DIPOLE MOMENT AND MOLECULAR STRUCTURE

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Received October 17, 1936

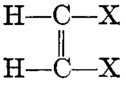
This subject is practically the growth of the last eight years. Several of us remember the eagerness with which we learned, at the meeting of the Bunsen Gesellschaft in Munich in 1928, what the moments of a few of the most familiar molecules were; we now know those of some twelve or fifteen hundred compounds.

The methods of measurement usually employed are well known; most of them depend on the determination of the molecular polarization of the substance, either as a gas or in dilute solution in a non-polar solvent; the electronic (and to a certain extent the atomic) polarization is eliminated by making the measurements over a considerable range of temperature, or by observing the refractivity in the visible, or sometimes by measuring the dielectric constant of the substance in the solid state. There are also one or two methods of an entirely different kind, which are of value in particular cases, as well as being important in confirming the general theory. The best known of these is the "molecular beam" method (41, 5; see also 8), an adaptation of the famous Stern and Gerlach experiments for the determination of the magnetic moments of atoms. In this a thin ribbon of molecules at very low pressure is passed through a highly inhomogeneous electric field, and from the observed spreading of the beam an approximate value of the dipole moment can be obtained. A still more recent and as yet little developed method is that depending on the determination of the dielectric losses, that is, of the energy lost as heat when the substance is exposed to a rapidly alternating electric field (3).

The investigation of the dipole moment in its relation to the structure, like that of all new physical properties, has been passing through two stages, the first more or less qualitative, and the second quantitative. There was a whole series of structural problems in which the moments of the alternative structures differed so widely that a rough measurement of the moment was enough to decide between them. The extreme cases were where one of the alternative formulas was polar and the other non-polar. In many of these the conclusions derived from the dipole measurements have been confirmed and extended by other methods, such as those depending on the absorption spectra and the crystal structures, but the dipole method was among the earliest to give us the information we needed. Examples of various structures established in this way are the following: symmetrical (not pyramidal), methane, carbon tetrachloride, and the XCl_4 compounds in general; plane, bismuth trichloride; pyramidal, ammonia, phosphine, phosphorus trichloride; linear, carbon dioxide, carbon disulfide; triangular, water, sulfur dioxide.

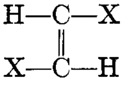
Then there were a variety of more special types of molecules, where the alternative structures that were chemically possible, though both polar, differed markedly in moment. Of fundamental importance here were the halogen hydrides—hydrogen chloride, hydrogen bromide, and hydrogen iodide—with the moments 1.03, 0.78, and 0.38 *D*, respectively (42), because of the light they threw on the distinction between covalent and electrovalent links. The distance between the atomic nuclei in gaseous hydrogen chloride has been shown to be 1.273 A.U. Hence if the molecule is ionized, and the charges can be regarded as located on the nuclei, its moment should be $4.77 \times 1.273 = 6.1\ D$. The actual value is 1.03 *D*, which is only 17 per cent of this. If the binding pair of electrons in H—Cl could be regarded as equally shared between the atoms the moment would of course be zero. It is thus evident that though the condition of the molecule is in some sense intermediate between the two extremes, it comes much nearer to the covalent state. This conclusion is supported by the observed values for other covalent links which are of the same order of magnitude, and also by the observation of Wrede (41) that the moments of true salts, such as the alkaline halides, in the gaseous state are much larger, and of the order of 10 *D*, their theoretical value for complete ionization being between 10 and 20 *D*.

The dipole evidence was also able to solve a variety of other problems of a less general kind: (*1*) The correct structures of the dihalogen substitution products of ethylene



$$\begin{array}{c}\mathrm{H{-}C{-}X}\\ \|\\ \mathrm{H{-}C{-}X}\end{array}$$

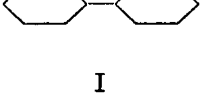
cis; polar



$$\begin{array}{c}\mathrm{H{-}C{-}X}\\ \|\\ \mathrm{X{-}C{-}H}\end{array}$$

trans; non-polar

could be assigned as soon as the moments had been measured, and this was done by Errera (4). (*2*) In the same way the *trans*-configuration of azobenzene was definitely proved by showing that it is non-polar (2). (*3*) The formula (II)



