THE STRUCTURE OF MOLECULES AS REVEALED BY DIELECTRIC CONSTANT DATA

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There has been a tendency among American chemists to regard the electromagnetic properties of molecules as being of particular importance. Thus Langmuir (1) defines surface tension as a measure of the potential energy of the electromagnetic stray field which extends out from the surface layer of atoms. Harkins (2) speaks of an electromagnetic theory of surfaces and surface energy, and Lewis (3) finds little of value in the electrochemical viewpoint but elaborates a magnetochemical theory to account for the properties of molecules. On the other hand European scientists of the same period appear to have favored the electrostatic or electrochemical viewpoint. For example, Fraenkel (4) and Debye (5) have developed electrical theories of surface tension, the latter actually making considerable progress in calculating the magnitude of the surface tension in a number of cases; Guyot (6) and Frumkin (7) have studied the potential differences at interfaces for a considerable number of both aliphatic and aromatic compounds; and Debye (8) has successfully shown how one may have a dielectric constant, or rather a portion of it that varies with the absolute temperature if it be assumed that there exist permanent electrical dipoles in certain of the molecules. In recent years, with the impetus of results of dielectric constant studies such as are to be reported in this paper, the electrical nature of molecules seems again to be coming to the fore.

It would of course be desirable to be able to calculate the properties of molecules, inorganic as well as organic. We are certain that spatial considerations and calculations based on what the physicist calls classical mechanics are not fruitful. And whether it will be possible to calculate the properties of any but the simplest "dumbbell" type of molecules by means of the Heisenberg quantum mechanics or the Schroedinger wave mechanics still remains to be seen. Therefore, it seemed practical to determine certain fundamental properties of the molecules from experimental data which are related to the actual electrical structure.

The property of the molecule chosen in the work I am to report to you was the electric moment.

There are, as far as the author is aware, but two methods for the accurate determination of the electric moment of a molecule:

1. A study of the temperature variation of the dielectric constant of the molecule in the gaseous condition.

2. A study of the dielectric constant and density data for suitable binary mixtures, that is, dilute solutions in which the solvent is of zero polarity and the solute is the molecule in question.

The data to be discussed in this article were, unless otherwise indicated, obtained by the second method. The dipole theory, and, in addition, the method of calculation of an electric moment has been given in a previous paper (9). Therefore, it is necessary for me simply to give the equations and to define the symbols as they will be used in the rest of the article. The equations are as follows:

$$P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_1M_1 + f_2M_2}{d} = f_1P_1 + f_2P_2 \qquad (1)$$

where $P_{1,2}$ = molar polarization of the solution
P_1 = molar polarization of the solvent
P_2 = molar polarization of the solute
f_1 = mole fraction of the solvent
f_2 = mole fraction of the solute
M_1 = molecular weight of the solvent
M_2 = molecular weight of the solute
d = density of the solution
ϵ = dielectric constant of the solution.

The quantity, P_2 is obtained from the equation

$$P_2 = \frac{(P_{1,2} - f_1P_1)}{f_2} = P_2' + P_2'' \qquad (2)$$

The assumption is made in this method of treatment that the polarization due to the non-polar solvent is always directly proportional to its mole fraction in solution. The molar polarization of the solute, P_2, is obtained either by taking a tangent to the $P_{1,2}$ versus mole fraction of the solvent curve at the point where the mole fraction of the solvent is unity, and prolonging it until it cuts the axis where the mole fraction of the solute is unity, or by plotting a number of P_2 values obtained directly from equation (2) for dilute solutions and extrapolating the curve back to infinite dilution of the solute. In this manner the effect of a single solute molecule between the plates of the condenser is obtained, and effects which might be caused by an association of molecules are avoided. There must, of course, be no chemical reaction between solvent and solute.

In equation (2), P_2'' = polarization due to deformation of the molecule =

$$\frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M_2}{d'} \tag{3}$$

P_2' = polarization due to orientation of the molecule =

$$\frac{4\,\pi}{3} N \frac{\mu^2}{3\,kT} \tag{4}$$

where n_D = refractive index (D-line) for solute molecule
d' = density of solute molecule
N = Avogadro number = 6.06×10^{23}
μ = electric moment of the solute molecule
k = Boltzmann constant = 1.372×10^{-16}
T = Absolute temperature; in the work to be reported = 298°.

It will be evident that the polarization due to the deformation of the molecule cannot always be determined using the Lorentz-Lorenz formula at the temperature of the experiment; however, it is always possible to approximate this part of the total polarization in one of several ways, as follows:

1. By adding the individual atomic refractivities, making proper allowance for different types of linkages.

2. By determining the refractive index and density of the substance at some other temperature. (P_2'' is practically independent of state. Thus, for ethyl alcohol in the vapor state, $P_2'' = 13.2$ cc. and for ethyl alcohol in the liquid state, $P_2'' = 12.8$ cc.)

3. By following the suggestion of Errera that

$$P_2'' = \frac{\bar{\epsilon} - 1}{\bar{\epsilon} + 2} \frac{M_2}{\bar{d}},$$

where $\bar{\epsilon}$ and $\bar{d}$ are the dielectric constant and density of the molecule in question in its solid state.

Having the total molar polarization of the solute molecule and that part of the polarization which is due to the deformation of the molecule, the part of the polarization due to the orientation of the molecule is readily obtained. The calculation of the electric moment follows directly from equation (4). The effect of any atomic polarization has been neglected in the results to follow, since it is generally of the order of magnitude of the error in P_2'', and is without significance for the work to be discussed in this article.

One might expect that the electric moment of a molecule determined in different non-polar solvents might vary somewhat, since the dielectric constant of the solvent changes. It may be said, however, that within the limits of the experimental error of a series of determinations for which all the precautions of precision measurements were taken, such is not the case. In other words the molar polarization, and therefore the electric moment of a solute molecule, is independent of the non-polar solvent used. This fact is illustrated in table 1 (9).

The purpose of this paper is two-fold:

I. To discuss the use of electric moment data in giving information concerning the structure of molecules.

II. To discuss the relation between the results of these studies and certain other well-known phenomena of physics and physical chemistry.

PART I

The material to be treated in this part has been divided into the following sections:

a. Mono-, di-, and tri-substituted benzenes.

b. Derivatives of diphenyl.

c. Derivatives of methane in which all four valences are satisfied by like atoms or groups of atoms. Type $C\alpha_4$.

d. Typical inorganic molecules.

