potassium hydroxide, while *o*-benzoyl-*m*-cresol gives a good yield of *m*-homosalicylic acid when treated in the same way.

When *m*-cresyl benzoate reacts with aluminum chloride without a solvent at about 130° it is converted practically quantitatively into the *o*-benzoyl-*m*-cresol. Apparently, high temperatures favor the formation of the *ortho* isomer.

o-Benzoyl-*p*-cresol, $C_6H_3.(OH).(CH_3).(COC_6H_5)(1,4,2)$. **Action of Anhydrous Aluminum Chloride on *p*-Cresyl Benzoate.**—This ketone is formed when 40 g. of the chloride is added in small portions to 50 g. of the ester which is stirred and heated to 140° for 15–20 minutes. The reaction is completed at 200°. The solid residue which results upon decomposing the melt is purified by repeatedly dissolving it in 20% sodium hydroxide solution and reprecipitating with hydrochloric acid. The dry residue weighs 47 g.

p-Homosalicylic acid is formed when *o*-benzoyl-*p*-cresol is fused with potassium hydroxide.[7]

Summary

Direct action of anhydrous aluminum chloride on the cresyl benzoates offers a good method for producing benzoyl cresols in excellent yields. The method possesses advantages over that of Friedel and Crafts.

The constitution of the benzoyl cresols has been proved by converting them into hydroxytoluic acids of known constitution by means of fused potassium hydroxide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE ELECTRIC MOMENTS OF SUBSTITUTED BENZENE MOLECULES AND THE STRUCTURE OF THE BENZENE RING

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Information concerning molecular structure may often be obtained from a consideration of the distribution of the electric charges in a molecule as revealed by the dielectric behavior of the substance. If the center of gravity of the positive charges does not coincide with that of the negative, the molecule may be regarded as containing an electric doublet, that is, two charges of equal size but opposite sign, very close together, the imaginary line joining the two charges being termed the axis of the doublet and the magnitude of the doublet being measured by its electric moment, the product of one of the charges by the length of the axis. A method of calculating the electric moment of a molecule from its structure has been discussed in an earlier paper.[1] It may be convenient to resolve the system of positive and negative charges in a molecule into two or more doublets, the resultant of the moments of these doublets being the moment of the molecule as a whole.

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[7] Jacobsen, *Ber.*, **14**, 2352 (1881).

[1] Smyth, *Phil. Mag.*, **47**, 530 (1924).

A method developed[2] for the calculation of the approximate value of the electric moment from the dielectric constant and other experimental data was used to secure the moments of a large number of hydrocarbon molecules.[3] The moment obtained for the benzene molecule was only 0.2×10^{-18} e.s.u., a value so small as to be indistinguishable from 0 by the method of calculation employed, a result recently confirmed by Sänger[4] who, after a detailed treatment of the subject, concluded that the benzene molecule had no moment. It appeared, however, that when a methyl group replaced a hydrogen atom to give toluene, a small doublet was formed in the molecule (see Table II). The axis of the doublet thus formed would lie on the line joining the carbon atom of the methyl group to the carbon atom of the benzene ring to which it is attached. Since the methyl group is regarded as positive, the positive end of the doublet might be expected to point toward the methyl carbon atom. When a second doublet of the same kind was introduced by the attachment of another methyl group to give a xylene, the moment of the molecule varied from a maximum in the case of the *ortho* compound, in which the two doublets might be pictured as reinforcing each other, to a minimum in that of the *para* compound, in which the two doublets apparently tend to oppose and nullify each other. Although it was recognized that the absolute error in these values was probably not less than 50%, it was believed that the differences between them were significant and possibly explicable on the supposition that the structure of the benzene molecule was the conventional hexagon with all the carbon atoms in the same plane. It appeared that the introduction of larger doublets, the values for the moments of which would be relatively more accurate, should provide a valuable means of investigating the structure of the ring.

