

888. *The Electric Dipole Moments of a Vinylenic Series.*

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The dipole moments of a series of compounds  $\text{Me}_2\text{N}\cdot[\text{CH}\cdot\text{CH}]_n\cdot\text{CHO}$ , from  $n = 0$  (dimethylformamide) to  $n = 4$ , have been measured in benzene at  $25^\circ$ . End-to-end charge transfers have been calculated on two very different stereochemical models, a stick-like and a snake-like one. The conclusions, which are qualitatively independent of the model used, are that this charge transfer falls off quickly as  $n$  increases. Each end-group appears to have a limited sphere of action extending over about three vinylene units.

THE effect of conjugation on the dipole moments of aliphatic chain systems has received little investigation. Kushner and Smyth<sup>1</sup> measured dipole moments of individual dyes and compared observed moments with the number of possible ionic structures. Everard and Sutton<sup>2</sup> measured several series of compounds containing conjugated ring systems: they found that (with the exception of styrene derivatives) the mesomeric moments increased linearly with the length of the system.

Spectroscopists have investigated several series of vinylenic compounds: among recent publications Bohlmann and Mannhart<sup>3</sup> have confirmed the simple prediction by Lewis and Calvin<sup>4</sup> that for polyenes  $\lambda_{\text{max.}} \propto \sqrt{n}$  (where  $n$  is the number of vinylene links). Whiting and Malhotra (unpublished work) subsequently observed that cyanines correspond to the other Lewis and Calvin model, with  $\lambda_{\text{max.}} \propto n$ , but that the vinylogues of dimethylformamide do not correspond to either model.

Simple treatment of conjugated aliphatic systems offers two alternative predictions for a rigid, "stick-like" model, wherein the end-dipoles of a series such as we have investigated would have relative orientations unaltered by the interpolation of extra vinylene links:

(a) Provided that the end-groups do not interact, the dipole moment of the series will be independent of  $n$ . (b) If, on the other hand, the end-groups do interact to give a charge transfer from end to end, the dipole moment will be a linear function of the product  $(\delta e \cdot \mathbf{r})$  where  $\delta e$  is the charge transferred, and  $\mathbf{r}$  the distance between the end-groups. Clearly  $\mathbf{r}$  is a linear function of  $n$ , and so the dipole moment will also be if  $\delta e$  is constant.

Measurement of the dipole moments of a series of compounds with the same end-groups should enable us to distinguish between the two possibilities (a) and (b). If the results indicate some combination of the two, then we should be able to infer to what extent "conjugation" amounts to an end-to-end charge transfer. Therefore this has been done for several vinylogues of dimethylformamide.

## EXPERIMENTAL

Benzene of analytical grade was purified as described by Hill and Sutton.<sup>5</sup> The compounds  $\text{Me}_2\text{N}\cdot[\text{CH}\cdot\text{CH}]_n\cdot\text{CHO}$  ( $n = 0-6$ ) were prepared by Dr. M. C. Whiting and Dr. S. S. Malhotra (to be published).

Electric dipole moments were determined by measuring dielectric constants and specific volumes at  $25^\circ$  by the methods described by Everard and Sutton<sup>6</sup> for their small-scale technique, with the heterodyne-beat capacitance meter described by Hill and Sutton.<sup>7</sup> The dielectric constant of benzene was assumed to be 2.2750.<sup>8</sup> The pycnometer was calibrated with air-free distilled water. Owing to strong absorption of light by all the solutes save dimethylformamide, refractive-index measurements were not satisfactory, and values of  $\epsilon_P$  were calculated from

<sup>1</sup> Kushner and Smyth, *J. Amer. Chem. Soc.*, 1949, **71**, 1401.

<sup>2</sup> Everard and Sutton, *J.*, 1951, 2818.

<sup>3</sup> Bohlmann and Mannhardt, *Chem. Ber.*, 1956, **89**, 1307.

<sup>4</sup> Lewis and Calvin, *Chem. Revs.*, 1939, **25**, 273.

<sup>5</sup> Hill and Sutton, *J.*, 1949, 746.

<sup>6</sup> Everard and Sutton, *J.*, 1951, 16.