The data to be used in the discussion are, with few exceptions, those of the author and his collaborators (10) and are presented in table 2. Where other data are used in the text they will be introduced with suitable references.

TABLE 1

Polarization in non-polar solvents

MOLECULE	P_2	P_2''	P_2'	$\mu \times 10^{18}$
Solvent: benzene (ϵ = 2.280)				
Nitrobenzene	348.0	32.0	316.0	3.90
Chlorobenzene	82.0	31.0	51.0	1.52
Phenol	89.0	27.5	61.5	1.70
Solvent: carbon disulphide (ϵ = 2.633)				
Nitrobenzene	346.0	32.0	314.0	3.89
Chlorobenzene	82.5	31.0	51.5	1.52
Phenol	83.6	27.5	56.1	1.64
Naphthalene	54.0	43.5	10.5	0.69
Solvent: hexane (ϵ = 1.904)				
Nitrobenzene	346.0	32.0	314.0	3.89
Chlorobenzene	84.0	31.0	53.0	1.55
Naphthalene	55.0	43.5	11.5	0.72

a. Mono-, di-, and tri-substituted benzenes

Benzene itself is a typical non-polar molecule, but when one of its hydrogen atoms is replaced by any other atom or by a group of atoms a polar molecule will be formed. Thus, the introduction of a chlorine atom, a methyl group, a hydroxyl group, etc., will cause the formation of a molecule whose polarity is quantitatively measured by the magnitude of its electric moment. Sufficient electric moment data are now available to indicate

TABLE 2

Electric moments of some derivatives of benzene, diphenyl and methane, and also of some typical inorganic molecules

MOLECULE	P_2	P_2''	P_2'	$\mu \times 10^{18}$
Solvent: benzene (25°C)				
Toluene	36.3	30.3	6.0	0.52
o-Xylene	40.8	35.0	5.8	0.52
p-Xylene	36.7	35.5	1.2	0.06
o-Dinitrobenzene	800	35	765	6.05
m-Dinitrobenzene	338	35	303	3.81
p-Dinitrobenzene	37.0	34	3	0.32
1,3,5-Trinitrobenzene	55.0	40	15.0	0.80
o-Nitrotoluene	331	38	293	3.75
m-Nitrotoluene	407	38	369	4.20
p-Nitrotoluene	463	38	425	4.50
Benzoic acid	43.5	24.6	18.9	1.0
Bromobenzene	82	33	49	1.5
Benzaldehyde	190	35	155	2.75
p-Nitrobenzaldehyde	158	38	120	2.4
p-Nitrobenzoic acid	300	40	260	3.5
p-Chlorobromobenzene	40	39	1	0.2
o-Cresyl methyl ether	57	37	20	1.0
m-Cresyl methyl ether	65	37	28	1.17
p-Cresyl methyl ether	68	37	31	1.20
o-Cresol	74	32	42	1.44
m-Cresol	84	32	52	1.60
p-Cresol	87	32	55	1.64
o-Chlorophenol	68	34	34	1.3
m-Chlorophenol	130	34	96	2.17
p-Chlorophenol	148	34	114	2.4
o-Nitrophenol	235	33	202	3.1
m-Nitrophenol	348	33	315	3.9
p-Nitrophenol	563	33	530	5.05
p-Phenylenediamine*	45	35	10	0.7
Hydroquinone diethyl ether	116	50	65	1.7
Hydroquinone diacetate	150	50	100	2.2
Terephthalic acid dimethyl ester	152	50	102	2.2
Mesitylene	42	41	1	0.2
1,3,5,-Triethylbenzene	56	55	1	0.2
Phloroglucinol trimethyl ether	130	55	75	1.8
Phloroglucinol triacetate	185	65	120	2.4
Diphenyl	50	50	0	0
4,4′-Dichlorodiphenyl	63	63	0	0
4,4′-Dinitrodiphenyl	65	65	0	0
4,4′-Diaminodiphenyl	100	60	40	1.3

TABLE 2—*Concluded*

MOLECULE	P_2	P_2''	P_2'	$\mu \times 10^{18}$
Solvent: benzene (25°C)—*Concluded*				
4,4'-Diethoxydiphenyl	150	75	75	1.9
4,4'-Diacetylphenyl	155	80	75	1.9
Hexane	30.5	29.6	0.9	0.05
Carbon disulphide	22.2	21.1	1.1	0.06
Chloroform	47.5	21.3	26.2	1.10
Carbon tetrachloride	28.2	28.3	0	0
Ethyl ether	54.5	23.0	31.5	1.22
Iodine	60.2	28.0	32.2	1.2
Stannic iodide	26.7	30	0	0
Silver perchlorate	477.0	16	461.0	4.7
Water	64	4	60	1.7
Antimony triiodide	80	76	4	0.4
Tetranitromethane	32.5	31	1.5	0.2
Pentaerythritol tetrabromide	56	56	0	0
Pentaerythritol tetraacetate	140	70	70	1.9
Solvent: carbon tetrachloride				
Benzene	26.7	25.8	0.9	0.06
Toluene	33.7	30.3	3.4	0.40
Chloroform	49.8	21.3	28.5	1.15
Ethyl ether	56.0	23.0	33.0	1.24
Methyl acetate	78.0	18.0	60.0	1.67
Ethyl acetate	87.0	22.2	64.8	1.74
Acetone	170.0	16.0	154.0	2.70
Ethyl alcohol	73.5	16.0	57.5	1.63
Isoamyl alcohol	86.0	13.0	73.0	1.85

* Redetermination of the electric moment of this molecule gives a value slightly higher than that originally reported (J. Am. Chem. Soc. 50, 2332 (1928)). The substance is so difficulty soluble in benzene that an exact determination is impossible with the apparatus now available. The value given, however, must be approximately correct. Thus, the original conclusion with regard to the structure of the benzidene molecule is unchanged.

that an atom or group of atoms when introduced into a molecule may be considered as an electrical vector, having both magnitude and direction. The idea to be conveyed here is that each atom or group is characterized by a more or less definite moment, and not that each will always necessarily produce exactly the same moment when introduced into methane, ethane, benzene, or a hydrogen molecule. This is evident from table 3.

