491. *The Dipole Moments of Some Aliphatic Aldimines, with Special Reference to the Moment of the* C=N *Bond.*

By K. B. Everard and L. E. Sutton.

The electric dipole moments of a series of aliphatic aldimines have been measured in order to provide a relatively reliable value for the C=N bond moment. This proves to be 1·4 D. The dipole moments vary from member to member of the series, and these variations are compared with those which have been reported in other homologous series.

The difference between aliphatic and aromatic values for the bond is also considered.

There does not appear to be any generally accepted value for the C=N bond moment in the literature. Smyth gives it as 0·9 D. (*J. Amer. Chem. Soc.*, 1938, **60**, 183), and Sutton as 2·4 D. (*Trans. Faraday Soc.*, 1934, **30**, 789). Bergmann and Weizmann (*Chem. Rev.*, 1941, **29**, 553)

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* The orientation of this compound is known unambiguously, without the aid of dipole data, because the isomers are all known (Carter, Race, and Rowe, *J.*, 1942, 236).

attempt to calculate it from the dipole moment of benzophenone anil, using Sidgwick, Sutton, and Thomas's value (*J.*, **1933**, 406) of 1·34 D. for the Ph–N: moment; but doubts have been cast on the correctness of the latter value by Bennett and Glasstone (*Proc. Roy. Soc.*, 1934, **145**, *A*, 71), who substitute 0·21 D. for it; and in any case, the moment of such an aldimine, with benzene rings attached, is liable to be altered by resonance. The estimate 2·27 D. of the C=N bond moment derived therefrom is consequently of doubtful validity.

Aliphatic aldimines offer the advantages of simplicity in preparation and the lack of complications (such as mesomeric moments) in evaluating the bond moment. They show tautomerism similar to keto-enol tautomerism, but the concentration of the enamine form in aliphatic aldimines is negligible (von Auwers and Wunderling, *Ber.*, 1932, **65**, 70). They are not, however, stable substances. They are prone to aerial oxidation (Chancel, *Bull. Soc. chim.*, 1894, **11**, 933); the simpler ones are apt to polymerise to cyclic trimers (Henry, *Bull. Acad. roy. Belg.*, 1895, **29**, 489); others undergo aldol-like condensations (Kharasch, Richlin, and Mayo, *J. Amer. Chem. Soc.*, 1940, **62**, 494).

These difficulties were met in a way described in the experimental section, but even so, it was found that the "scatter" of measurements was somewhat more than that encountered with more stable compounds. This, however, is taken into account in estimating the error of each moment. The entire preparation and measurement of one compound were repeated, and the two values differed by only 0·01 D. The purity of each compound was assessed by analysis, the results of which, however, are not of course affected by polymerisation. Some of the lower members of the series polymerise too readily to make examination worth while (Henry, *loc. cit.*).

EXPERIMENTAL.

(Analyses by Mr. F. C. Hall.)

The method used for the preparation of these aldimines was essentially that of Campbell, Sommers, and Campbell (*J. Amer. Chem. Soc.*, 1944, **66**, 82). The aldehydes and amines used as starting materials were B.D.H. specimens, except for acetaldehyde and ethylamine. Acetaldehyde was distilled before use; ethylamine was liberated from its hydrochloride by alkali, dried, and condensed in a spiral cooled with solid carbon dioxide.

The first aldimine so prepared, n-*butylidene*iso*butylamine*, was twice distilled under atmospheric pressure using a 4-in. Dufton column. The product gave an unsatisfactory analysis, however, so all the other aldimines (and subsequently this one too) were distilled under reduced pressure without an air-leak in the Claisen flask, and were analysed and used within 24 hours.

All the aldimines became yellow when kept for periods of a few hours to a few days. The fractional redistillation of those affected the most was carried out in several parts immediately before solutions were made up for polarisation measurements.

The average yield of purified material was about 50%.

B. p.s and analytical results are entered in Table I.

TABLE I.