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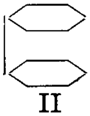
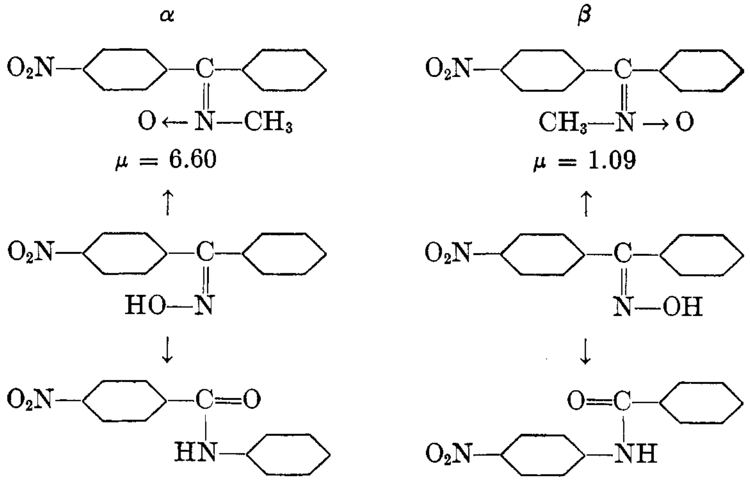


II

proposed by Kaufler for diphenyl was shown by the work of Williams, Weissberger, and Sängewald (40, 35, 38) to be impossible. They showed that the moments of the *p,p'*-diderivatives are practically identical with those of the *p*-disubstituted benzenes having the same substituents; where the moment of the substituent group is symmetrical to the central line of the molecule the compound is non-polar, otherwise it is polar. It follows that the Kaufler formula must be given up, and that the two phenyl groups lie in the same plane (formula I). (*4*) The controversy as to the structures of the isomeric oximes, between the original Hantzsch–Werner view and that of Meisenheimer, was finally settled in favor of the latter by the measurement of the moments of the oxime ethers. Taylor and Sutton (33) showed, for example, that the isomeric α- and β-*N*-methyl ethers of *p*-nitrobenzophenone had moments of 6.60 and 1.09 *D*, respectively; this made it clear that in the former the highly polar $—NO_2$ and N→O groups were acting in the same direction, while in the latter they were opposed to one another. Since the former ether is obtained from the oxime which in the Beckmann reaction is converted into the anilide of *p*-nitrobenzoic acid, it follows that the Beckmann change is a *trans* and not a *cis* migration, and that Meisenheimer's view is correct:

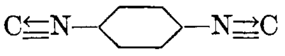


(*5*) The plane structures of the benzene and naphthalene molecules were established by means of the moments of their derivatives before they had been proved by the crystal structure. For benzene this was implicit in the very ingenious method used by Williams (37) to determine the direction of the moments of groups by balancing them against one another in the para position in benzene; and its truth was shown by his discovery that both the compounds p-$C_6H_4X_2$ and 1, 3, 5,-$C_6H_3X_3$ always had approximately zero moment if the C–X dipoles lay in the direction of the valence joining C to the next atom of the X group. For naphthalene the decisive test is the moment of the 2,6-di derivative (39; for more recent work on the naphthalene derivatives see reference 34). (*6*) The structure of the divalent carbon compounds, such as carbon monoxide and the isocyanides, was investigated by means of the moments, which entirely confirmed the structures proposed by Langmuir, as opposed to those of Nef (10; see also 20):

Structures proposed by Nef: $\mathrm{C{=}O}$ $\mathrm{R{-}N{=}C}$

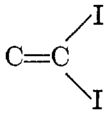
Structures proposed by Langmuir: $\left\{\begin{array}{ll}\mathrm{C}\overset{\leftarrow}{\equiv}\mathrm{O} & \mathrm{R{-}N}\overset{\rightarrow}{\equiv}\mathrm{C}\\ \overset{-}{\mathrm{C}}\equiv\overset{+}{\mathrm{O}} & \mathrm{R{-}}\overset{+}{\mathrm{N}}\equiv\overset{-}{\mathrm{C}}\end{array}\right.$

The essential points are the minute polarity of carbon monoxide, showing that there has been an electronic transference from the oxygen to the carbon, and in the isocyanides the magnitude and direction of the moment of the —N—C group, in which it was shown that the terminal carbon atom is at the negative end of the dipole, which supports the same view. A final test is the observation (30) that *p*-diisocyanobenzene is non-polar; this must be so according to the Langmuir structure (I) but not according to that of Nef (II).