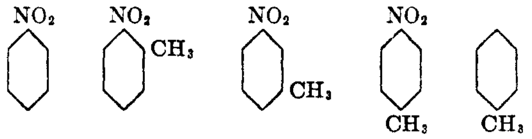
Thus, the introduction of an OH group into methane, benzene and hydrogen gives a moment of magnitude, $\mu = 1.65 \times 10^{-18}$ e.s.u., and the introduction of an NH_2 group into benzene and hydrogen gives a moment of magnitude, $\mu = 1.5 \times 10^{-18}$ e.s.u. This agreement is, however, probably due to internal compensations. There are many ways in which the vector value of the group may be altered, since when such an atom or group is introduced the number of electrons present in the molecule is changed.

TABLE 3

Substitution of atoms in non-polar molecules

ATOM OR GROUP	ELECTRIC MOMENT $\times 10^{18}$		
	For $C_6H_5\alpha$	For $CH_3\alpha$	For $H\alpha$
Cl	1.52	2.0 (14)	1.04 (11)
Br	1.51	1.86	0.79 (11)
I		1.6	0.38 (11)
CN	3.85	3.4	
OH	1.65	1.64	1.7
NO_2	3.9	3.1 (12)	
NH_2	1.5		1.53 (13)

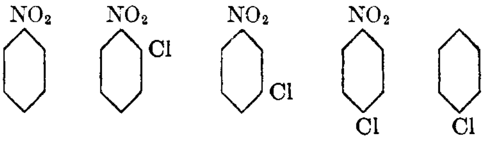
When two of these groups are substituted in benzene, the second in various positions with respect to the first, it is possible to assign an electrical character to each of these groups, the only limitation being that one of the groups must be used as a reference. The table to be presented was formed making the assumption that the methyl group is positive in nature. From the data for the nitrotoluenes it will be evident that if the CH_3 group has a positive character, the NO_2 group must have a negative character.



$\mu \times 10^{18} = 3.9$ 3.75 4.2 4.5 0.4

The moment of the nitrotoluene molecule steadily increases as the CH_3 group moves from the *ortho*, through the *meta*, to the *para* position.

The data for the chloronitrobenzenes, taken from Höjendahl (12), illustrate the fact that the Cl atom and NO_2 group exert like electrical effects, since as the Cl atom moves from the *ortho*, through the *meta*, to the *para* position the moment steadily decreases.

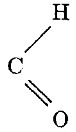
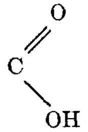


$\mu \times 10^{18} = 3.9$ 4.3 3.4 2.6 1.5

In this manner charges and approximate values have been assigned to certain atoms and groups. These are given in table 4.

TABLE 4

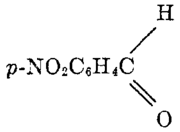
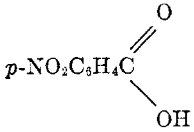
Characteristic moments of atoms or groups

GROUP	MOMENT	GROUP	MOMENT
NO_2	-3.9		
	-2.8		-0.9
OH	-1.7	CH_3	$+0.4$
Cl	-1.5	NH_2	$+1.5$
Br	-1.5		

Assuming for the present that we are dealing with a benzene molecule in which the six carbon atoms are found in a single plane, one might assume that the vectors characteristic of the various atoms or groups would also act in this plane. It is probable that in the case of the substitution of a single atom and in the case of certain very simple groups, this assumption will not lead to any particular difficulty, but the author wishes emphatically to point out that in general this assumption may not be made. These statements are of interest in connection with an article by Thomson (15), written before data such as are given in this paper were available. Thomson makes essentially the same assumption that is noted above in the statement, "neglecting the deflection of the two doublets due to their action on each other," which precedes the equations given to calculate the moment of disubstituted benzenes. These equations or their equivalents have been used by Höjendahl (16) to treat the data for the various chloronitrobenzenes and dinitrobenzenes and by Smyth and Morgan (17) to treat the data for the dichlorobenzenes and cresols. The data for the dichlorobenzenes, chloronitrobenzenes, and dinitrobenzenes could be treated in this manner because only atoms and simple groups are involved, but in the case of the cresols it was necessary to assume values for the CH_3 and OH groups which are hard to justify experimentally. The reason why these simple equations cannot be used in the case of the cresols appears to be that the stereochemistry of the oxygen atom of the hydroxyl group was not taken into account.

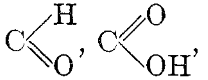
TABLE 5

Electric moment data for disubstituted benzenes

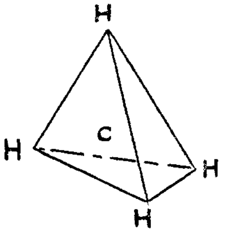
MOLECULE	OBSERVED MOMENT	CALCULATED MOMENT
 $p\text{-}NO_2C_6H_4CHO$	2.4×10^{-18}	1.1×10^{-18}
 $p\text{-}NO_2C_6H_4COOH$	3.5×10^{-18}	3.0×10^{-18}
$p\text{-}NO_2C_6H_4NH_2$	7.1×10^{-18}	5.4×10^{-18}
$p\text{-}ClC_6H_4OH$	2.4×10^{-18}	0.2×10^{-18}
$p\text{-}NO_2C_6H_4OH$	5.1×10^{-18}	2.2×10^{-18}

Further evidence that the assumption of vectors acting in the plane of the benzene ring is untenable is presented in table 5.

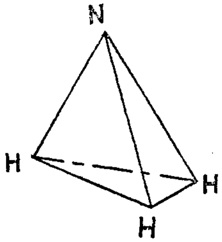
The conclusion to be drawn from these data is that in the case



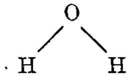
of $C\begin{matrix}H\\ O\end{matrix}$, $C\begin{matrix}O\\ OH\end{matrix}$, NH_2 and OH groups the vector is directed in space rather than in the plane of the benzene ring, due to the fact that it is joined to the benzene nucleus by a carbon, nitrogen or oxygen atom. The structure for the methane, ammonia, and water molecules has been worked out in more or less detail (18) and may be represented by the following diagrams:



Methane



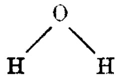
Ammonia



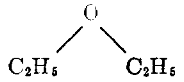
Water

This indicates that atoms and groups replacing the hydrogen atoms will be projected into space rather than in a plane; in the case under discussion, the plane of the benzene nucleus. Höjendahl (12) has termed such groups as those just mentioned "inclined" groups. Inclined groups must of course be in the great majority in chemistry.