Aldehyde residue.	Amine residue.	B. p.	Pres. (mm.).	Found, %. C.	H.	N.	Calc., %. C.	H.	N.
n-Bu	*iso*-Am	61°	20	76·8	13·5	10·1	76·6	13·5	9·9
n-Bu	*iso*-Bu	142·5 * 35	(1) atm. (2) 11	75·6	13·5	11·2 (2)	75·6 †	13·4 †	11·0 †
n-Bu	*n*-Bu	56	29	75·6	13·5	11·0	75·6	13·4	11·0
n-Bu	*iso*-Pr	30	29	74·2	13·3	12·5	74·3	13·3	12·4
n-Bu	*n*-Pr	46	39	74·4	13·5	12·4	74·3	13·3	12·4
n-Bu	Et	50	134	72·4	13·0	12·8	72·7	13·1	14·1
Pr	*n*-Bu	54	65	73·9	13·5	12·6	74·3	13·3	12·4
Et	*n*-Bu	51	121	—	—	14·3	—	—	14·1

* Corrected. † Required values (new compound).

The purification of benzene and the physical measurements were carried out as described in the preceding paper. All dipole moments are given in Debye units.

Results.

n-Butylidene*iso*amylamine.

ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.	ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.
0·004626	2·2808	1·1458	0·00059	0·018824	2·3019	1·1480	0·00232
0·007052	2·2840	1·1461	0·00089	0·019080	2·3026	1·1481	0·00233
0·011882	2·2907	1·1468	0·00147				

$$\varepsilon_{12} = 2{\cdot}2734 + 1{\cdot}511\omega_2;\quad v_{12} = 1{\cdot}1450 + 0{\cdot}157\omega_2;\quad \Delta n = -\,0{\cdot}00004 - 0{\cdot}121\omega_2;$$
$$_{\mathrm{T}}P_2 = 95{\cdot}04\ \text{c.c.};\quad _{\mathrm{E}}P_2 = 44{\cdot}64\ \text{c.c.};\quad \mu = 1{\cdot}57 \pm 0{\cdot}05.$$

n-Butylidene*iso*butylamine (1).

ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.	ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.
0·003222	2·2767	1·1459	0·00040	0·009579	2·2875	1·1470	0·00132
0·008000	2·2856	1·1468	0·00111	0·016148	2·2980	1·1482	0·00210

$$\varepsilon_{12} = 2\cdot2719 + 1\cdot634\omega_2;\ v_{12} = 1\cdot1454 + 0\cdot177\omega_2;\ \Delta n = -\ 0\cdot00002 - 0\cdot131\omega_2;$$
$${}_{\mathrm{T}}P_2 = 89\cdot32\text{ c.c.};\ {}_{\mathrm{E}}P_2 = 40\cdot20\text{ c.c.};\ \mu = 1\cdot55 \pm 0\cdot03.$$

n-Butylidene*iso*butylamine (2).

ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.	ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.
0·002303	2·2767	1·1452	0·00033	0·014258	2·2966	1·1474	0·00193
0·004797	2·2815	1·1456	0·00066	0·015564	2·2978	1·1477	0·00203

$$\varepsilon_{12} = 2\cdot2733 = 1\cdot598\omega_2;\ v_{12} = 1\cdot1447 + 0\cdot190\omega_2;\ \Delta n = -\ 0\cdot00003 - 0\cdot131\omega_2;$$
$${}_{\mathrm{T}}P_2 = 88\cdot84\text{ c.c.};\ {}_{\mathrm{E}}P_2 = 40\cdot59\text{ c.c.};\ \mu = 1\cdot54 \pm 0\cdot03.$$

n-Butylidene-*n*-butylamine.

ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.	ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.
0·007287	2 2852	1·1464	0·00094	0·016599	2·3005	1·1483	0·00202
0·011180	2·2926	1·1472	0·00139	0·018202	2·3062	1·1485	0·00231
0·012066	2·2938	1·1474	0·00152				

$$\varepsilon_{12} = 2\cdot2719 + 1\cdot819\omega_2;\ v_{12} = 1\cdot1451 + 0\cdot188\omega_2;\ \Delta n = -\ 0\cdot00004 - 0\cdot122\omega_2;$$
$${}_{\mathrm{T}}P_2 = 94\cdot17\text{ c.c.};\ {}_{\mathrm{E}}P_2 = 41\cdot22\text{ c.c.};\ \mu = 1\cdot61 \pm 0\cdot03.$$

n-Butylidene*iso*propylamine.

ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.	ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.
0·002612	2·2792	1·1454	0·00031	0·008602	2·2913	1·1466	0·00125
0·003803	2·2816	1·1454	0·00050	0·010820	2·2959	1·1474	0·00154

$$\varepsilon_{12} = 2\cdot2739 + 2\cdot022\omega_2;\ v_{12} = 1\cdot1446 + 0\cdot240\omega_2;\ \Delta n = 0\cdot00008 - 0\cdot151\omega_2;$$
$${}_{\mathrm{T}}P_2 = 89\cdot74\text{ c.c.};\ {}_{\mathrm{E}}P_2 = 36\cdot45\text{ c.c.};\ \mu = 1\cdot61 \pm 0\cdot01.$$

n-Butylidene-*n*-propylamine.

ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.	ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.
0·002642	2·2778	1·1452	0·00036	0·010027	2·2921	1·1469	0·00135
0·004692	2·2824	1·1459	0·00064	0·014058	2·2994	1·1477	0·00190

$$\varepsilon_{12} = 2\cdot2732 + 1\cdot867\omega_2;\ v_{12} = 1\cdot1448 + 0\cdot207\omega_2;\ \Delta n = 0\cdot00000 - 0\cdot135\omega_2;$$
$${}_{\mathrm{T}}P_2 = 85\cdot35\text{ c.c.};\ {}_{\mathrm{E}}P_2 = 36\cdot45\text{ c.c.};\ \mu = 1\cdot55 \pm 0\cdot02.$$

n-Butylidene-ethylamine.

ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.	ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.
0·003878	2·2826	1·1460	0·00056	0·009530	2·2964	1·1473	0·00135
0·005732	2·2866	1·1463	0·00082	0·012804	2·3057	1·1480	0·00185

$$\varepsilon_{12} = 2\cdot2721 + 2\cdot594\omega_2;\ v_{12} = 1\cdot1452 + 0\cdot219\omega_2;\ \Delta n = 0\cdot00000 - 0\cdot144\omega_2;$$
$${}_{\mathrm{T}}P_2 = 88\cdot78\text{ c.c.};\ {}_{\mathrm{E}}P_2 = 31\cdot73\text{ c.c.};\ \mu = 1\cdot67 \pm 0\cdot05.$$

Propylidene-*n*-butylamine.

ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.	ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.
0·004614	2·2818	1·1460	0·00063	0·011016	2·2955	1·1470	0·00148
0·007546	2·2877	1·1466	0·00099	0·016104	2·3054	1·1482	0·00216
0·009976	2·2921	1·1469	0·00133				

$$\varepsilon_{12} = 2\cdot2722 + 2\cdot059\omega_2;\ v_{12} = 1\cdot1452 + 0\cdot178\omega_2;\ \Delta n = 0\cdot00001 - 0\cdot134\omega_2;$$
$${}_{\mathrm{T}}P_2 = 88\cdot56\text{ c.c.};\ {}_{\mathrm{E}}P_2 = 35\cdot43\text{ c.c.};\ \mu = 1\cdot61 \pm 0\cdot02.$$

Ethylidene-*n*-butylamine.

ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.	ω_2.	ε_{12}.	v_{12}.	$-\Delta n$.
0·003896	2·2829	1·1457	0·00055	0·009741	2·2964	1·1468	0·00134
0·006647	2·2882	1·1461	0·00097	0·012905	2·3043	1·1474	0·00179

$$\varepsilon_{12} = 2\cdot2730 + 2\cdot408\omega_2;\ v_{12} = 1\cdot1450 + 0\cdot188\omega_2;\ \Delta n = -\ 0\cdot00003 - 0\cdot135\omega_2;$$
$${}_{\mathrm{T}}P_2 = 84\cdot83\text{ c.c.};\ {}_{\mathrm{E}}P_2 = 31\cdot44\text{ c.c.};\ \mu = 1\cdot61 \pm 0\cdot03.$$

DISCUSSION.

The results in Table II show a variation in the moments of these aldimines, albeit a small one (no two moments lie more than 0·12 apart). Similar variation has been observed in a number of other homologous series which have been investigated [see tables given by Wheland (" The Theory of Resonance," Wiley, 1944, p. 123) and by Groves and Sugden (*J.*, 1937, 158)].

TABLE II.

