Summary

1. The number of molecules of gas uncondensed by liquid air formed per quantum absorbed has been determined for the photochemical decomposition of both liquid and gaseous formic acid. A similar determination of the number of additional molecules uncondensed by carbon dioxide snow and ether has been made.

2. The quantum efficiency increases with frequency in the case of the liquid. The vapor absorbs only at short wave lengths and variations of frequency were not made.

3. Possible mechanisms for the reaction have been discussed.

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[CONTRIBUTION FROM THE PHYSIKALISCHES INSTITUT DER UNIVERSITÄT, LEIPZIG]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. VIII. THE ELECTRIC MOMENT AS A VECTOR QUANTITY

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Electric moment data for a number of molecules, organic and inorganic in nature, have been presented in the previous papers of this series.[2] The moments have been calculated from dielectric constant and density data for suitable binary mixtures, using the Debye modification of the Clausius–Mosotti Law. The purpose of the present article is to give the results of further experimental work in this field and to suggest the significance of these data.

The apparatus used for the determination of the dielectric constants of the binary mixtures was designed and constructed especially for the purpose by the author. It has been very briefly described in a previous article.[2e] Dielectric constant and density determinations were made at 25°, using a carefully regulated thermostat and observing the usual precautions for precision work. In every case the solvent used was benzene.

Purification of Materials

All substances used for the measurements herein reported were subjected to a careful purification. For that purpose the customary methods of crystallization or distillation or both were resorted to. It is considered unnecessary to give the outline of the method for each particular substance—suffice it to say that in no case did the observed physical constants,

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[2] (a) Williams and Krchma, THIS JOURNAL, **49**, 1676, 2408 (1927); (b) Williams and Allgeier, *ibid.*, **49**, 2416 (1927); (c) Williams and Ogg, *ibid.*, **50**, 94 (1928); (d) Williams and Schwingel, *ibid.*, **50**, 362 (1928); (e) Williams and Weissberger, *ibid.*, **50**, 2332 (1928).

melting point or freezing point, differ appreciably from those given in the standard tables.

Results

The results of the experimental determinations and calculations are given in Table I. The symbols of the previous articles have been retained throughout. In the interest of a saving of space the dielectric constant and density data for the binary mixtures have been omitted; they are in all respects similar to those previously given. Their accuracy is fully as great in practically every case.

TABLE I

ELECTRIC MOMENT DATA FOR SOLUTE MOLECULES

Molecule	P_2	P_2''	P_2'	$\mu \times 10^{18}$
Bromobenzene	82	33	49	1.51
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	0.1
Hydroquinone diethyl ether[a,b]	116	50	65	1.7
Hydroquinone diacetate[a,b]	150	50	100	2.2
Mesitylene	42	41	1	0.1
sym.-Triethylbenzene	56	55	1	0.1
sym.-Trinitrobenzene	54	40	14	0.8
Phloroglucinol triacetate[b]	185	65	120	2.4

[a] Previously reported in a preliminary note, Williams, *Physik. Z.*, **29**, 271 (1928).

[b] The author takes this opportunity to thank Dr. A. Weissberger of the Chemisches Laboratorium der Universität, Leipzig, for the preparation and purification of these chemicals.

The polarization due to the deformation of the molecule, P_2'', was calculated by taking the sum of the atomic refractions or by means of the familiar Lorenz-Lorentz formula. In either case the molar refraction is obtained. That this method of procedure leads to a slight inaccuracy is well known;[2a] however, it does not in any way interfere with the significance of the results as discussed below.

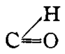
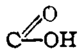
Discussion

The molecules for which electric moment data are presented above are derivatives of benzene of one form or another. They are discussed in the order of an increasing number of substituent atoms or groups of atoms. The simplest case is, of course, that in which only one of the hydrogens of the benzene is replaced. Since benzene itself is a non-polar substance, any such substitution of an atom or group will cause the formation of a polar molecule. Sufficient electric moment data are now available to indicate that an atom or group when introduced into a molecule may be considered as a vector and acting in a certain direction. For example, the introduction of an OH group into methane, ethane, propane or benzene gives a moment of magnitude, $\mu = 1.7 \times 10^{-18}$ e.s.u., while the NO_2 group substituted into benzene gives a moment of magnitude, $\mu = 3.9 \times 10^{-18}$ e.s.u. This statement must not be understood to mean that the moment of any compound formed by the substitution of an atom or group into methane will be exactly the same as the moment formed when the same atom or group is substituted into benzene or other non-polar molecule; the idea to be conveyed is that each atom or group is characterized by a more or less definite moment. There are many ways in which the vector value of this moment may be somewhat altered, since when such an atom or group is introduced the number of electrons present in the molecule is changed and internal compensations may take place. If such a group be introduced into the benzene nucleus (which for the purpose of discussion is considered as two-dimensional) it is natural to assume that the vector will act in the direction of the plane. On the basis of this assumption an approximate moment may be assigned to each of nine atoms or groups from the data of this and the previous articles.[2] The data are taken entirely from electric moment data for derivatives of benzene.