If the molecules of a substance are free to assume a perfectly random orientation, their electric moment may be calculated from the Debye equation[5]

$$[(\epsilon - 1)/(\epsilon + 2)](M/d) = MR_{\infty} + (4\pi N/9k)(\mu^2/T) \qquad (1)$$

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[2] Smyth, *Phil. Mag.*, **45**, 849 (1923).

[3] Smyth, THIS JOURNAL, **46**, 2151 (1924).

[4] Sänger, *Physik. Z.*, **27**, 165 (1926).

[5] This equation was derived on the basis of the classical mechanics. The application of the older quantum theory to diatomic molecules led to equations which gave values for the electric moment differing greatly from the values yielded by the Debye equation. [Pauli, *Z. Physik*, **6**, 319 (1921). Pauling, *Proc. Nat. Acad. Sci.*, **12**, 32 (1926); *Phys. Rev.*, **27**, 568 (1926).]

However, recent applications of the newer quantum mechanics to simple poly-atomic molecules give equations from which results practically identical with those of the Debye equation may be obtained. [Kronig, *Proc. Nat. Acad. Sci.*, **12**, 488, 608 (1926). Mensing and Pauli, *Physik. Z.*, **27**, 509 (1926). Manneback, *ibid.*, **27**, 563 (1926). Van Vleck, *Nature*, **118**, 226 (1926). Ebert, *Naturwissenschaften*, **14**, 919 (1926).] It seems probable, therefore, that the application of the Debye equation to complex in which ϵ is the dielectric constant, M the molecular weight, d the density, MR_∞ the molecular refraction for light of infinite wave length, calculable approximately, in the absence of infra-red absorption bands, by extrapolation of the refraction in the visible region, N is the number of molecules in a gram molecule, $= 6.061 \times 10^{23}$, k the molecular gas constant, $= 1.372 \times 10^{-16}$, T the absolute temperature and μ the electric moment of a single molecule; $[(\epsilon-1)/(\epsilon+2)](M/d)$, called the molecular polarization, may be replaced by P, the expression being analogous to the familiar Lorenz-Lorentz formula for molecular refraction.

The molecular polarization of a mixture of two substances, 1 and 2, is given according to Debye by the expression

$$P_{1,2} = [(\epsilon - 1)/(\epsilon + 2)][(c_1M_1 + c_2M_2)/d] = c_1P_1 + c_2P_2 \qquad (2)$$

in which c_1 and c_2, M_1 and M_2, and P_1 and P_2 are, respectively, the mole fractions, molecular weights, and polarizations of the individual components.

When molecules containing electric doublets are in close proximity to one another, at least a partial orientation normally occurs. In order to eliminate the effect of this orientation upon the value of the polarization and the moment calculated from it, the chlorobenzenes which were selected for investigation because of the large doublets in their molecules were dissolved in benzene or in hexane which, like benzene, has a molecule of zero moment.[3] The values of the polarization for solutions of different concentrations were extrapolated to infinite dilution, where the molecules containing doublets should be free to assume a random orientation, and Equation 1 was then applied to calculate the moment.

In order to secure the necessary data for these calculations the densities and dielectric constants of mixtures of monochlorobenzene and the dichlorobenzenes with benzene and with hexane were measured at 0°, 25° and 50°, the materials having been carefully purified by standard methods. The densities were determined by means of an Ostwald-Sprengel pycnometer and the dielectric constants were measured in a gold-plated cell inserted in one arm of a capacity bridge, in which a current of 600 meters' wave length was used. The experimental details and actual data will be given in another paper. The molecular refractions were calculated from the data in Landolt-Börnstein-Roth-Scheel[6] and "International Critical Tables."

Because of the uncertainties in the theory of dielectrics, there is some doubt as to the absolute correctness of the values calculated for the mo-

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molecules is not without justification, and it appears almost certain that the results obtained for molecules of similar character, if not absolutely correct, are at least directly comparable with one another.

[6] Landolt-Börnstein-Roth-Scheel, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 5th ed., 1923.

ments, but the accuracy of the experimental data and the extrapolation is such that relative to one another they should not be in error by more than 5%.