I

II

(*7*) A question arising out of this is the structure of acetylene and its derivatives. Nef maintained that, in particular, diiodoacetylene had not the obvious linear structure I—C≡C—I, but the tautomeric form  .

The former should obviously be non-polar, while the latter should have a considerable moment. The substance was examined, and shown to be non-polar, so that it must have the linear formula (31).

With all these molecules the differences in the moments to be expected on the alternative theories are so large that quite rough determinations of the moments are sufficient to settle the questions at issue.

This stage of the investigations is nearly complete, and all the more obvious plums have been gathered, although we shall always have new problems arising which can be settled in this way. We have now entered on the more advanced and more quantitative branch of the subject, where we endeavor to draw conclusions from small differences of moment. Here we meet with various difficulties, which are essentially of two kinds, the first being in the accurate measurement of the moments, and the second in their interpretation.

The difficulties of measurement are two, one depending on the allowance to be made for the atomic polarization, and the other on the effect of the solvent.

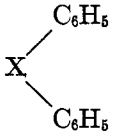
The atomic polarization for some time afforded a refuge to chemists who found moments that were incompatible with their preconceived ideas; it was always possible to explain them away by the supposition that some of the compounds in question had abnormally large atomic polarizations. Recently this loophole has been fairly well closed. The atomic polarization can be measured by determining the polarization in the gas over a considerable range of temperature, since P_E and P_A are independent of temperature, and so can be separated from P_0. Another method is to measure the dielectric constant of the solid, in which the orientation of the molecules is fixed, so that the polarization depends on P_E and P_A alone; this may however need some modification in view of the frequent rotation of atomic groups in crystals. The general result of these measurements has been to show that the atomic polarization is never large, and seldom, in molecules of the size with which we are ordinarily concerned, exceeds some 4 cc. or so (24, 26, 12).

The influence of the solvent on the polarization was first pointed out by Horst Müller (17), who showed that the value of P_α for chlorobenzene varied by about 10 per cent in different non-polar solvents, being greatest in those with the lowest dielectric constant. Subsequent work has shown that this phenomenon is practically universal, and further that it is highly specific, so that no general relation can be established for correcting the observed moment for the effect of the solvent. The influence depends, as we might expect, for any given solvent on the magnitude of the moment of the solute, and also on the shape of the polar molecules and the position which the dipole occupies in them. Higasi (11) and Frank (6) have tried with some success to examine the relation of these properties, but no complete theory has been reached, or is probably to be expected until the physical theory of liquids has been developed considerably further than it has at present.

This influence of the solvent also affects the accuracy of the determination of the moment by the temperature method in solution, which was previously regarded as exceptionally accurate, since it appears to determine and eliminate the atomic polarization. It is, however, obvious that, since the dielectric constant of the solvent changes with the temperature, the effect on the polarization of the solute will also change. The effect may not be large, but it may seriously change the slope of the polarization–temperature curve, and also the intercept. It will thus give a false value both of the moment and of the atomic polarization; moreover, owing to the highly specific character of the influence, it is not at present possible to apply a satisfactory correction. In the present state of our knowledge it seems that the accurate determination of the dipole moment is possible only by the measurement of the polarization of the gas over a large temperature range. The next best measurements are those obtained by determining the polarization of the vapor at one temperature, and allowing for the electron polarization through the refractivity.

It is evident that the restriction of accurate measurements to substances whose polarization can be measured in the gaseous state constitutes a very serious limitation of the applicability of the moments, and it is very much to be hoped that it will be possible to discover the general relation between the gaseous and the solution values, so that we may be able to assign moments to molecules that cannot be measured in the gaseous state.