Aldehyde residue.	Amine residue.	Moment.	Uncertainty (±).
n-Butylidene	*iso*Amylamine	1·57	0·05
,,	*iso*Butylamine	1·55, 1·54	both 0·03
,,	*n*-Butylamine	1·61	0·03
,,	*iso*Propylamine	1·61	0·01
,,	*n*-Propylamine	1·55	0·02
,,	Ethylamine	1·67	0·05
Propylidene	*n*-Butylamine	1·61	0·02
Ethylidene	,,	1·61	0·03

Changing the aldehyde residue appears not to affect the moment: this may seem strange in view of variations of up to 0·4 in, for example, the alkyl halide series, but Cowley and Partington (*J.*, 1935, 604) have found that the moments (in solution) of the somewhat analogous *n*-butyl, *n*-propyl, and ethyl cyanides are all 3·57 (though that of methyl cyanide is 0·13 lower). The moments (in solution) of another similar series, the aldehydes, vary only from 2·49 for acetaldehyde to 2·60 for *iso*valeraldehyde (Coomber and Partington, *J.*, 1938, 1444), whilst those measured in the gas phase of acetaldehyde (2·72), propaldehyde (2·73), and *n*-butaldehyde (2·72) are sensibly the same (Hurdis and Smyth, *J. Amer. Chem. Soc.*, 1943, **65**, 89). It is hoped to perform gas-phase measurements on the aldimines for comparison with the latter work.

As the size of the amine residue is increased, the moment tends to diminish (though the *n*-propyl compound is irregular); this trend might be expected if it is due to the greater polarisability of the higher alkyl groups, for an increase in the N–R moment in the grouping $C{-}N{=}R$ not only partly opposes the resultant moment of the system, but also results in the nitrogen atom becoming less electronegative, which should diminish the $C{=}N$ bond moment.

The chief peculiarity seems to be the effect of chain branching, which appears to cause a decrease in moment of 0·06 when the alkyl residue is butyl, and an increase of 0·06 when it is propyl. The same thing is evident in the chloride series where the changes are minus and plus 0·05 (Wiswall and Smyth, *J. Chem. Physics*, 1941, **9**, 356). The reason for this is obscure, but, as it may conceivably be a result of measuring these dipole moments in solution, discussion is deferred until some measurements in the gas phase have been carried out.

Despite these variations, we can give a better estimate than any hitherto of the $C{=}N$ bond moment.

It is necessary to know the values of the H–C and C–N bond moments. Those of bonds between any element and quadrivalent carbon, as usually evaluated, depend necessarily on the former moment, which must therefore be considered first. There seems to be fairly general agreement that its magnitude is 0·3—0·4, but there has been some controversy recently as to its direction, following Coulson's statement (*Trans. Faraday Soc.*, 1942, **38**, 433) on the basis of some wave-mechanical calculations that the positive pole was situated nearer the carbon atom. It had previously been assumed that the opposite was the case, as the greater electronegativity of carbon would require. Coulson included for the first time in a bond moment the effect of sp^3 hybridisation of the bonding orbitals of carbon, which results in a lop-sided distribution of the negative charge constituting each bond.

This emphasises the rather arbitrary nature of the definition of a bond moment. Such a moment arises partly from the atomic dipole as above, partly from the covalent dipole, and partly from the ionic dipole (for references, see, *e.g.*, Cottrell and Sutton, *Quart. Reviews*, 1948, **2**, 260). The relevant definition is really determined by the nature of the observation; and the fact that in bending movements of certain benzene compounds the moving H–C dipole has its positive pole towards the hydrogen (Bell, Thompson, and Vago, *Proc. Roy. Soc.*, 1948, **192**, *A*, 498) suggests that for many purposes a definition excluding the atomic dipole is more useful. We shall use this in the present context, and so take the H–C dipole to be H^+C^- and of magnitude 0·4.

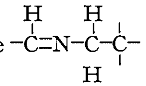
As for the C–N bond moment, Hammick, New, and Sutton (*J.*, 1932, 742) have given 1·2 for the moment of the grouping $CH_3{-}N$, obtained vectorially from the moments of ammonia and methylamine; assuming that the methyl group moment ($= \mu_{H-C}$) is 0·4, this gives $\mu_{C-N} = 0{\cdot}80$. Bennett and Glasstone (*loc. cit.*) give 0·71 for the $CH_3{-}N$ moment, corresponding to a C–N bond moment of 0·31. Smyth quotes the latter as 0·45 (*loc. cit.*). This value will be taken as the most probable, because it agrees with that which can be calculated from a recent determination of the trimethylamine moment, 0·86 (benzene solution; Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374). Since the valency angles are tetrahedral, or nearly so [electron-diffraction work on trimethylamine gives the value 108° ± 4° for the C–N–C bond angle (Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036); *X*-ray diffraction in the vapour phase gives 110° (Richter, *Physikal. Z.*, 1935, **36**, 85)], this must be the $CH_3{-}N$ moment, so on this basis the C–N moment is 0·46.

