

3. A study has been made of the limitations of temperature and acidity for which the various indicators are suitable.

4. Colors ranging from red through yellow, green, blue and violet are included. Interfering colored ions may therefore be counteracted by the selection of the proper indicator color from the group described.

5. All the indicators described are suitable for use in the quantitative estimation of trivalent arsenic with an accuracy ordinarily required from the usual volumetric determinations.

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THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. XII. DIPOLE MOMENT DATA FOR (A) NAPHTHALENE AND CERTAIN OF ITS DERIVATIVES. (B) ALPHA AND BETA BENZENE HEXACHLORIDES

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RECEIVED MARCH 19, 1931

PUBLISHED JUNE 8, 1931

In the last years it has been amply demonstrated that the symmetrical hydrocarbons have zero dipole moments. Such a molecule will become electrically dissymmetrical and possess a finite dipole moment if one of its hydrogen atoms is replaced by another atom or group of atoms; furthermore the moment will vary with the nature of the substituent. When two of its hydrogen atoms are replaced by these substituents, it will not generally be possible to compute the electric moment of the resulting molecules from the assumption that it is the vector sum of individual moments characteristic of the substituent groups because (a) it is necessary to take into account the stereochemistry of the atoms forming the substituent group and (b) it is necessary to take into account mutual attractions or repulsions between the groups unless they be sufficiently removed from one another in the molecule. These factors, first suggested by one of us¹ as possibilities in order to explain the fact that hydroquinone diethyl ether possesses a finite dipole moment, have now been quite completely described.^{2,3} These studies, and now many others, have assisted materially in assigning configurations to benzene, methane and ethane, cyclohexane and certain of their derivatives.

In a few individual cases difficulties with the measurement and interpretation of the electric moment data have been encountered. Thus, iodine, symmetrical trinitrobenzene, and naphthalene have appeared to

¹ Williams, *Physik. Z.*, 29, 271 (1928).

² Højendahl, "Dissertation," Copenhagen, 1928; *Physik. Z.*, 30, 391 (1929).

³ Williams, *THIS JOURNAL*, 50, 2350 (1928); *Z. physik. Chem.*, [A] 138, 75 (1928); Williams and Fogelberg, *THIS JOURNAL*, 52, 1356 (1930).

possess finite dipole moments although one would expect them to be non-polar from structural considerations. In a review of earlier work from this Laboratory,⁴ these molecules were classified as being molecules for which the existence of a finite moment seemed questionable. There has been a considerable amount of work done since in order to clear up this apparent difficulty. In the case of trinitrobenzene Parts⁵ has made a careful study of the polarization at several temperatures and has verified the value previously reported for its electric moment, ($\mu = 0.8 \times 10^{-18}$ e. s. u.) assuming that the atom polarization is zero. In order for the moment to be zero the atom polarization would have to be 14 cc., a value which is probably much too high. It appears therefore that the molecule actually is polar. Interpreted, this would mean that the vectors characteristic of the three NO_2 groups do not act in the plane of the benzene ring.

The difficulty in the case of iodine was assumed to be the result of chemical changes due to the solvent. This has definitely been established by Müller and Sack,⁶ who found that when either hexane or cyclohexane was used as solvent the moment was zero. They were also able to find finite values of like magnitude as those reported by us when the iodine was dissolved in benzene.

The data of this article show conclusively that naphthalene has no moment. The value reported by Williams and Ogg,⁷ $\mu = 0.7 \times 10^{-18}$ e. s. u., is too high because at the time the measurements were made it was impossible to measure with sufficient accuracy the dielectric constant changes produced in extremely dilute solutions. For this reason in the earlier papers the molar polarization of the solute molecule was determined by taking a tangent to the $P_{1,2}$ curve (molar polarization of the solution) at the point where the mole fraction of the reference liquid is unity, and prolonging it until it cut the axis where the mole fraction of the solute is unity. This is also the explanation for the fact that in so many cases the molar polarization of the solute appeared to be exactly constant. More recently the measurement of the dielectric constant in these extremely dilute solutions has been improved to such an extent that it has been possible to obtain the molar polarizations of the solute molecules for each concentration by means of the equation

$$P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_1 M_1 + f_2 M_2}{d} = f_1 P_1 + f_2 P_2$$

where the symbols have their usual significance. The P_2 values, obtained in this manner, are extrapolated back to zero concentration in order to measure the molar polarization of a free polar molecule not in interaction

⁴ Williams, *Physik. Z.*, 29, 174 (1928).