<sup>7</sup> Hill and Sutton, *J.*, 1953, 1482.

<sup>8</sup> Hartshorn, Parry, and Essen, *Proc. Phys. Soc.*, 1955, **68**, B, 422.

refractivity values. The numerical values used<sup>9</sup> were: H = 1.10, C = 2.42, tertiary N = 2.84, carbonyl O = 2.21, increment for (C=C) = 1.73 c.c. The derived  ${}_E P$  values can be summarised by the equation  ${}_E P(n) = 20.0 + 8.75n$  (where  ${}_E P$  is expressed in c.c. and  $n$  is the number of vinylenic groups). For dimethylformamide (see Table 1) the agreement between the observed value and that so calculated was fair.

The computation of moments and the notation used follow the pattern set by Everard, Hill, and Sutton,<sup>10</sup> so that no allowance has been made for atom polarisation other than that implicit in using  $[R]_D$  values. As the moments are large ( $\mu > 3$  D), the uncertainties in  ${}_E P$  and in  ${}_A P$  are unimportant.

The solubility in benzene falls off rapidly with increase in  $n$ , and no satisfactory results could be obtained for the compounds with  $n = 5$  or 6. The results for  $n = 0-4$  are shown in Table 1 and plotted in Fig. 1.

FIG. 1. Electric dipole moment as a function of chain length.

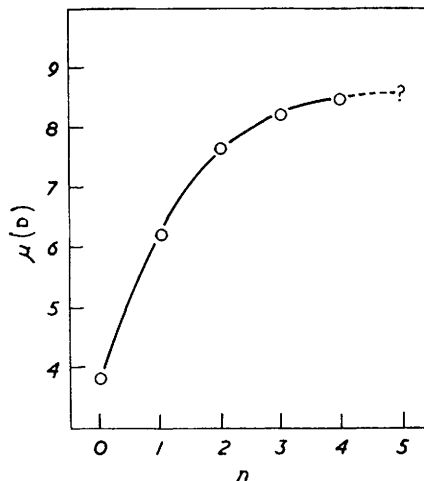


TABLE 1.

	$\epsilon$	$v$	$-10^5 \cdot \Delta n$	$10^6 w$	$\epsilon$	$v$
Dimethylformamide ( $n = 0$ )					$(n = 3)$	
1243	2.3028	1.1445	8.5	608	2.3046	1.1448
1908	2.3164	1.1447	12.4	1559	2.3521	1.1448
4739	2.3784	1.1446	31.4	2361	2.3903	1.1447
4958	2.3836	1.1446	33.2	3316	2.4363	1.1448
$\epsilon = 2.2751_4 + 21.83w$ , $v = 1.1446 + 0.003w$ , $\Delta n =$				$\epsilon = 2.2753 + 48.68w$ , $v = 1.1448 - 0.01w$ , ${}_T P_2$		
$-0.067w$ , ${}_T P_2 = 324.9$ c.c., ${}_E P_2$ (calc.) = 20.0 c.c.,				$= 1434.2$ c.c., ${}_E P_2$ (calc.) = 46.2 c.c.		
${}_E P_2$ (obs.) = 21.8 c.c.						
$\mu = 3.86 \pm 0.01$ D.				$\mu = 8.24 \pm 0.02$ D.		
$(n = 1)$				$(n = 4)$		
685	2.3029	1.1446		433	2.2937	1.1447
2065	2.3619	1.1444		631	2.3023	1.1448
2611	2.3860	1.1445		775	2.3094	1.1449
3913	2.4416	1.1443		1182	2.3271	1.1447
$\epsilon = 2.2743 + 42.71w$ , $v = 1.1446 - 0.06w$ , ${}_T P_2 =$				$\epsilon = 2.2747 \pm 44.20w$ , $v = 1.1448 - 0.003w$ ,		
$827.4$ c.c., ${}_E P_2$ (calc.) = 28.7 c.c.				${}_T P_2 = 1532.9$ c.c., ${}_E P_2$ (calc.) = 54.9 c.c.		
$\mu = 6.24 \pm 0.02$ D.				$\mu = 8.50 \pm 0.04$ D.		
$(n = 2)$						
855	2.3194	1.1447				
1021	2.3286	1.1446				
1134	2.3327	1.1446				
2459	2.4005	1.1446				
$= 2.2755 + 50.94w$ , $v = 1.1446 - 0.002w$ , ${}_T P_2 =$						
$1240.7$ c.c., ${}_E P_2$ (calc.) = 37.5 c.c.						
$\mu = 7.67 \pm 0.05$ D.						