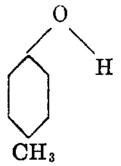
The writer has studied the stereochemistry of the oxygen atom by considering the effect of the substitution of several simple atoms or groups into the various positions in phenol. It is immediately evident that these compounds cannot be treated as derivatives of benzene in the simple sense referred to above (15). It has been pointed out (19) that the values obtained for the cresols and cresyl methyl ethers may best be accounted for by assuming that these compounds have a structure similar to that which has been proved for water and to that which has been assumed for the ethers. These different structures may be represented schematically as follows:



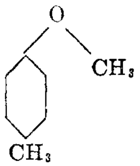
Water.



Ether.



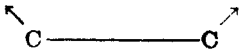
p-Cresol.



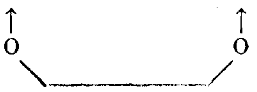
p-Cresyl methyl ether.

The electric moments for the chlorophenols and nitrophenols have been taken from unpublished data of Mr. Fogelberg, working with the writer at the University of Wisconsin. A glance at the results for these molecules, which have also been included in table 2, will show that the electric moment increases sharply when the hydroxyl group is moved from the *ortho*, through the *meta* to the *para* position. According to the equations of Thomson (15), based on the consideration of a simple benzene formula and a vector representation of the polarity of the substituent groups, the value should decrease sharply, in fact, in the case of *p*-chlorophenol, the electric moment should practically vanish. It is possible to account for the experimentally determined values when a structure similar to water and ether is assumed. A careful study of the infra-red absorption bands for these various substituted phenols should enable one to determine whether or not this structure is the correct one.

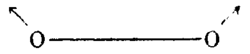
The data for certain like *para* di-substituted benzenes are of considerable interest because they also show the effect of the inclination of groups and interactions between them. According to the equations of Thomson, all like *para* di-substituted benzenes should have a zero moment. Reference to table 2 will show that in the cases of (1) the dimethyl ester of terephthalic acid, (2) hydroquinone diacetate, and (3) hydroquinone diethyl ether such is far from the truth. These molecules must have a structure similar to that indicated in the following diagrams



1.



2.



3.

It is probable, also, that the structure of hydroquinone should be given by one of these formulas. In the case of the derivatives of hydroquinone there is as yet no means of differentiating between formulas No. 2 and No. 3. The study of potential differences at interfaces has led Frumkin (20) to favor formula No. 3. At any rate the data for these compounds show clearly that the stereochemistry of the atom joined to the benzene nucleus, in this case, carbon and oxygen, respectively, must be considered.

It may be said from studies such as are reported in this article that both the carbon and oxygen atoms are tetrahedral in nature. It will be evident, also, that when the few data necessary become available the stereochemical properties of a number of other atoms may be worked out in some detail.

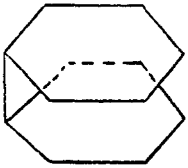
In connection with the discussion of these *para* substituted dioxybenzenes the writer would like to call attention to the fact that these results are *not* in contradiction to what one should expect on the basis of the classical stereochemistry, although this interpretation has been placed upon them by Ebert, Eisenschitz and v. Hartel (21). As has been pointed out, it is exactly this stereochemistry which would lead one to expect the results which have actually been found to exist.

The data for the symmetrical tri-substituted derivatives of benzene lead to definite conclusions concerning the structure of the benzene nucleus. If any of the formulas proposed by Körner (22), Baeyer (23), and Ladenburg (24) are correct, a finite electric moment for *every* like tri-substituted compound of the symmetrical type should result. The evidence is conclusive in the case of mesitylene and 1,3,5-triethylbenzene (see table 2) and in the case of 1,3,5-tribromobenzene (12) that no such moment results, a fact which clearly and definitely indicates that the six carbon atoms in the benzene nucleus lie in a single plane.

In the same way that it is possible for a like *para* disubstituted derivative of benzene to have a finite moment, it is also possible to have a like 1,3,5-trisubstituted derivative of benzene which will show a finite moment. The presence of a finite moment in the case of the two derivatives of phloroglucinol is indicated in the data of table 2.

b. Derivatives of diphenyl

A study of the chemical properties of diphenyl and its derivatives has led to interesting speculations concerning the structures of the various molecules. Adkins, Steinbring and Pickering (25), as a result of their chemical studies, conclude that the non-formation of the anhydrides is due to the fact that in the dinitro and dihydroxy acids the rings are extended as in the conventional formula, while in the amino or benzidine type of acids the rings are superimposed. Kuhn and Albrecht (26), discussing the same question, "come to the conclusion that it is not possible to explain diphenyl and its derivatives by means of a single space formula." In the case of the *p,p′*-disubstituted diphenyl compounds, two types of formula are discussed, as follows: (1) A formula in which the axes of the two benzene rings lie in a straight line; (2) A formula in which the axes of the two benzene rings make an angle with each other *or* are directed parallel to each other, as indicated in the following diagram.

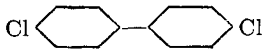


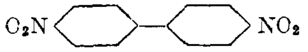
In the discussion of the results of electric moment studies for the various derivatives of diphenyl, it is necessary to consider the data not only for the particular derivatives of diphenyl but also for the corresponding derivatives of benzene. These data, with the exception of the value of the electric moment for *p*-dichlorobenzene which has been given by Smyth and Morgan (17) are given in table 2.

With regard to the structure of the several derivatives of diphenyl, the following statements may be made.

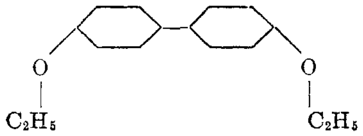
(1) Since the electric moments of the compounds *p*-dichlorobenzene and 4,4′-dichlorodiphenyl, and of *p*-dinitrobenzene and 4,4′-dinitrodiphenyl, are zero, and since the introduction of a single Cl atom or NO_2 group into the benzene nucleus causes

a highly unsymmetrical molecule, the conclusion is definite that in the case of the compounds, 4,4′-dichlorodiphenyl and 4,4′-dinitrodiphenyl the rings of the diphenyl nucleus are co-axial. They are represented diagrammatically in the following sketches.