⁵ Parts, *Z. physik. Chem.*, B4, 227 (1929).

⁶ Müller and Sack, *Physik. Z.*, 31, 815 (1930).

⁷ Williams and Ogg, *THIS JOURNAL*, 50, 94 (1928).

with any other polar molecules of the same kind. The use of a non-polar solvent precludes the possibility of the polar molecule being in interaction with other polar molecules of unlike kind.

The data of Section A give definite information with regard to, first, the importance of the so-called atom polarization, and, second, the structure of naphthalene and certain of its simple derivatives. The data of Section B are of interest in connection with the stereochemistry of derivatives of cyclohexane.

Experimental

The electric moments of naphthalene, 2,6-dichloronaphthalene, α -benzene hexachloride and β -benzene hexachloride have been determined by the method of the binary mixture, using benzene as solvent. All dielectric constant and density determinations were made in a thermostat carefully regulated to $25 \pm 0.05^\circ$. All chemicals were subjected to rigorous purifications—in short it may be claimed that every known precaution for precision measurements was taken. A frequency of 10^6 cycles was used for the dielectric constant measurements. The dielectric constant differences, obtained using the heterodyne beat method consisting of standard oscillator, variable oscillator and detector-amplifier circuits previously described,⁸ are believed to be accurate to ± 0.0002 .

The dielectric constant and density data are presented in Table I. The symbols of the previous articles have been retained throughout, f_1 is the mole fraction of the solvent, in this case benzene; d_4^{25} is the density of the solution; ϵ is its dielectric constant; $P_{1,2} \left(= \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_1 M_1 + f_2 M_2}{d} \right)$ is the molar polarization of the solution; and P_2 is the molar polarization of the solute molecule.

TABLE I
DIELECTRIC CONSTANT AND DENSITY DATA
Naphthalene

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.0000	0.8735	2.276	26.66	43.3
0.9972	.8741	2.277	26.71	43.2
.9931	.8751	2.279	26.77	43.0
.9862	.8766	2.282	26.89	43.8
.9723	.8796	2.288	27.12	43.3
2,6-Dichloronaphthalene				
1.0000	0.8735	2.276	26.66	54.3
0.9982	.8748	2.277	26.71	55.0
.9955	.8769	2.280	26.79	56.2
.9928	.8788	2.283	26.89	58.3
.9866	.8833	2.289	27.09	58.8

⁸ Williams, *Fortschritte Chem., Physik physik. Chem.*, 20, 257 (1930).

TABLE I (Concluded)
 α -Benzene Hexachloride

f_1	d_4^{25}		$P_{1,2}$	P_2
1.0000	0.8735	2.276	26.66	156
0.9988	.8755	2.285	26.82	159
.9969	.8782	2.298	27.06	156
.9939	.8830	2.319	27.45	155
.9909	.8877	2.340	27.83	155
β -Benzene Hexachloride				
1.0000	0.8735	2.276	26.66	66.9
0.9988	.8755	2.277	26.71	66.7
.9975	.8774	2.278	26.76	67.3
.9969	.8783	2.279	26.79	66.7

In Table II are presented the electric moments of the solute molecules, calculated from the P_2 values in infinitely dilute solution. The latter were obtained by direct extrapolation of the P_2 values calculated for the dilute solutions. The quantity P_2'' is that part of the total polarization of the solute molecule contributed by the deformation of the molecule and is given by the quantity $\frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{d}$, where n_D is the refractive index for the "D" line at 25°, and P_2' is that part of the total polarization of the solute molecule contributed by its actual orientation in the field and is given by the quantity $\frac{4\pi}{3} N \frac{\mu^2}{3kT}$, where μ is the electric moment of the molecule in question.

 TABLE II
 ELECTRIC MOMENTS OF SOLUTE MOLECULES

Molecule	P_2	P_2''	P_2'	$\mu \times 10^{18}$
$C_{10}H_8$	43.3	43.3	0	0
2,6- $C_{10}H_6Cl_2$	54.3	54.2	0.1	0
α - $C_6H_6Cl_6$	156	57.5	98.5	2.15
β - $C_6H_6Cl_6$	66.9	57.5	9.4	0.70