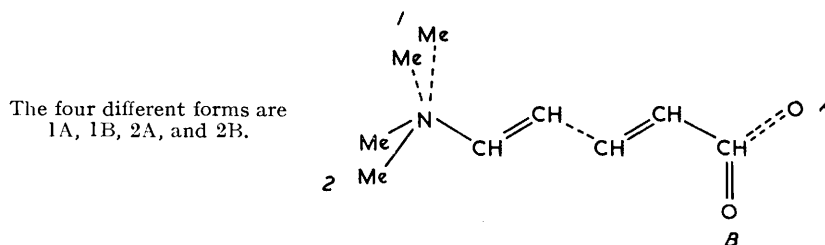
<sup>9</sup> Landolt and Börnstein's "Tabellen," Springer Verlag, Berlin, 1923, 985.

<sup>10</sup> Everard, Hill, and Sutton, *Trans. Faraday Soc.*, 1950, **46**, 417.

## DISCUSSION

It is immediately apparent from Fig. 1 that neither of the simple treatments, (a) or (b), is adequate to explain the observed results. We have therefore attempted to combine the two. This requires that we consider in some detail the configuration of the polyene chain.

As with any polyene system, these compounds may, in principle, have a very large number of stereoisomers. If free rotation around the "single bonds" can occur, the number of forms is infinite. If, however, we may postulate a planar skeleton we reduce isomerism to *cis-trans* and *cisoid-transoid* (*s-cis-s-trans*) types. Experimental justification for doing this comes from the examination of butadiene<sup>11</sup> and of acraldehyde<sup>12</sup> by electron diffraction and by microwave spectroscopy, respectively. The scattering pattern for butadiene can be adequately accounted for by a *transoid* structure, with no evidence for *cisoid*. Similarly, the spectrum of acraldehyde gives no definite evidence of any species being present but the *transoid*; and it is consistent with a potential function for rotation about the central C-C bond which has the *cisoid* form approximately 2.5 kcal. mole<sup>-1</sup> above the *transoid*, and a *transoid* barrier height of 5 kcal. mole<sup>-1</sup>.



Two principal models have been considered: (a) The all-*trans*, all-*transoid* "stick" model in which there are only four non-equivalent forms (see diagram) depending upon the orientation (in the plane) of the end-groups relative to the skeleton. (b) A "snake" model, in which no restrictions are placed upon configuration except those of planarity and the preservation of normal bond angles. This requires consideration of  $2^{2n+1}$  possible isomers, although some of them are equivalent.

For both models, all carbon-carbon distances were assumed to be 1.40 Å; this does not lead to any major error in calculating overall lengths and vector angles in the molecules. Also all  $\angle CCC$  were assumed to be 120°. We have further simplified the treatment by assuming that for any given compound the charge transfer  $\delta e$  is the same for all the configuration isomers. Therefore we regard the overall dipole moment of a particular isomer ( $\mu_T$ ) as being made up of a charge-transfer moment ( $\delta e \cdot r$ ) and the vector sum of the end-group moments ( $\mu_D$ ). If  $\theta$  is defined as the angle between the vector  $\mu_D$  and the charge-transfer moment, then

$$\mu_T^2 = \mu_D^2 + (\delta e \cdot r)^2 - 2\mu_D(\delta e \cdot r) \cos \theta \quad . \quad . \quad . \quad (1)$$

Since our models have more than one configuration isomer, we must take a mean of their polarisations (which are individually proportional to  $\mu_T^2$ ) in order to calculate an observable dipole moment. The correct mean, fortunately, is the arithmetic one, so that if each is assumed to have the same weighting factor, we have the simple relation

$$\mu_{\text{obs}}^2 \equiv \langle \mu_T^2 \rangle = \langle \mu_D^2 \rangle + \langle r^2 \rangle (\delta e)^2 - 2\langle \mu_D r \cos \theta \rangle (\delta e) \quad . \quad . \quad . \quad (2)$$