(2) The electric moments of the compounds hydroquinone diethyl ether and 4,4′-diethoxydiphenyl (1.7 and 1.9 × 10^{-18} e.s.u., respectively) must be considered to be of the same order of magnitude. The reason why hydroquinone diethyl ether gives a finite moment has been discussed above. Since the magnitude of the moment of the corresponding diphenyl derivative is the same, it is highly probable that its structure is similar. The conclusion to be drawn from these considerations is, again, that the benzene rings are extended. This structure is suggested in the following diagram.



In this connection it may be pointed out that until more accurate experiments are available for this and similar substances, the possibility of a slight deformation from the extended position is not excluded.

(3) The electric moment data for the compounds *p*-phenylenediamine and 4,4′-diaminodiphenyl distinctly indicate a collapsed or perhaps folded structure for the latter substance, at least in benzene solution (27). The electric moment of the similar benzene derivative is small; thus there is only a slight tendency for the NH_2 groups to be bent from the plane of the benzene ring. 4,4′-Diaminodiphenyl has a comparatively large moment, $\mu = 1.3 \times 10^{-18}$ e.s.u. If the benzene rings of the diphenyl were extended, as has been shown to be the case for the dichloro-, dinitro- and diethoxy-derivatives, there can be little question that a much smaller moment would have resulted for the benzidine molecule as well.

Thus the electric moment data indicate the truth of the statement quoted above from the article of Adkins, Steinbring and Pickering, namely, that in the dinitro- and dihydroxy-derivatives of diphenyl the rings are extended as in the conventional formula, while in the amino or benzidine type the rings are folded. They are also in accord with the conclusions of Kuhn and Albrecht. It is evident, however, that these data are as yet insufficient to establish the general truth of these conclusions.

c. Derivatives of methane of type $C\alpha_4$

There are found in table 2 data for but four derivatives of methane of the type $C\alpha_4$. Electric moment data for molecules of this type are of great significance because of the structural considerations involved, and to properly discuss the point it will be necessary to introduce certain of the more numerous data of Ebert, Eisenschitz and v. Hartel (21) as well.

TABLE 6

Electric moment data for molecules of type $C\alpha_4$

MOLECULE	FINITE ELECTRIC MOMENT
$C(OCH_3)_4$	Present
$C(OC_2H_5)_4$	Present
$C(CH_2Cl)_4$	Absent
$C(CH_2OOCCH_3)_4$	Present
$C(COOCH_3)_4$	Present
$C(COOC_2H_5)_4$	Present
CCl_4	Absent

Until within recent years scientists had been satisfied with the classical idea of the tetrahedral carbon atom in spite of the fact that there could be no real evidence in its favor. When x-ray methods for the determination of the structure of matter were made available, it became important to show that the tetrahedral carbon atom actually did exist. This was readily accomplished. The question then arose as to whether or not the carbon atom might not also show different stereochemical properties from that of the tetrahedron, and it appeared, to certain investigators at least, that such was actually the case. For our present purpose it is necessary to mention only the papers on this subject by Weissenberg (28) in which it was claimed that polar molecules of the type $C\alpha_4$ possessed the symmetry of a pyramid instead of that of a tetrahedron.

The electric moment data for this type of compound may be conveniently divided into two classes; (1) those molecules whose electric moment is zero, and (2) those molecules which possess a finite electric moment. Concerning the interpretation of the results for the molecules of the first group, there can be no question. The four valences of the central carbon atom are directed toward the corners of a regular tetrahedron.

To account for the presence of a dipole moment in the case of molecules of the second group, two explanations have been given. The first, due to Ebert, Eisenschitz and v. Hartel (21) and to Weissenberg (28), assumes that the four valences of the central carbon atom are directed toward the corners of a regular pyramid. It can readily be seen that if the carbon atom may assume this form and the four valences are satisfied by like groups, a molecule possessing a finite dipole moment must result. This explanation denies the existence of the classical tetrahedral carbon atom in these particular cases.

The second explanation has been given by the writer (29) and by Höjendahl (12). It retains the idea of the tetrahedral carbon atom and accounts for the asymmetric properties of molecules of the second class now under discussion, as being caused by the stereochemistry of the groups which satisfy the four valences of the carbon atom and by the interaction between these groups as their lengths and complexities are increased. It may be pointed out that in every case of a molecule of the type $C\alpha_4$ known to date which has a finite moment there is an oxygen atom in each group, either attached directly to, or very close to, the central carbon atom. The effect of the presence of an oxygen atom in the various phenols and dioxy- and trioxybenzenes has been discussed at some length, and it is only reasonable to suppose that where such an atom is present in the part of each group directly attached to the central carbon atom of a molecule of the type $C\alpha_4$ a similar asymmetry may be introduced. Thus, such a molecule may have a tetrahedral central carbon atom and still be asymmetrical as a whole because the groups attached to the central atom are bent from the directions of the valences of the central tetrahedral carbon atom. In spite of the fact that Ebert, Eisenschitz and v. Hartel (21) do not calculate the exact dipole moments of their various compounds, a careful inspection of their data shows that as the length and complexity of the substituent group increases, the polarity of the molecule increases strongly. It would seem if the explanation of the pyramidal carbon atom were the correct one that an increase in the length of hydrocarbon chain would have little or no effect on the polarity of the molecule, as has actually been shown to be the case for the simple aliphatic alcohols and ketones. The data for $C(OCH_3)_4$, $\mu = 0.7 \times 10^{-18}$ e.s.u., and $C(OC_2H_5)_4$, $\mu = 1.1 \times 10^{-18}$ e.s.u., calculated from the polarization values given by Ebert, Eisenschitz and v. Hartel, show a distinct increase in polarity as the complexity of the molecule changes but slightly.

Further evidence for the explanation which retains the tetrahedral carbon atom and ascribes the polar properties of this class of molecules to properties of the substituent groups is to be found in the study of the surface properties of the molecule pentaerythritol tetrapalmitate reported by Adam (30). The cross-sectional area of this molecule was found to be 100×10^{-16} sq. cm., but was easily reducible by compression to 80×10^{-16} sq. cm., or almost exactly four times the cross-sectional area of a single closely packed hydrocarbon chain. The conclusion drawn by Adam was that the four chains (substituent groups) must lie parallel, two of them having been bent back through a large angle. Thus the four substituent groups are easily pliable and interactions between them could produce asymmetry in the molecule. This molecule differs from pentaerythritol tetraacetate, for which electric moment data are given by both Ebert and his co-workers (21) and in table 2, only by the lengths of the hydrocarbon chains.