When two of these groups are substituted into 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. In the table given below the CH_3 group is considered to be positive in nature. It was shown[3] from the data for the nitrotoluenes that if the CH_3 group has one kind of electrical effect, the NO_2 group must have the opposite kind of electrical effect. If, on the other hand, the data for the chloronitrobenzenes[4] are considered, it is seen that the electric moment of the molecule becomes smaller and smaller as the second substituent moves from the ortho through the meta to the para position. This indicates that the Cl atom and the NO_2 group have like electrical effects—also, if the CH_3 group is positive, then both must be negative. In this manner charges and approximate values have been assigned to the atoms or groups given in Table II.[5]

TABLE II

CHARACTERISTIC MOMENTS OF ATOMS OR GROUPS

Group	Moment	Group	Moment
NO_2	−3.9	OCH_3	−1.2
 $C\overset{H}{=}O$	−2.8	 $C\overset{O}{-}OH$	−0.9
OH	−1.7	CH_3	+0.4
Cl	−1.5	NH_2	+1.5
Br	−1.5		

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[3] Williams, *Physik. Z.*, **29**, 174 (1928).

[4] Höjendahl, *Nature*, **117**, 892 (1926).

[5] The classification of the NH_2 group was made possible by the kindness of Dr. Höjendahl who communicated the results of unpublished data on the nitranilines.

To this point Höjendahl[4] and Smyth and Morgan[6] have discussed their data in a similar manner.

These data are of interest in connection with an article by Thomson[7] written before these and similar data were available. Considering the case when both substituents are of the same kind, this author concludes that "neglecting the deflection of the two doublets due to their action on each other that: 1. If the second constituent goes into the para position the resultant moment is zero. 2. If it goes into the ortho position the resultant moment is

$$(I^2 + I^2 + 2I^2 \cos 60°)^{1/2} = \sqrt{3}I$$

3. If it goes into the meta position the resultant moment is

$$(I^2 + I^2 + 2I^2 \cos 120°)^{1/2} = I$$

where I = moment characteristic of the atom or group."

The results of recent researches[4,6,8] on disubstituted benzenes of this type have in every case been treated in the manner suggested above, assuming always that the vectors which represented the groups acted in the plane of the benzene ring. It was found that the experimental data could without serious difficulty be represented by the formulas of Thomson or their equivalent. However, the fact that hydroquinone diethyl ether and hydroquinone diacetate have rather large dipole moments indicates clearly that the simple assumption of no interaction between the two groups cannot always be made. It is becoming more and more evident that as the substituted groups become longer or more complex the greater is the interaction between them—in other words, it is only in the case of the substitution of atoms and smaller groups that the vectors may be considered to act approximately in the plane of the benzene ring, and that when sufficient data are accumulated the cases where there is appreciable interaction will be in the majority. It is only because the simplest substances have been investigated first that the para disubstituted benzenes have previous to this article appeared always to have moments indistinguishable from zero.

Thomson further considers the case in which the second substituent is not the same as the first. In this case the "moment of the molecule if the second substituent goes into: (1) the para position is $I - I'$; (2) the ortho position is $(I^2 + I'^2 + II')^{1/2}$; (3) the meta position is $(I^2 + I'^2 - II')^{1/2}$; where I' = moment characteristic of the second atom or group." As in the case of two like substituents, it is found that in certain cases (atoms and smaller groups) the assumption of vectors directed in the plane of the benzene nucleus does not lead to any appreciable difficulty. This is rather nicely illustrated in the case of para chloro-

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[6] Smyth and Morgan, THIS JOURNAL, **49,** 1030 (1927).

[7] Thomson, *Phil. Mag.*, [6] **46,** 497 (1923).

Errera, *Physik. Z.*, **27,** 764 (1926).

bromobenzene tabulated above, which gives a moment indistinguishable from zero. The moments of chlorobenzene ($\mu = 1.52 - 1.55 \times 10^{-18}$) and bromobenzene ($\mu = 1.51 \times 10^{-18}$) are very nearly alike, so that when one vector acts in opposition to the other a cancellation results. Other cases of this type have been sufficiently discussed. However, it is becoming more and more apparent, as before, that this is true only in the cases where simple substituents are present in the benzene nucleus, and that as the substituent groups become more complex the effect of the interaction between the groups becomes more pronounced. As evidence for this statement Table III has been prepared. It contains data for several substituted nitrobenzenes. The moment has in each case been calculated in the manner suggested by Thomson.