(the assumption that  $\delta e$  is constant enables us to take it outside the average bracket). By rearrangement, we can obtain a simple quadratic in  $\delta e$ :

$$\langle r^2 \rangle (\delta e)^2 - 2\langle \mu_D r \cos \theta \rangle (\delta e) - (\mu_{\text{obs}}^2 - \langle \mu_D^2 \rangle) = 0 \quad . \quad . \quad . \quad (3)$$

<sup>11</sup> Bastiansen, personal communication.

<sup>12</sup> Wagner, Fine, Simmons, and Goldstein, *J. Chem. Phys.*, 1957, **26**, 634.

To obtain values of  $\mu_D$  we have used aliphatic group moments taken from a critical survey:<sup>13</sup> C=O = 2.75 D along C=O, C-NMe<sub>2</sub> = 0.86 D at 109° to the N-C vector. This use of aliphatic moments attributes any mesomeric moment to the charge transfer.

From the form of the curve (Fig. 1) it is clear that it might be possible to extrapolate to obtain an approximate value for the dipole moment of the  $n = 5$  compound. Linear extrapolation from the values of the  $n = 3$  and  $n = 4$  compounds gives the moment of  $n = 5$  as  $8.75 \pm 0.15$  D; we also fitted a curve to the observed values, on the assumption that for large  $n$  the moment would reach a constant value. The curve employed was of the form  $\mu = p - q(1 + rn)e^{-sn}$ . This gave a value of 8.61 D for the  $n = 5$  compound and a limiting value of 8.66 D. For the purposes of subsequent calculation we shall use the value of 8.6 D.

TABLE 2. *Derived charge transfer values* (in units of electron charge or units of 4.8 e.s.u.).

$n$	0	1	2	3	4	5
<i>a</i> Stick model .....	0.49	0.34	0.26	0.21	0.17	0.14 †
<i>b</i> Snake model (all forms) .....	0.48	0.38	0.34	0.29	0.25 *	0.22 *†
<i>c</i> Snake model (Class 2 forms) ...	0.49	0.41	0.33 <sub>s</sub>	0.27	0.23 *	0.20 *†

\* By graphical extrapolation of coefficients in equation (3).

† Using the extrapolated value for  $\mu_{obs.} = 8.6$  D.

(a) *The stick model.* The results of the solution of equation (3) for the stick model are shown in Table 2, row *a*, and are plotted in Fig. 2. The single, most stable form (from dipole-dipole energies) gives results differing by less than 0.01e electron charge from this mean value.

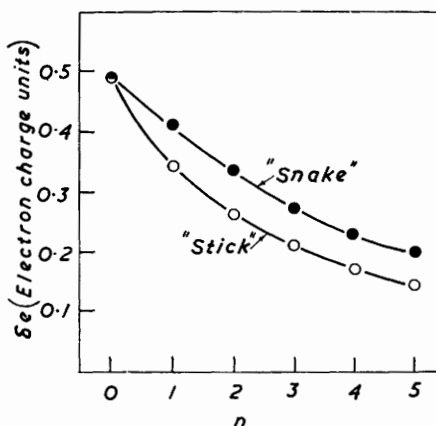


FIG. 2. *Charge transfer as a function of chain length.*

(b) *The snake model.* Although the same in principle, the averaging of the coefficients in equation (3) for the snake model is more complicated than for the stick model because of the  $2^{2n+1}$  configurations that it may have. Certain simplifying results emerge, the principal one being that there are only six possible values of the  $\mu_D$  vector. Nevertheless, the calculation becomes rather lengthy as  $n$  gets larger (there being 128 sets of terms for  $n = 3$  and 512 for  $n = 4$ ); so, for the compounds with  $n > 3$  it was decided to extrapolate graphically to obtain the necessary coefficients. The  $\langle r^2 \rangle$  coefficients fall on a straight line, while the curve for the  $\langle \mu_D^2 \rangle$  values is monotonic in form, in the region  $n = 0$  to  $n = 3$ : thus there is little error in a graphical extrapolation of the two sets of values  $\langle r^2 \rangle$  and  $\langle \mu_D^2 \rangle$ . On the other hand, the cross-terms ( $\langle \mu_D r \cos \theta \rangle$ ) lie on a curve with a maximum between  $n = 1$  and  $n = 2$ , so that graphical extrapolation was not very accurate. Fortunately, the derived value of  $\delta e$  is much less sensitive to this term than to the other two.