To summarize, it may be pointed out that electric moment data for molecules of the types 1,4-$C_6H_4\alpha_2$, 1,3,5-$C_6H_3\alpha_3$, and $C\alpha_4$ are now available which indicate that in the case of very simple substituents, a symmetrical molecule is formed, but that as the substituents become more and more complex, asymmetrical molecules result. Complexity in groups seems in general to be caused by the presence of such atoms as oxygen (and it may be predicted that such atoms as sulphur, nitrogen, phosphorus and others will produce similar effects), which have definite spatial configurations, and by interactions between groups as their length and shapes change. The presence of finite dipole moments in molecules of these types need not disturb in any way our feeling for the simple configuration of the benzene nucleus with the six carbon atoms lying in a single plane, and the tetrahedral model of classical stereochemistry for the methane molecule.

d. Typical inorganic molecules

It might be predicted that the method which has been used to determine the electric moment of the molecules discussed to this point could not be used to determine the moments of inorganic molecules. This method, it will be recalled, depends upon a study of dielectric constant and density data for dilute solutions in which the solvent is non-polar in character. Such is, however, not the case, although it is true that there have been comparatively few such measurements made because the present experimental difficulties are greater. Inorganic molecules are generally but slightly soluble in such solvents as benzene, hexane, and carbon tetrachloride, but it is not at all impossible that other non-polar solvents which will dissolve this type of molecule can be found.

The value obtained for the water molecule from dielectric constant and density data for a saturated solution of water in benzene (31), $\mu = 1.7 \times 10^{-18}$ e.s.u., must probably be considered to be slightly in error because Sänger and Steiger (32), in a very careful and painstaking research, have obtained the value, $\mu = 1.85 \times 10^{-18}$ e.s.u., from a study of the temperature variation of the dielectric constant of water vapor. The accuracy of the result obtained from dielectric constant and density data for solutions depends very considerably upon the exactness with which the concentration of the solute in solution is known. In this particular case, since water is but difficulty soluble in benzene, it is extremely difficult to determine the solubility of water in benzene with a degree of accuracy sufficient for the purpose. The value used in the calculation was that of Hill (33), a value in good agreement with values which had previously been reported by Groschuff (34) and by Richards, Carver and Schumb (35). It is of interest that after this value was reported the results of a new solubility determination were communicated to the author, these results changing the value for the electric moment of water to 1.87×10^{-18} e.s.u., that is, practically the identical result of Sanger and Steiger.

The result for stannic iodide, $\mu = 0$, indicates that it has a structure similar to that which has been proposed for methane. The four iodine atoms are attached to the four valences of the tin atom at the corners of a regular tetrahedron. Thus it appears that the tetrahedral arrangement for atoms at the center of the periodic table (carbon, silicon, germanium, tin) is quite common.

Antimony triiodide appears to have a very small electric moment. In the series NH_3, $\mu = 1.5 \times 10^{-18}$ e.s.u., PH_3, $\mu = 0.5 \times 10^{-18}$ e.s.u., and AsH_3, $\mu = 0.15 \times 10^{-18}$ e.s.u., studied by Watson (36) it is apparent that as the size of an atom in any given group in the periodic table increases, the moment of any simple molecule in which this atom appears will decrease. This effect is also evident in the data for the halogen acids due to Zahn which have been presented in table 3, and in other data, and appears to be a quite general phenomenon. It is highly probable that all the atoms of Group V (nitrogen, phosphorus, arsenic, antimony) have their valences directed as shown in the diagram for ammonia which has previously been given.

Again, the electric moment for hydrogen sulphide, $\mu = 1.1 \times 10^{-18}$ e.s.u. (37), is considerably smaller than the moment of the water molecule, and it may be predicted that the moment for hydrogen selenide will be even smaller.

As yet there are but few data available for compounds of the metals of the first and second groups with strongly electronegative atoms or groups of atoms. The result for silver perchlorate, measured in benzene solution and given in table 2, indicates that these molecules will have a very high polarity. Thus, molecules formed by the atoms near the middle of the table are much less polar in character than those formed by the strongly electro-positive (and strongly electro-negative) groups; further, those molecules formed by atoms with the larger radii will be less polar than those formed by atoms with the smaller radii.

Therefore, in spite of the fact that so few data are as yet available, it seems possible to conclude that there is no abrupt transition between what have been termed homopolar and heteropolar linkages in molecules.

PART II

The material to be treated in this part shows the relation between the results of dielectric constant studies and

a. X-ray analysis.
b. Adsorbed film data.
c. Association.
d. Compound formation.

a. X-ray analysis

At first thought it might appear that it should always be possible to compare the results of such studies as have been described above, that is, data concerning the structure of molecules in the dissolved state, with their structure in the solid state as determined by x-ray analysis. A comparison of the results of both methods is now possible in a few cases, and it appears quite definitely that one may not assume that simply because a molecule is symmetrically built in the solid state it must also be symmetrical in the dissolved state, and vice versa. Indeed, this is not a surprising result when the nature of the forces operative in the case of a crystal is compared with the nature of the forces which would be expected in the case of a liquid or dissolved substance.

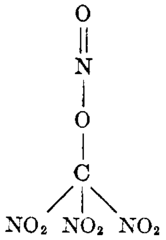
As examples of molecules in which the atoms are simply and symmetrically arranged about a central atom in both the solid and dissolved states, one may mention stannic iodide and carbon dioxide. The case of carbon dioxide is extremely interesting, because although the results of x-ray studies (38) have indicated without any question a linear and symmetrical arrangement of the three atoms which make up the molecule, it was thought that the molecule possessed a finite electric moment which would indicate a triangular arrangement of the atoms. Data for the infra-red absorption bands for carbon dioxide have led to both conclusions (39). Recently its electric moment has been redetermined by Stuart (40) who gives as his result the value, $\mu = 0$. The experimental work was carefully done, and it appears definitely that carbon dioxide has a zero moment. The temperature coefficient of the dielectric constant of the vapor was studied in this research. The three atoms must, therefore, have a linear and symmetrical arrangement in the gas phase as well as in the solid form.

