para*-substituted acetophenones. We now obtain 132°, in good agreement, from the moments of acetophenone and *p*-diacetylbenzene.*

The directions of the constituent moments having been established, it is a simple matter to obtain the mesomeric moments. A list of those that will be needed is given in Table I.

TABLE I.

Mesomeric moments of 4-substituted compounds.

|	NO_2.	Ac.	CN.	NH_2.	NMe_2.	Br.	Cl.
Benzene	0·76	0·46	0·45	1·02	1·66	0·43	0·41
Styrene †	1·10	—	—	—	2·14	0·33	0·40
Diphenyl	1·16	—	0·73	1·44	2·14	0·35	0·37
Stilbene	1·31	0·61	0·82	1·73	2·54	0·33	—
1 : 4-Diphenylbutadiene	1·50	—	—	—	2·72	—	—

† It is assumed that styrene has a moment of 0·12 (see below).

They are based on the dipole moments given in Parts I and III. No distinction is made between electron-releasing and electron-accepting groups; *i.e.*, the direction of μ_m has not been specified.

In order to exhibit the dependence of mesomeric moments on the conjugated systems to which they relate, the former have been plotted against the lengths of the latter from end to

* Weissberger (*J. Amer. Chem. Soc.*, 1945, **67**, 778) gave the moment of *p*-diacetylbenzene as 2·71. A study of his measurements suggests, however, that he made an error in ε_1 of 0·028. The dipole moment has accordingly been recalculated by Halverstadt and Kumler's method, and the revised value of 3·10 obtained.

end (Fig. 1). Although we have actually plotted the length, it would doubtless be possible to have taken some other extensive property of the systems, such as their molar volumes or molar refractions. With the lengths, however, a series of straight lines is obtained, the slopes of which are characteristic of the substituent groups. The linear relationship is remarkably

Fig. 1.
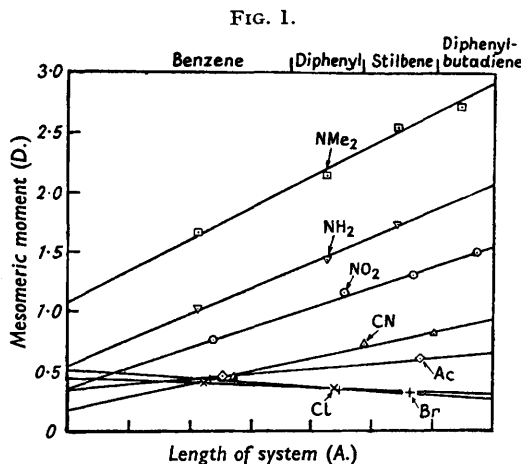
exact; the standard deviation of the points from their respective lines (Ac and Cl being omitted) is 0·03 D. It could be explained very simply by supposing that the charge leaving the polarising group is independent of the attached system and is distributed evenly over it. Notwithstanding, two facts point to its being accidental.

Fig. 2.
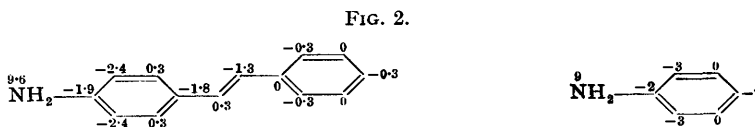
The net charges on the atoms are shown in units of $-e/100$: *i.e., positive charges are given a positive sign.*

(i) A. Pullman (*Compt. rend.*, 1948, **226**, 486) calculated the π-electron distribution in 4-aminostilbene, and found that, quite apart from alternating polarity effects, the formal charge distribution is very uneven, there being more charge on the β-carbon atom than on the whole of the second benzene ring. Coulson and Jacobs (*J.*, 1949, 1983), using a different method of computation, confirmed this result and also performed calculations on aniline; their results are reproduced in Fig. 2. The pattern of distribution is likely to be similar for other groups.

(ii) The mesomeric moments of styrene derivatives do not lie on the lines through the other points. The discrepancies in the ordinates are shown in Table II, row 1.

Table II.

Substituent.	4-NMe$_2$.	4-NO$_2$.	4-Cl.	4-Br.	β-NO$_2$.	β-Ac.	β-Br.	Root mean square.
μ (" obs.") $\atop$ $-\mu$ (interpolated) $\}$	0·35	0·01	0·12	0·08	0·33	0·19	$-0·02$	0·22
Ditto (corrected)...	0·02	0·02	$-0·02$	0·02	$-0·06$	$-0·02$	$-0·11$	0·03

Three β-substituted styrenes have been included, but we cannot be sure that they should be comparable. The reliability of the measurements on which the values for β-bromo- and β-acetyl-styrene are based is unknown. β-Nitrostyrene, however, has been re-examined recently (Part I).

Better agreement and consistency are obtained, as shown in Table II (row 2), by making two assumptions : (*a*) that styrene itself has a dipole moment, not of zero, but of about 0·12, in such a sense that the vinyl group accepts electrons from the phenyl group (cf. Part I) ; and (*b*) that the abscissæ for styrene derivatives in Fig. 1 are increased by *ca.* 1·5 A.

The need for increasing the abscissæ of the 4-substituted styrenes would be expected by reference to Fig. 2, if substitution of the second benzene ring in 4-aminostilbene by hydrogen had only a minor effect on the electron distribution in the rest of the system, and, in particular, on the large charge on the β-carbon atom; in this connexion it is noteworthy that the moments of 4-dimethylaminostyrene and of 4-dimethylamino-2′ : 4′ : 6′-trimethylstilbene are similar (2·15 and 2·11), for the second ring in the latter is prevented from conjugating (Part II). The fact that these moments are nearer to that of 4-dimethylaminostilbene (2·41) than to that of dimethylaniline (1·61) supports the view that the charge migrating to the second benzene ring is smaller than that on the β-carbon atom. It must be remembered also that the former charge migrates further than the latter; consequently, the dipole moment to which it gives rise is proportionately, though not actually, greater.

The mesomeric, or π-bond moments of aniline and 4-aminostilbene, may be calculated from the charges given in Fig. 2. They are 1·17 and 1·63, respectively. The observed ones are 1·02 and 1·73. The agreement is much better than that usually obtained in comparisons of this sort (see, *e.g.*, Hill and Sutton, *J.*, 1949, 746; Bentley, Everard, Marsden, and Sutton, *J.*, 1949, 2957; Orgel, Cottrell, Dick, and Sutton, *Trans. Faraday Soc.*, 1951, **47**, 113); and it might be better still, for the charge distributions are not given to sufficient figures to make the last figure of the moments significant. Evidently, Coulson and Jacobs's statement (*loc. cit.*) that " our charge migrations are probably too large," is too conservative. It may be because the charge migrating is so small relative to that in these other cases, that the agreement is so good.

Pullman's charge distributions (see above) lead to a π-bond moment of 4·34 for 4-aminostilbene. It seems that her treatment exaggerates some of the formal charges.

PHYSICAL CHEMISTRY LABORATORY, OXFORD.