TABLE III

ELECTRIC MOMENT DATA FOR PARA DISUBSTITUTED BENZENES

	Molecule	Observed moment	Calculated moment
1.	$NO_2C_6H_4CHO$	2.4×10^{-18}	1.1×10^{-18}
2.	$NO_2C_6H_4COOH$	3.5×10^{-18}	3.0×10^{-18}
3.	$NO_2C_6H_4NH_2$	7.1×10^{-18}	5.4×10^{-18}
4.	$NO_2C_6H_4Cl$	2.5×10^{-18}	2.4×10^{-18}
5.	$NO_2C_6H_4CH_3$	4.5×10^{-18}	4.3×10^{-18}

It is at once evident that in the case of the first three molecules there is appreciable interaction between the substituents. The data for the last two molecules, cases in which the second substituent (Cl or CH_3) is of simpler type, have been included only for purposes of comparison. Other tables might be prepared from data now available which would illustrate the same point.

To summarize: it would appear that when two atoms or groups of atoms (like or unlike) are substituted into the benzene nucleus, the assumption that there is no interaction between them can be made only when the groups are of very simple type. *In general* the vectors characterizing the groups *cannot* be considered to act in the direction of the plane of the benzene ring, so that in any vectorial considerations a three dimensional rather than a two dimensional molecule must be considered.

In the above discussion the various molecules have been considered as derivatives of benzene. Recent data of the author indicate that in the case of the substitution of certain groups (OH and OCH_3, for example) the role played by the benzene nucleus may become insignificant and that the molecules are best treated from another point of view. These data are reserved for a later communication.

The data for the symmetrical trisubstituted derivatives of benzene are of interest in connection with the question of the structure of the benzene nucleus. If the Körner formula[9] were the correct one, a finite electric

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[9] Körner, *Gazz. chim. ital.*, **4**, 444 (1874). See also Huggins, THIS JOURNAL, **44**, 1607 (1922); **45**, 264 (1923).

moment for every like trisubstituted compound of the symmetrical type should result. The same supposition may be made in the cases of the formulas of Baeyer[10] and of Ladenburg.[11] The evidence is conclusive that in the case of mesitylene and symmetrical triethylbenzene no such moment results. The same is true in the case of symmetrical tribromobenzene, where a moment indistinguishable from zero has been reported by Höjendahl.[4] In a previous article Williams and Schwingel[2d] reported a value, $\mu = 1.08 \times 10^{-18}$, for symmetrical trinitrobenzene, but stated that from theoretical considerations a zero value should have resulted. However, a value of such magnitude should be distinguishable from zero;[2] therefore this substance was reinvestigated with extreme care. The result given in Table I was kindly communicated to me by Mr. Schwingel from the Laboratory of Physical Chemistry, University of Wisconsin as the result of careful measurements on trinitrobenzene which had been "recrystallized from benzene ten times and dried *in vacuo* at 35° to constant weight." A repetition of the work by the author in this Laboratory gave a result 5% higher. Therefore the original result is essentially correct and it indicates that symmetrical trinitrobenzene has a finite electric moment. The explanation is, without doubt, to be found in a consideration similar to that given to the disubstituted compounds. The interaction between the groups causes them to be extended (only slightly in this case) above the plane of the benzene nucleus.

There can be no doubt that measurements of this type, made at a single temperature and using benzene as a solvent, will indicate a finite moment for *sym.*-trinitrobenzene. However, in order to remove any question, it would be desirable to supplement these measurements by others at different temperatures.

Concerning the data for phloroglucinol triacetate there can be no question. This substance, a symmetrically trisubstituted benzene, has a comparatively large dipole moment, the explanation of which is to be found in a strong interaction between the groups. The case is exactly analogous to that of hydroquinone diethyl ether and hydroquinone diacetate[12] and will not be discussed further at this point.

In the case of the trisubstituted benzenes, then, it is predicted that as the groups which are substituted into the benzene nucleus become more complex, the greater will be the interaction between them. This point is now being investigated more thoroughly by the author.

In the above discussion the phrase "the plane of the benzene ring" has been more or less frequently used, although it has not been directly proved that the six carbon atoms of the benzene nucleus are in one plane.

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[10] Baeyer, *Ann.*, **245**, 103 (1888).

[11] Ladenburg, *Ber.*, **2**, 140 (1869).

[12] In this connection see also Williams, *Physik. Z.*, **29**, 271 (1928).