The derivatives of methane of the type $C\alpha_4$ were studied in order to compare the results with those obtained from x-ray determinations. At the time the work was started there was considerable discussion about the structure of pentaerythritol, $C(CH_2OH)_4$. The early interpretations of the x-ray diagrams, due to Mark and Weissenberg (41) and to Huggins and Hendricks (42), appeared to indicate a structure in which the four carbon atoms attached to the central carbon atom were located in a plane. If this were correct, then one should expect that pentaerythritol, and perhaps also its simple halogen derivatives, $C(CH_2Cl)_4$ and $C(CH_2Br)_4$, should have finite electric moments. It is quite impossible to dissolve pentaerythritol in sufficient quantity in any of the non-polar solvents now commonly used for electric moment determinations, so that there are as yet no data available for this substance. The derivatives $C(CH_2Cl)_4$ and $C(CH_2Br)_4$ gave zero moments, indicating a tetrahedral rather than a pyramidal arrangement of groups about the central carbon atom. This does not mean, however, that pentaerythritol itself must have a zero moment; indeed, like hydroquinone and phloroglucinol, it probably has a small but finite moment.

By this time considerable curiosity had been aroused in this apparently new type of carbon atom in pentaerythritol, and the conclusions of Mark and Weissenberg and of Huggins and Hendricks were questioned, first by Nitta (43) and later by a number of other investigators, with the result that it is now definitely established that a mistake was made in the earlier interpretation of the diagrams.

A similar difficulty has appeared in the case of the tetraacetate of pentaerythritol, for which it will be recalled both Ebert, Eisenschitz and v. Hartel and the author (table 2) found rather large electric moments. Gerstäcker, Möller, and Reis (44) reported, as a result of their x-ray investigations, that in this molecule the four carbon atoms attached to the central carbon atom were to be found in a single plane. These conclusions have been questioned by Knaggs (45) who has shown beyond reasonable doubt that the interpretation of the previous experiments was incorrect, and that here again the central carbon atom has its four valences directed to the corners of a regular tetrahedron. The large electric moment of this molecule is explained by Ebert as being caused by a change in the form of the molecule as it is dissolved. The author feels, however, that the results of the x-ray and electric moment studies are in substantial agreement, each indicating that the central carbon atom is of the tetrahedral form, the molecule having a finite electric moment in solution because of the stereochemistry of the groups attached to this tetrahedral central carbon atom and because of interactions between them.

Tetranitromethane has been studied in both solid and dissolved states. As a result of their x-ray studies Mark and Noethling (46) conclude that the four NO_2 groups attached to the central carbon are not alike but are arranged as follows:



These authors point out that their result is in agreement with that obtained by earlier investigators who have studied the relation between various physical properties and the constitution of the molecule in the liquid state. The conclusion is perfectly definite, however, that the electric moment of the molecule is zero—in short, the two results appear to be directly in conflict.

The simplest case from the standpoint of the electric moment data is that of benzene. These data clearly indicate a structure in which all of the six carbon atoms lie in a single plane. From the results of x-ray studies, however, it appears at present impossible to decide in favor of either a plane or space arrangement of the carbon atoms. This point has been briefly discussed by Clark (47).

The comparison of the results of the two types of study is possible in certain other cases, all of which appear to be more difficult of interpretation and which will not be discussed here. Certain progress is being made by Mr. Greene, working in the author's laboratory, and will be reported in another place.

b. Adsorbed film data

The potential differences at interfaces in their relation to the polarity and orientation of molecules have been studied by several investigators (48) (49) (50). It is unfortunate that it is as yet impossible to compare accurate electric moment and potential difference at interface data for some simple molecule. Considerable progress has been made with electric moment data in the case of derivatives of benzene, but for this same type of compound interfacial potential difference data are meagre. On the other hand, interfacial potential difference data for compounds of the aliphatic type are numerous and lead to rather simple interpretations, but electric moment data are available in but comparatively few cases.

Rideal (50) calculates the electric moment of a molecule from interfacial potential difference data in the following manner. The potential difference at the interface must be due to the orientation of molecules which have a definite electric moment. This potential difference is, therefore, proportional to the electric moment of the molecule in question. It is further proportional to the number of molecules at the interface, that is, the surface concentration which may be calculated from the Gibbs adsorption isotherm. Therefore:

$$E = 4 \pi N \Gamma \mu$$

where E = potential difference at the interface.
N = Avogadro number = 6.06×10^{23}
Γ = surface concentration in gram molecules per square centimeter.
μ = electric moment of the molecule adsorbed at the interface.

For *n*-butyric acid Rideal calculates

$$\mu = \frac{1.16 \times 10^{-3}}{3.79 \times 10^{15}} = 0.3 \times 10^{-18}$$

In this calculation the assumption is made that the dielectric constant of the surface layer is unity.

The electric moment of *n*-butyric acid has not as yet been accurately determined from dielectric constant and density data, but it appears certain, from preliminary measurements of the author, that it will be of the order of magnitude, $\mu = 1 \times 10^{-18}$ e.s.u. It appears from these and other data which have not been introduced, that the electric moment determined by means of suitable dielectric constant studies will always be larger by a factor of from three to six than those obtained by the method outlined by Rideal. Further, the writer insists that the dielectric constant methods are the only methods now available by which quantitative electric moment data may be obtained. The chief difficulty in the method of Rideal appears to lie in the assumption of unit dielectric constant for the oriented molecule at the interface.

In order to explain why the electric moment of a molecule cannot at present be calculated from potential difference data, Frumkin and the writer (51) have suggested four possible reasons.

1. Incomplete orientation of the molecules at the interface.
2. A disturbing influence of the neighboring water molecules or ions.

3. To determine the values of the electric moment one must know the single potential difference, but the experiments give only a differential effect related to some arbitrary zero point.
4. The polarization of the oriented molecules by the neighboring molecules, assuming the orientation to be always complete.