Discussion, Section A

The molar polarization is made up of two parts, a polarization due to deformation or distortion, and a polarization due to orientation. In order to determine the electric moment of a molecule from dielectric constant and density data at a single temperature, it is necessary to be able to evaluate the polarization by deformation. The latter may be defined as the limiting value that the optical polarization (obtained by means of the Lorentz-Lorenz formula) attains on passing to the limit for zero frequency when the orientation effect which would set in for smaller frequencies is disregarded. But this extrapolation cannot be carried out accurately with the dispersion measurements now at our disposal, so that the extrapolation to zero frequency cannot be used when *absolute* accuracy

is necessary. From a practical standpoint, however, this aspect is entirely changed, for if we take non-polar molecules and compare the value of the dielectric constant with the square of the refractive index for the "D" line, the differences are found to be small. The method of the Lorentz-Lorenz formula will therefore be very satisfactory for the determination of the distortion contribution to the polarization except in the case when it is necessary to decide whether a molecule is but slightly polar or not polar at all. In the latter case there is considerable difference of opinion concerning the magnitude of the inaccuracy introduced. Thus Smyth⁹ considers the difficulty to be a serious one, while the authors are of the opinion that even here the difficulty can have but little practical importance, especially now that it is possible to make very accurate determinations of the dielectric constant differences between that of the pure solvent and the extremely dilute solutions. An inspection of the data for the naphthalene and 2,6-dichloronaphthalene molecules shows that the difference between the total polarization of each, determined from dielectric constant studies, and the polarization due to deformation of each, calculated from the Lorentz-Lorenz formula using the refractive index for the "D" line, is so small as to be absolutely negligible, leaving no doubt that the polarity of each is zero.

It may be mentioned here that Morgan and Lowry,¹⁰ in trying to account for the moment, $\mu = 0.7 \times 10^{-18}$ e. s. u., previously reported for the naphthalene molecule, have assumed the difficulty to be a result of the fact that this deformation part could not be calculated in the way described above. That this cannot be true is evident from the original data⁷ which are reproduced in Table III. The only change that has been made is in the determination of P_2 , which this time is simply calculated for each concentration of naphthalene in solution without any attempt being made to determine the limiting value.

TABLE III
DIELECTRIC CONSTANT AND DENSITY DATA FOR NAPHTHALENE SOLUTIONS IN CARBON BISULFIDE

f_1	d_{25}^{25}	ϵ	$P_{1,2}$	P_2
1.000	1.2591	2.633	21.27	...
0.999	1.258	2.641	21.37	120
.994	1.255	2.646	21.55	66
.983	1.246	2.654	21.93	46
.973	1.240	2.663	22.25	45
.965	1.235	2.673	22.59	45
.935	1.225	2.680	23.30	42

If the last four values of P_2 had been used to determine the limiting value instead of having to make use of a value weighed by the first two values

⁹ Smyth, *THIS JOURNAL*, **51**, 2051 (1929).

¹⁰ Morgan and Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

as well in the extrapolation there would have been little, if any, doubt that naphthalene was non-polar. The result of early experimental difficulties was quite often a molar polarization, and therefore an electric moment, which was somewhat high. The calculation of a moment for the anthracene molecule was not attempted⁷ because it was realized that the solutions were too dilute for determinations of the dielectric constant differences with sufficient accuracy for the purpose.

Smyth, Morgan and Boyce¹¹ in presenting their result for the electric moment of monochlorobenzene ($\mu = 1.56 \times 10^{-18}$) make the statement "The value for the moment of monochlorobenzene agrees well with the figure 1.58×10^{-18} recently published by Höjendahl¹² and by Williams and Krchma¹³ who, being unable to take into account the small quantity P_A , obtained a slightly high value." The value reported from this Laboratory was $\mu = 1.55 \times 10^{-18}$. The quantity P_A referred to is the atom polarization, which is ordinarily defined as the difference between the total induced polarization and that due simply to electronic shifts, that is, it is a quantity which measures the polarization due to the shifting of position of atoms and groups of atoms. Values of P_A have been determined by Errera¹⁴ by making the assumption that when the molecules are held in the solid state they are unable to orient themselves in an applied field and therefore cannot contribute to the dielectric constant of a solid. The difference between the total polarization in the solid state and the electron polarization calculated from optical data should therefore be atom polarization. The assumption that molecules in solid substances are unable to orient themselves in an alternating field is hardly a safe one, for as Errera¹⁵ himself has shown the dielectric constant of ice varies with the applied frequency. Furthermore, unpublished work from this Laboratory shows definitely that the dielectric constant of solid nitrobenzene changes with frequency. In all probability the orientation of molecules in the solid state will prove to be quite a general phenomenon and an excellent way in which to study it will be by means of dielectric constant determinations. This rotation of molecules in the solid state has recently been discussed from a theoretical point of view by Pauling.¹⁶ For the problem at hand it is evident that care will have to be exercised in assigning a magnitude to P_A . It may also be claimed that other methods of determining it are not without difficulty. In this series of articles the molar refraction for the "D" line has been subtracted from the total polarization, and the electric moment has been calculated from the difference. This procedure certainly

¹¹ Smyth, Morgan and Boyce, *THIS JOURNAL*, 50, 1536 (1928).