The $-C{=}$ and ${=}N-$ angles in aldimines have not been determined, but it will be assumed that they are each 120°. This has been confirmed in the case of some molecules having ethylenic carbon atoms (see, *e.g.*, Gallaway and Barker, *J. Chem. Physics*, 1942, **10**, 88) and of a few molecules containing doubly-bound nitrogen [*e.g.*, Robertson finds the ${=}N-$ angles in *trans*-azobenzene to be 121° (*J.*, 1939, 232), and Hughes finds 120° in dicyandiamide (*J. Amer. Chem. Soc.*, 1940, **62**, 1258), both by *X*-ray diffraction methods].

It may be assumed that the alkyl groups are disposed in the *trans*-configuration about the double bond in aliphatic aldimines, as is found with benzylideneaniline (de Gaouck and Le Fèvre, *J.*, 1938, 741). Thus if the alkyl group moments, being opposed, cancel, we are left with three bond moments, H–C, C=N, and N=C, which have a resultant of 1·54—1·67. The direction of the C=N bond moment may be assumed to be the same as that of the C–N and C≡N moments (*i.e.*, C^+N^-); so its evaluation consists in the solution of a vector quadrilateral. A trigonometrical solution gives the values 1·38 and 1·52 for the C=N bond moment, according as the lowest or highest aldimine moment is taken, or 1·44 from the arithmetic mean, 1·59, of all the aldimine moments.

This bond moment may be compared with those of C–N (0·45) and C≡N (3·2 from solution measurements, 3·6 from gas). The moments of carbon–nitrogen bonds evidently do not rise linearly with the multiplicity as do the energies (Pauling, " Nature of the Chemical Bond," Cornell, 2nd ed., 1940, pp. 53, 131); on the contrary, the difference between the triple and the double bond moments markedly exceeds that between the double and the single. This may be because the C≡N bond owes its large polarity chiefly to the atomic dipole provided by the unshared electrons on the nitrogen (see Coates and Sutton, *J.*, 1948, 1187). If this be so, it lends weight to Cowley and Partington's explanation (*loc. cit.*) of the fact that, despite the large polarising power of the cyanide group, alkyl cyanides higher than methyl have the same moment: they suggested that this was due to the location of the dipole far away from the attached alkyl groups.

The C=N bond moment is a little more than half as polar as the C=O (2·4), and the same is true of the single bond moments. This parallels the electronegativity differences of carbon and nitrogen and of carbon and oxygen, which are in the approximate ratio of 1 : 2.

It is noteworthy that the indication given by the present work, of the decrease in the polarity of the C=N bond with increase in the molecular weight of the amine, and a statement by Coates and Sutton (*loc. cit.*) that " . . .thermal data suggest that the C=N bond heat of formation will be large in imines only when it has large alkyl groups attached," may appear to be related by a principle enunciated by Walsh (*J.*, 1948, 398), that the more polar a bond is the weaker it is. Both the moment attributed to the C=N bond and its heat of formation are, however, residual, formal values. It would be better to say that the moment of the  $-\overset{H}{\overset{|}{C}}{=}N-\overset{H}{\overset{|}{\underset{H}{C}}}-\overset{|}{\underset{|}{C}}-$ grouping decreases when its heat of formation increases. Our view of the former change is that it is due to one bond increasing in polarity while another decreases; and we cannot attribute the latter change to any one bond. Such a comparison, therefore, does not provide unambiguous support for Walsh's principle.