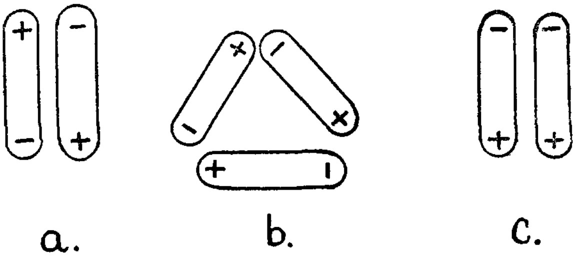
The fourth possibility appears to be the most promising one. If the oriented molecules are polarized by the presence of the neighboring molecules, that is, a polarization exactly analogous to the polarization due to the deformation of a molecule in the Debye theory, a dielectric constant of the order of magnitude of three or four, instead of one, might be accounted for. Suitable experiments have been designed to test this possibility and are being carried out in this laboratory.

Although this difference in the order of magnitude of the electric moment calculated from the two types of measurement is as yet incompletely accounted for, there are a number of marked parallelisms between the results of the different experimental studies:

1. The results in each case indicate that polar molecules may be considered to be made up of polar parts and non-polar parts—a conclusion of considerable importance for the study of molecular structure.
2. A definite electrical character, positive or negative, may be assigned to various atoms and groups of atoms which have been substituted into hydrocarbon residues by each method, and in all cases in which a simple interpretation is possible there is good agreement between the results of the two methods.
3. The order of magnitude of the electrical effects for the alcohols, ketones, acids and halogen derivatives appears to be relatively the same as the dipole effect for the same types of compounds. The somewhat greater relative electrical effects in the case of ethers and esters may be accounted for by the assumption of a more complete bending of the group, thus increasing the degree of orientation.

c. Association

One of the most difficult problems in chemistry is to define exactly what is meant by the term association when applied to a liquid. There have been numerous methods proposed by which it is supposed to be possible to calculate the degree of association. It has, however, always been a serious difficulty that the results obtained by the different methods have not always agreed. Discussion of the problem has been revived in recent years due to the rapid accumulation of electric moment data for the more common organic liquids, without doubt because Debye (52) has proposed a physical theory for association which depends on the mutual interaction of the dipoles of the liquid. In the neighborhood of these polar molecules there exist strong fields of force which tend to associate the molecules of the liquid. The effects of this association become evident in a study of the dielectric constant and density data for the binary mixtures from which the electric moments of the various solute molecules are calculated. It will be recalled that in the calculation the molar polarization of the solute molecule is determined by extrapolating the P_2 versus mole fraction of solute curve to the position which corresponds to infinite dilution, that is, to a concentration which corresponds to a single solute molecule dissolved in the inert solvent to avoid any effect due to association of solute molecules. The course of the P_2 versus mole fraction of solute curves indicates clearly the effect of several postulated types of association. Thus, if two molecules associate in the manner (a), or if three molecules associate in the manner (b), the molar polarization of the solute will decrease with increasing solute concentration. On the other hand, if two molecules associate in the manner (c), the molar polarization of the solute will increase with increasing solute concentration. Thus, an association of type (a) is sup-



posed to account for the behavior of nitrobenzene dissolved in benzene, while a combination of associations of types (b) and (c) is supposed to account for the behavior of ethyl alcohol dissolved in benzene. These cases have been discussed by Debye and will not be detailed here. It must, however, be repeated here that such considerations as these can be but qualitative in nature.

To illustrate the type of article now becoming popular the work of Rolinski (53) may be mentioned. This author outlines a method of calculating the degree of association, making use of a modification of the Debye-Clausius-Mosotti law which has been used to determine the electric moments reported in his article. The assumption is made that in the liquid studied, the resultant dipole moment of two associating molecules is exactly zero. The relation used by Rolinski is

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\,\pi}{3} N\,\gamma' + \frac{4\,\pi}{3} N_0 \frac{\mu^2}{3\,kT} \tag{5}$$

where γ' = constant, the polarization due to deformation
N = total number of molecules
N_0 = number of non-associated molecules
and the other symbols have their usual significance.

Using the electric moment found in the ordinary way, the degree of association, α, is given by the equation

$$\alpha = 1 - \frac{N_0}{N} \tag{6}$$

The difficulties with such a treatment have been discussed in some detail in another place (54). They may be summed up by saying that the mutual potential energy of two dipoles depends not only upon their magnitude, as is assumed by Rolinski, but also upon their arrangement and distance between them. Association must, therefore, be dependent also upon the shapes of the molecules, since it will determine the minimum distance to which the polar parts of a molecule may approach.

In conclusion, it may be said that while these considerations may give a qualitative measure of the degree of association and can distinguish various types of association, it has not as yet given a quantitative explanation. There appears to be absolutely no relation between the conclusions concerning association which have been drawn from cryoscopic measurements and those which result from a consideration of the polarization data for the same systems. The data for phenol may be mentioned. Freezing point measurements show a rapidly increasing molecular weight when this substance is dissolved in benzene, yet the molar polarization values calculated from dielectric constant and density data are perfectly constant over the same range of concentrations.

d. Compound formation

Considerable space has been devoted to a detailed discussion of electric moment data, and it has been shown that these data are intimately related to the results of other types of study. To suggest that the utility of this type of measurement is not limited to the several fields which have just been considered, the application to a field which is as yet practically untouched will be mentioned. Again, it is but one of several important problems about which dielectric constant studies should give important information.

In the previous section there was indicated the manner in which the association of like molecules became apparent from molar polarization data. It may be reasoned that if two substances which will combine to form a compound are dissolved together in a non-polar solvent, the molar polarization of the new compound will differ by a considerable amount from the average molar polarization of the two components, each measured separately. As far as the author is aware, such a study has been attempted in but a single case. Ebert (55) has shown that when ethyl alcohol and hydrochloric acid are mixed, the molar polarization obtained is considerably higher than that of either of the components, the interpretation being that a compound is formed between them. In order to explain the mechanism of many reactions in both inorganic and organic chemistry the existence of an intermediate compound is postulated; it would seem, therefore, that such a study as suggested would be invaluable in the detection of compound formation in solution. Definite progress has already been made on this problem in our laboratory.

In conclusion, it is my privilege to be able to acknowledge my indebtedness to Professor P. Debye for many valuable suggestions. A considerable portion of the experimental work reported herein was done in his laboratory. It is also a pleasure to acknowledge the contributions of a number of my students, both past and present.

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