¹² Höjendahl, *Nature*, 117, 892 (1926).

¹³ Williams and Krchma, *THIS JOURNAL*, 49, 1676 (1927).

¹⁴ Errera, *Physik. Z.*, 27, 764 (1926).

¹⁵ Errera, *J. phys.*, [6] 5, 304 (1924).

¹⁶ Pauling, *Phys. Rev.*, 36, 430 (1930).

reduces any error caused by the failure to subtract the atom polarization to a quantity of little or no practical significance. The data for the electric moment of monochlorobenzene introduced at the beginning of this chapter and the data of Table II for naphthalene and 2,6-dichloronaphthalene demonstrate the truth of this statement.

The data of this section are also of interest in connection with the structure to be assigned to naphthalene and its derivatives. There is certain chemical evidence that the 2,6 and 2,7 positions are closer than the ordinary plane formula appears to indicate, and that the 1,8 positions have a relationship approaching that of an ortho compound.^{17,18} This is interpreted to mean either that the two rings are completely folded over each other, or make a very small angle with each other. The data of Höjendahl² for α -nitronaphthalene, $\mu = 3.6 \times 10^{-18}$ e. s. u., 1,5-dinitronaphthalene, $\mu = 0.6 \times 10^{-18}$ e. s. u. and 1,8-dinitronaphthalene, $\mu = 7.1 \times 10^{-18}$ e. s. u., and the data of this article indicate that in these simpler compounds the two rings must be extended. The most important fact leading to this conclusion is the absence of a finite moment in the case of 2,6-dichloronitronaphthalene. If the rings were folded, either completely or in such a way as to make a small angle with each other, a finite moment would have to exist. If they were folded completely, that is, superimposed on one another, the moment should correspond almost identically with that of *o*-dichlorobenzene, for which $\mu = 2.3 \times 10^{-18}$ e. s. u.

The data of Höjendahl alone are probably insufficient to distinguish between a completely folded and a completely extended model if we assume with Höjendahl that the moment reported for 1,5-dinitronaphthalene should be zero, rather than the small finite value reported, $\mu = 0.6 \times 10^{-18}$ e. s. u. The latter value has resulted from experimental inaccuracy in the earlier work of the type referred to in the case of naphthalene itself. It is evident that if the rings were completely folded, the moment of the molecule would correspond to that of *p*-dinitrobenzene, which is known to be zero. The moment for 1,8-dinitronaphthalene is approximately, though not quite, twice that of α -nitronaphthalene. Considered vectorially, each nitro group is acting to produce its characteristic electrical dissymmetry in the same direction, instead of in opposite directions as in the case of 1,5-dinitronaphthalene. This result might have been expected either on the basis of a folded or extended structure. The situation may be compared with that of benzene itself in which it has been pointed out⁴ that data for like para disubstituted benzenes are insufficient to determine whether or not the six carbon atoms lie in a plane, but when data for the corresponding symmetrically trisubstituted benzenes are considered the plane formula is definitely indicated.

¹⁷ Kauffer and Karrer, *Ber.*, **40**, 3262 (1907).

¹⁸ Raiford and Clark, *THIS JOURNAL*, **48**, 483 (1926).

Discussion, Section B¹⁹

In one of the previous papers of this series²⁰ electric moment data for cyclohexane and some of its simple derivatives were presented and discussed. It was stated that the extension of these studies to more complicated derivatives will be difficult and somewhat involved because of the possibilities of isomerism in these compounds. There should, for example, be four benzene hexachlorides. In addition to the more common α - and β -forms having melting points 157 and 310°, respectively, two other forms²¹ having melting points 112 and 129° have been prepared.

From theoretical considerations there should be four principal isomers, one in which all six chlorine atoms lie above the plane of the carbon atoms, one with five above and one below, one with four above and two below, and finally a symmetrical form with three above and three below.