The moment of the C=N bond in aromatic aldimines might perhaps be expected to differ from that found above. We must, however, be quite clear what we mean by it. It may be defined in two ways: (1) That moment which, when vectorially added to the H–C bond moment, the Ph–N σ-bond moment *, and the total mesomeric moment, gives the correct magnitude and direction to the observed moment of the molecule; this definition gives a quantity which excludes the mesomeric effect; it therefore closely corresponds to the thermochemical quantity, bond energy term, and like it should be constant. It may be distinctively labelled the *bond moment term.* (2) That moment which gives the observed total moment when vectorially added to that of the H–C bond and to one in the direction of the Ph–N bond which is the algebraic sum of the Ph–N σ-bond moment and such mesomeric moment as there is in this line. This quantity might throw light on the actual electronic state of the C=N bond in this particular molecule; it would be expected to vary from one molecule to another, and it might be relevant to any relation between bond moment and local bond properties.

The direction of the benzylideneaniline moment can be got from the moments of this substance (1·57) and of either *p*-chlorobenzylideneaniline (1·77) or *p*-chlorobenzylidene-*p*-toluidine (2·06) (de Gaouck and Le Fèvre, *loc. cit.*) with either chlorobenzene (1·55) or *p*-chlorotoluene (calculated as 1·95): the two values agree within 2°. We need next to know the directions of all the bonds, the moment of the H–C bond and, for definition (1) above, the direction of the mesomeric moment in the molecule as a whole and the σ-bond moment of Ph–N (*i.e.*, excluding mesomeric moment). We assume as before that bonds around the carbon and nitrogen atoms have regular trigonal symmetry, that the H–C and Ph–N σ-bond moments

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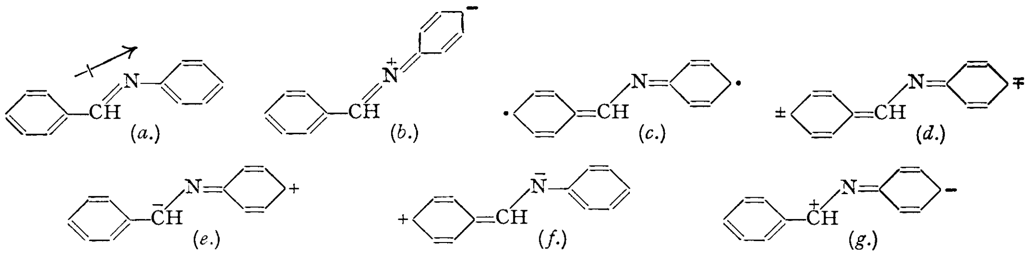
* This excludes the C–H bond moment of the Ph group because it is balanced by that in the other Ph group.

are 0·4 and 0·45 respectively, and that the direction * of the mesomeric dipole is from either of the central atoms to approximately the centre of the remote benzene ring (see below). The vector polygons are then solved. We find that by definition (1) the C=N moment is 1·06 and the mesomeric moment is 0·68 in the sense shown over structure (*a*); by definition (2) the former is 1·30.



The justification for ascribing the above direction to the mesomeric moment is the following. Coates and Sutton (*loc. cit.*) have pointed out that a structure of type (*b*) would be unimportant in benzylideneaniline because it would require the molecule to be differently shaped; so contributions from it must be ignored, though they would assist in explaining the sign of the mesomeric moment. The important types of structure are likely to be (*a*), (*c*), (*d*), (*e*), (*f*), and (*g*), of which (*a*), (*c*), and (*d*) make no contribution to the mesomeric moment; (*e*) would give a moment in the opposite sense to that observed; and (*f*) and (*g*) would give the observed sense. It is inferred that (*f*) and (*g*) together are more important contributors to the hybrid than (*e*), as would be expected from the electronegativity of nitrogen being greater than that of carbon.

When structures with charges on the *ortho*-positions are also taken into account, it appears that the most likely position of a mesomeric charge centroid in a ring is at about the centre; but there is some uncertainty in this, hence in the direction of the mesomeric moment, and so in the moments we have given under definition (1). We estimate this uncertainty to be $\pm 0{\cdot}1$.

The apparent reduction of the C=N bond moment term in benzylideneaniline from the pure double-bond value (1·44) towards that of the pure single bond (0·45) must be due to some other cause than mesomerism (the effect of which has been separately assessed). This cause is probably to be sought in the different states of hybridisation of the bond orbitals in the aliphatic and aromatic molecules. It is noteworthy that the bond energy term of this C=N bond (96 kcals.) is also reduced from the pure double-bond value (106) towards that of the pure single bond (52·5) (Coates and Sutton, *loc. cit.*).

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