The difficulties of the interpretation of the moments, are not, like those of measurement, obstacles to be got out of the way as soon as possible; they are due to the complications of the molecular structure itself, which is the problem we are trying to solve. They are mainly concerned with two factors,—the mutual polarization of the dipoles and the effects of resonance. One of the chief problems which have so far been attacked by the exact measurement of the moments is that of the valency angles. The resultant of two moments is their vector sum, and so if we know the individual values and the sum we know the angle between them. The difficulty is that the individual moments affect one another by induction; in the chloro derivatives of methane it has been shown (28) that the value may be diminished by as much as 30 per cent. This source of error can only be avoided by having the dipoles whose inclination is to be determined remote from one another. The theory has been discussed by Smallwood and Herzfeld (23) and by Frank (7); for its application in detail to the dichloronaphthalenes see Weissberger and Hampson (34). From this work it is clear that no satisfactory theoretical allowance for the mutual induction can be made unless the dipoles are more than 2 A.U. apart. In practice this means that we are almost confined to compounds of the type



where we can introduce polar groups into the para positions in the benzene rings with the certainty that the new dipoles will be collinear with the X–C valencies. This method has been applied by a number of workers with considerable success to such compounds as diphenylmethane, diphenyl ether, and diphenyl sulfide, and the consistency of the results indicates that it is on the whole trustworthy.[1] The importance of this work lies in the fact that the angle measured is that in which the valencies are attached to two phenyl groups; this may well differ from the angle between the valencies when they are joined to hydrogen or halogen atoms, or to methyl groups, for two reasons: (1) because of the steric interference of the phenyls, which again will vary with the radius of the central atom, and (2) because of the occurrence of resonance forms in which one of the valencies is double. A comparison of the valence angles in these various classes of compounds is thus of great interest. Now it is clear that in the simpler (halogen and alkyl) compounds the dipole method is useless on account of the mutual induction, while the method of electron diffraction is eminently suitable, owing to the relative simplicity of the molecules. In the phenyl derivatives on the other hand the large number of atoms in the molecule makes the calculation of the electron diffraction curves almost impossible, and the angles can only be determined from the dipole moments.

Another subject which has been attacked by the exact measurement of moments is that of the effect of rotating atomic groups, as for example in the ethylene dihalides. This is too complicated a subject to be dealt with here, but reference may be made to the work of L. Meyer (15), Smyth, Dornte, and Wilson (25), Lennard-Jones and Pike (13), and Altar (1).

The second difficulty in relating moment to structure arises from the effect of resonance, and this opens up the widest prospect for the future application of dipole moments.

I need say no more of the theory of reasonance than that it implies that certain molecules can have a structure intermediate between two formulas and partaking (but not necessarily in the same degree) of the properties of both. Some of the most convincing proofs of this theory are derived from the study of dipole moment. In no other way is it possible to explain the very small moments of nitrous oxide or of the azide group, where the only permissible structural formulas must have large moments in opposite directions. The simplest example is that of nitrous oxide. Here the spectrum shows that the molecule is linear, but not symmetrical. It must therefore be N—N—O, with either two double links, or one single and one triple. Assuming that so stable a substance must have its octets complete, there are two possible structures:

$$\overset{\longleftarrow\!\!\!\!-\!\!\!+}{\mathrm{N}\underline{\leftarrow}\mathrm{N}=\mathrm{O}} \qquad\qquad \overset{+\!\!\!\!-\!\!\!\!\longrightarrow}{\mathrm{N}\equiv\mathrm{N}\rightarrow\mathrm{O}}$$

Each of these will have a considerable dipole moment, and in opposite directions, as shown by the arrows. A tautomeric mixture of the two

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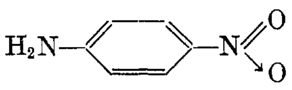
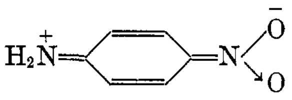
[1] For a summary of this work see reference 9; for a method of obviating certain difficulties due to resonance see reference 29.