It is claimed that the data presented cannot be explained by the use of such a formula as that suggested by Körner, Baeyer or Ladenburg and that they can be accounted for by the assumption of a plane formula. The results are strongly indicative of the latter type of arrangement.

Smyth and Morgan,[6] from a consideration of their electric moment data for certain of the disubstituted benzenes conclude that "it appears logical to suppose that the benzene nucleus is a regular hexagon with all the carbon and hydrogen atoms in the same plane, although substitution may possibly distort the hexagon to a somewhat puckered ring." The results of the present investigation must be considered to strengthen materially the argument in favor of the plane ring, particularly in view of the limitations which must be placed upon any conclusions drawn from considerations of the disubstituted compounds. The limitations are, briefly, (1) the fact that any para like-disubstituted benzene forms a symmetrical molecule cannot be considered as proof for a special configuration of the benzene nucleus,[3] and (2) the effect of the interaction between groups which is emphasized in this article is certain to obscure the treatment.

The results of this article are also of interest in connection with those recently reported by Ebert and v. Hartel[13] for molecules of the type CX_4. Certain molecules of this type, CCl_4, CH_4, $C(CH_2Cl)_4$, and also from unpublished data of the author, $C(NO_2)_4$ and $C(CH_2Br)_4$ have zero moments and therefore are symmetrical, while others, such as $C(OCH_3)_4$, $C(OC_2H_5)_4$ and $C(CH_2OOCCH_3)_4$ are characterized by finite electric moments ($\mu = 0.8$, 1.1 and 2.6×10^{-18}, respectively). From these data as well it would appear that as the length or complexity of the substituent group is increased, the interaction between groups is increased. Thus electric moment data for molecules of the types 1,4—$C_6H_4X_2$, 1,3,5—$C_6H_3X_3$ and CX_4 are now available which indicate that in the case of simpler substituents (X) a symmetrical molecule is formed, but that as the substituent becomes more and more complex the effect of interactions between the groups becomes prominent and asymmetrical molecules result.

It would be desirable to have the x-ray diagrams in the cases of the molecules of the types 1,4—$C_6H_4X_2$ and 1,3,5—$C_6H_3X_3$ which give finite electric moments. One might expect in the case of compounds of the latter type, for example, that the ends of the substituted groups would be found in a plane above that of the benzene nucleus and that it should be possible to compare the results of such studies as these, that is, data concerning the structure of the molecules in the dissolved state, with their structure in the solid state as determined by x-ray analysis. However, at the present writing such a comparison is possible in but very few cases. It must be pointed out, too, that in certain of these cases, at least, the results are

[13] Ebert and v. Hartel, *Naturwissenschaften,* **15,** 668 (1927).

in direct conflict with each other, so that it cannot be said that such a comparison is always possible. This fact has been briefly discussed in another place.[14]

Conclusion

It appears from the data of this and previous articles that for both aliphatic and aromatic compounds an interaction between groups in a molecule is a common phenomenon. Thus formulas such as those of Thomson for the case of disubstituted benzene derivatives, which neglect the deflection caused by the interaction of two or more groups in a molecule, cannot be of general utility. In most cases the vectors characteristic of the groups must be considered to be acting in space rather than in a plane, making a three-dimensional analysis necessary.

The writer acknowledges with pleasure his indebtedness to Professor P. Debye for apparatus placed at his disposal and for the interest shown and counsel given by him during the progress of the work.

Summary

1. Dielectric constant and density data at 25° have been obtained for benzene solutions of bromobenzene, benzaldehyde, *p*-nitrobenzaldehyde, *p*-nitrobenzoic acid, *p*-chlorobromobenzene, hydroquinone diethyl ether, hydroquinone diacetate, mesitylene, *sym.*-triethylbenzene, *sym.*-trinitrobenzene and phloroglucinol triacetate. From these data the electric moments of the various solute molecules have been calculated and presented in a table.

2. It has been shown that an atom or group when substituted into a molecule is characterized by a more or less definite electric moment. This moment can be considered to be a vector quantity to which it is possible to assign an electrical character by making a simple assumption with regard to the electrical character of one group.

3. Interaction between groups in a molecule appears to be a common phenomenon; therefore the dipole moment of a molecule which contains several groups can be calculated in general only provided the vectors characteristic of the groups be considered to be acting in space.

4. The data are strongly indicative of a formula for benzene in which the six carbon atoms lie in one plane.

5. The possibility of comparing the molecular structure of molecules in the dissolved state, as indicated by electric moment data, with their structure in the solid state, as determined by x-ray analysis is briefly discussed.

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[14] Williams, *Physik. Z.*, forthcoming publication.