Using, then, the calculated values for the coefficients for  $n = 0$  to  $n = 3$  and extrapolated values for  $n = 4$  and  $n = 5$  (together with the extrapolated value of the dipole

<sup>13</sup> Katritzky, Randall, and Sutton, *J.*, 1957, 1769.

moment for  $n = 5$ ), we obtained the values shown in Table 2, row *b*. All the configurations were included in this average.

It seems clear, however, that all the possible configurations of these molecules will not be equally probable and that our previous assumption of equal weighting is not valid. We have, therefore, calculated the dipole-dipole interaction energies, by the standard method.<sup>14</sup> Comparing these with the thermal energy function  $kT$ , we found that the configurations fall into four classes: (1) those with large dipole-dipole attractive energies, but with steric hindrance; (2) those with smaller dipole-dipole attractive energies, and no steric hindrance; (3) those with small dipole-dipole repulsions, and (4) those with large dipole-dipole repulsions. Classes (1) and (4) can clearly be neglected. The configurations in each of classes (2) and (3) have energies corresponding to theoretical populations in a range of roughly 3 to 1. Since we intended to average with unit weighting or with zero weighting, we decided to consider only class (2). This contains approximately a third of the total possible configurations, for the lower members of the series.

Solving equation (3) for this type of configuration only, we obtained the values shown in Table 2, row *c*, and plotted in Fig. 2.

It seems surprising that the curves plotted in Fig. 2 should be so similar in form, but this result is very gratifying, for it means that the qualitative conclusions are insensitive to assumptions about the conformation of the chain itself and therefore are probably right. While the absolute values of the ordinates are dependent upon the detailed assumptions made, the relative values are affected very little.

In general terms we conclude that each polar end-group creates a disturbance in the conjugated chain which extends over a few links only. When two such groups, operating in the same sense, are placed so that their spheres of action overlap, they seem to create a perturbation which amounts to a considerable end-to-end charge transfer. As the groups are separated, however, this dies away. Eventually we should be left, at large values of  $n$ , with two separate dipoles, each perturbing several links of chain and causing local charge transfers, but not interacting. Thus the dipole moment should reach a constant value, and the value of  $\delta e$  should fall to zero. Our observations seem to be consistent with a range of action of about three vinylene groups from each of the end-groups studied.

Although these results appear to conflict with those of Everard and Sutton,<sup>2</sup> it should be stressed that these authors studied systems containing aromatic rings, while we have studied a series of aliphatic compounds. Further, they pointed out that their relationship between mesomeric moment and the length of system might be fortuitous, and they were unable to account for the styrene results on this picture.

It is possible to show that a benzene ring has a greater insulating effect than has a linear polyene chain of the same length. The value of the dipole moment of *p*-dimethylaminobenzaldehyde has been measured in benzene solution:<sup>15</sup> it is 5.6 D. The angular, *para*-end-groups have only two possible non-equivalent configurations; and solving equation (3) for either leads to a charge transfer of 0.21 electron.

Comparing this result with the "stick" values, Fig. 2, we see that a benzene ring seems to be equivalent to the  $n = 3$  compound: in other words, the insulating effect of a benzene ring is roughly equal to that of a conjugated chain of three vinylene groups, though the shortest vinylene system through the benzene ring corresponds to  $n = 2$ . This result accentuates the difference between aliphatic and aromatic systems.

We thank Dr. M. C. Whiting for calling our attention to the problem, Dr. S. S. Malhotra for supplying the compounds, and Dr. A. D. Buckingham for helpful discussions.

<sup>14</sup> See, e.g., Buckingham and Pople, *Trans. Faraday Soc.*, 1955, **51**, 1173.

<sup>15</sup> Weizman, *ibid.*, 1940, **36**, 329.