will also be found to have a considerable moment, since the polarization, from which the moment is calculated, is independent of the direction. Now the observed moment of nitrous oxide is only 0.17 *D*; this would only be possible for a tautomeric mixture if the time of interconversion were less than that (ca. 10^{-12} sec.) required for the rotation of the dipoles in the electric field. This practically implies that the molecule is in an intermediate state, which is what we mean by resonance. This conclusion is supported by the dimensions of the nitrous oxide molecule, as deduced from the spectrum (18). Precisely similar arguments apply to the organic azides (21). This is evidently a phenomenon that is peculiarly suited to investigation by means of the dipole moments. It is also one that is of fundamental importance, especially to the organic chemist. The modern theories relating organic reactivity to electron drift, which we owe to Lapworth, Robinson, Ingold, and others, obviously find their physical explanation in the theory of resonance, and should be capable of verification and extension by the dipole methods.

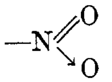
The first example of this is given by Sutton's examination (27) of the difference in moments of the alkyl and aryl compounds R—X, in which he showed that the sign of this difference determined whether further substitution occurred in the meta or in the ortho and para positions; this gave an experimental proof of the occurrence of an electronic drift which governed the reactivity.[2]

More recently, the investigation of resonance by means of dipole measurements has been pursued along a variety of lines. For example, it is known that *p*-nitroaniline has the abnormally high dipole moment of 6.2 *D*, exceeding by about 0.7 *D* the sum of those of aniline (1.52) and nitrobenzene (3.95). This is clearly due to resonance between the forms



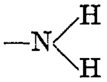


and this involves both the



$-NO_2$

and the



$-NH_2$

groups in the second formula lying in the plane of the ring. If it were possible to deflect these groups, or either of them, out of that plane, the resonance, and therefore the dipole moment, should be diminished. Now we have evidence that in durene (symmetrical tetramethylbenzene) the

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[2] For attempts toward a theoretical correlation of the resonance with the reactivity see references 32, 14, and 36.

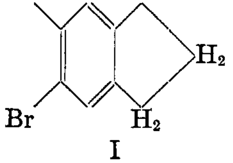
methyl groups should have this effect on an NH_2 or NO_2 placed between them, for in durene itself it has been shown, by x-ray analysis of the crystal (19), that the repulsion of the methyl groups is sufficient to deflect them some 3° from their normal positions. We should therefore expect to find that the moment of *p*-aminonitrodurene is less than that of *p*-nitroaniline, and that a similar reduction of moment occurred with the amino and also with the nitro compounds generally. This question has been investigated by Hampson and Birtles (unpublished work), who found the moments given in table 1 for the durene derivatives as compared with their benzene analogues. It will be seen that in every instance the methyl groups diminish the moment caused by NH_2 or NO_2, but that with the bromo compound, where no such interference with the resonance can occur, the moments of the durene and the benzene derivatives are identical.

TABLE 1

Moments of certain durene and benzene derivatives

GROUP	DURENE	BENZENE	DIFFERENCE
Nitro-	3.38	3.95	−0.57
Amino-	1.39	1.55	−0.16
Bromo-	1.55	1.52	+0.03
p-Nitroamino-	4.98	6.2	−1.2
p-Bromonitro-	2.36	2.65	−0.29
p-Bromoamino-	2.75	2.99	−0.24

Another question which can be examined by means of the moments is the effect of side rings on the resonance between the Kekulé structures in benzene. Mills and Nixon (16) pointed out that the addition of a side ring of five atoms to benzene, in hydrindene, may, for steric reasons, fix the double links in the benzene ring, with a single link common to the two rings; on the other hand a side ring of six atoms, as in tetralin, might also fix the benzene links, but with a double link common to the two rings. From the reactivities of certain derivatives they obtained evidence in favor of the occurrence of fixation of the links in these ways. It should be possible to test these conclusions by means of the dipole moments of the symmetrical compounds 5,6-dibromohydrindene (I) and 6,7-dibromotetralin (II). If



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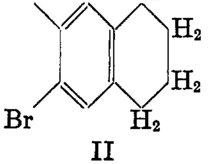