X-ray data²² have shown that the β -isomer is the symmetrical form having the chlorine atoms evenly distributed above and below the plane of the carbon atoms. No definite conclusions have been drawn concerning the structure of the other three isomers, although attempts have been made by studying the trichlorobenzenes obtained when the various benzene hexachlorides are treated with alcoholic potassium hydroxide.²¹

In this work the α - and β -isomers were prepared according to the method of Mathews²³ and their electric moments measured in benzene solutions. Their melting points agreed excellently with the values previously reported. Owing to the limited solubility of the β -compound in benzene, a maximum concentration of only 0.3 mole per cent. could be obtained, so that the moment, 0.7×10^{-18} e. s. u., may be appreciably in error. However, the

¹⁹ Since the completion of this manuscript the authors have noted that Hassel and Naeshagen [*Tids. Kemi Bergvesen*, 10, 126-127 (1930)] have made similar measurements for these compounds. The agreement is excellent in the case of the α -derivative but not in the case of the β -derivative. For the α -compound there is reported $\mu = 2.20 \times 10^{-18}$ e. s. u., but for the β -compound the value $\mu = 0$ is insisted upon. There are given reasons why the moment should be zero, then the statement is made, "the measurement has been carried out and it was found that this is certainly the case." An inspection of the data is not convincing. The melting point of the compound used is given as 297° but the commonly accepted value for the pure substance is 310°. The dielectric constant data are given not by recording the actual figures but by saying that the difference between the value for pure benzene and the value for a solution containing 1.2 g. per 100 cc. of benzene is less than 0.05. The data have been collected in such a way that one would have to assume the dielectric constant value of the solution to be the larger. (The $\Delta\epsilon$ value intended should undoubtedly be 0.005.) But in order for the electric moment of this molecule to be zero, the dielectric constant of the solutions must always be less than that of the pure benzene. Our $\Delta\epsilon$ would be less than 0.005 for a solution of this same concentration, yet it corresponds to a moment, $\mu = 0.7 \times 10^{-18}$ e. s. u.

²⁰ Williams, *THIS JOURNAL*, 52, 1831 (1930).

²¹ Van der Linden, *Ber.*, 45, 231 (1912).

²² Hendricks and Bilicke, *THIS JOURNAL*, 48, 3007 (1926).

²³ Mathews, *J. Chem. Soc.*, 59, 165 (1891).

measurements were of sufficient accuracy to show that the moment is not zero as might have been expected on the basis of the x-ray structure reported for the solid material. It does not necessarily follow, of course, that because a substance is symmetrical as a solid it should also be symmetrical in the dissolved state. Thus this case is quite analogous to that of the symmetrical trinitrobenzene referred to in the introduction. The measurements were repeated in dioxane, in which the hexachloride was more soluble, and a value of 2.0×10^{-18} was obtained. This was evidently due to an influence of the solvent on the somewhat non-rigid structure of the benzene hexachloride.

If there be assumed for the α -compound a configuration having all six of the chlorine atoms on the same side of the plane of the carbon atoms (this seems justified by the work of van der Linden), it is possible to calculate the angle that the vector characterizing the carbon to chlorine linkage makes with the plane of the carbon atoms. Taking the value of each carbon to chlorine linkage as 2.3×10^{-18} e. s. u., its value in chlorocyclohexane, an angle of 9° is obtained. This is considerably smaller than the 55° angle which would be predicted on the basis of tetrahedral carbon atoms with no mutual repulsion between the chlorine atoms. The small angle, 9° , is interpreted to mean that there is powerful mutual interaction between the chlorine atoms, a fact which might have been predicted because of the number and size of the latter. Also, it further emphasizes the fact pointed out in other papers from this Laboratory that the electric moment of a molecule cannot be properly calculated without taking into account mutual attractions and repulsions between substituted atoms and groups.

Summary

The method of the binary liquid mixture has been used to determine the electric moments of the naphthalene, 2,6-dichloronaphthalene, α -benzene hexachloride and β -benzene hexachloride molecules. In the discussion it has been shown that in order to account for the experimental data there must be considered both the spatial configurations of these molecules and the mutual interactions between their polar substituents.

In the case of the substituted naphthalenes the data indicated an extended arrangement of the benzene rings rather than a partially or completely folded one. The data for the benzene hexachlorides did not show what might have been predicted, namely, that the form in which the six chlorine atoms were located on one side of the plane of the six carbon atoms of cyclohexane would be very strongly polar, while the form in which three chlorine atoms were located on either side of the plane would be completely non-polar. The explanation is undoubtedly to be found in mutual interactions between the substituents, the chlorine and hydrogen atoms.