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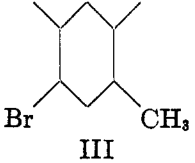


III

the links are fixed as Mills and Nixon suggest, the angle between the C–Br valencies should be larger in I than in II, and hence the moments of the systems should differ by an amount which can be calculated within narrow limits and which should be easily detected experimentally. The moments have been measured (22), and compared with those of the corresponding *o*-xylene derivative (III above) and of *o*-dibromobenzene. The results are given in table 2. The moment of the Br—C—C—Br system is obtained by subtracting from the moment of the dibromide that of the parent hydrocarbon together with a small correction (less than 0.2 *D*; see references 23, 7, 34) for the moment induced in the side system by the C–Br links.

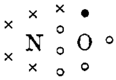
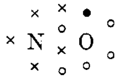
TABLE 2

Dipole moments

TYPE	MOMENT OF HYDROCARBON	MOMENT OF DIBROMIDE	INDUCED MOMENT	MOMENT OF Br—C—C—Br
Hydrindene	0.53	2.48	0.17	1.78
Tetralin	0.52	2.81	0.18	2.11
o-Xylene	0.59	2.86	0.14	2.13
Benzene	0	2.12	0	2.12

TABLE 3

Effect of resonance on moment

COMPOUND	RESONANCE STRUCTURES ⟵+	+⟶	OBSERVED MOMENT
Carbon monoxide	$C\overset{\leftarrow}{\equiv}O$	$C=O$	0.10 *D*
Nitric oxide			0.16 *D*
Nitrous oxide	$N\overset{\leftarrow}{-}N=O$	$N\equiv N\rightarrow O$	0.17 *D*
Organic azides	$—N\leftarrow N\equiv N$	$—N=N\underset{\rightarrow}{=}N$	ca. 0

Thus the dipole moments clearly indicate a fixation of the double links in the sense of the Mills–Nixon theory in the hydrindene system, but not in that of tetralin, where the structure appears to be the same as in the freely resonating systems of benzene and xylene. On the other hand in tetralin the evidence of Mills and Nixon leads to a different conclusion; it indicates that fixation occurs here too, though with a double link common to the two rings. It should be noticed that the evidence from the dipole moments is of a different kind from that derived from the reactivity. In the latter, a relatively small difference in the heat of activation between two molecules may produce a large change in the rate of reaction, as was pointed out by Sutton and Pauling (32), who concluded that a difference of 6 per cent in the ratio of the coefficients (i.e., in the predominance) of the two Kekulé forms was enough to account for the experimental results of Mills and Nixon. The moments, on the other hand, express the mean position of the atoms in the resting molecule.

In conclusion I may mention one or two points which have arisen from the study of dipole moments, and which still seem to need explanation.

The first concerns the coördinate, semipolar, or dative link. It has been established by a number of examples that this type of link always has a large dipole moment, as its formulation requires. But the moments which are found are much smaller than those required by the simple theory of the transference of an electron. The actual values found vary in different molecules, and often cannot be stated with any exactness, but on the average we take the moment to be about 3 to 4 *D*. Now the average length of the link in these compounds is about 1.5 A.U., so that if the coördination simply involved the transference of an electron from one atom to the other, the moment should be approximately $4.8 \times 1.5 = 7.2\ D$. The observed difference is presumably due to induction, in which the unshared electrons of the octet no doubt play a large part.

Another point is this. As we have seen, when there are two resonance structures with moments in opposite directions, the result of the resonance is to diminish the moment. The amount of the reduction should be different in every case, depending on the coefficients of the different structures and also on their respective moments, and we have no means of knowing how great it should be. The interesting point is that there is in fact a remarkable tendency for the resulting moment to be very nearly, but not quite, zero. Of this we have at least four examples (see table 3); in the last of them the exact moment of the N_3 group is not known, but that of the whole $C—N_3$ group is very nearly the same as that of a C—N link, so that the contribution of the N_3 part must be very small.

I should like to express my thanks to Dr. L. E. Sutton and Dr. G. C. Hampson for the kind assistance that they have given me in the writing of this paper.

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