The value 0.4×10^{-18} is calculated for the moment of *p*-dichlorobenzene from the small difference between $[(\epsilon-1)/(\epsilon+2)](M/d)$ and MR_∞ in Equation 1, a difference due to the unavoidable error in the extrapolation of MR from the visible region to infinite wave length. Analogous differences have given a value of 0.2×10^{-18} for benzene and a value of 0.48×10^{-18} for carbon tetrachloride, both of which have been shown by Sänger to have zero moment, and similar small values have been yielded by this method for other almost certainly symmetrical molecules. The variation of the polarization of *p*-dichlorobenzene with temperature is so small as to indicate that the term $(4\pi N/9k)(\mu^2/T)$ in Equation 1 differs from 0 by no more than the experimental error. The moment of the molecule must, therefore, be 0, or so close to 0 as to be indistinguishable from it by the methods employed here.[7]

The moment of monochlorobenzene, 1.61×10^{-18}, is that of the single doublet formed on attaching the chlorine atom to the benzene ring. As it may be supposed that the attachment of a second chlorine atom to the ring produces a similar doublet, the moment of the structure containing two chlorine atoms should be $2 \times 1.61 \times 10^{-18} \times \cos {}^1/_2 A$, where A is the angle between the directions of the axes of the two doublets. The angle A thus calculated is given in Table I together with the values of the moments.

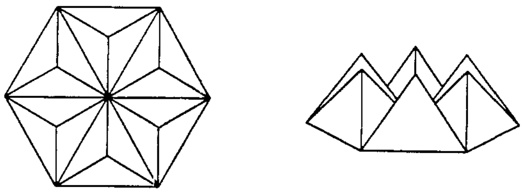
[7] Since this paper was submitted for publication, data have been published upon the dichloro-, dibromo- and di-iodobenzenes [Errera, *Physik. Z.*, **27**, 764 (1926)]. Errera calculated MR_∞ from measurements of the dielectric constants and densities of the solid substances, thus eliminating the error arising from the extrapolation of the molecular refraction. The value of MR_∞ obtained in this way for *p*-dichlorobenzene leads to a value of 0 for the moment, while the moment of *o*-dichlorobenzene is lowered by about 3% and that of the *meta* compound by about 4% by the use of these more accurate values for MR_∞, the smaller effect in the case of these latter compounds being due to the form of Equation 1. Errera's value for the polarization of *p*-dichlorobenzene agrees closely with that used in the present paper and his values for the pure *ortho* and *meta* compounds are less than 2% lower than those used here, but his values for the polarizations at infinite dilution obtained by extrapolation from the polarizations of solutions of these two compounds in benzene are considerably lower than ours and, therefore, lead to lower values for the moments, which, however, do not alter the conclusions to be derived from them. Since the values for *o*-dichlorobenzene and *m*-dichlorobenzene in the present paper are obtained as the results of measurements at three different temperatures in two different solvents, it is believed that confidence in their correctness is warranted. Measurements of the densities and dielectric constants of solutions of chlorobenzene in hexane at temperatures from —80° to +60° have just been completed with improved apparatus and will be published shortly. The range and accuracy of these measurements makes possible the calculation of the moment of chlorobenzene from the temperature variation of the polarization without the use of MR_∞, and the value, 1.55×10^{-18}, thus obtained differs by less than 4% from that used in this paper.

TABLE I

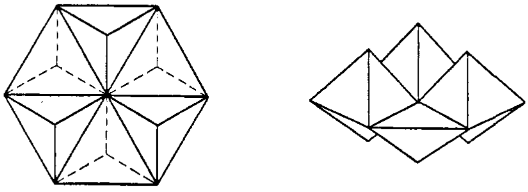
ELECTRIC MOMENTS AND THE ANGLES BETWEEN THE AXES

Substance	Moment × 10^{18}, e.s.u. Obs.	Calcd.	A°
C_6H_5Cl	1.61	..	..
o-$C_6H_4Cl_2$	2.30	2.79	89
m-$C_6H_4Cl_2$	1.55	1.61	122
p-$C_6H_4Cl_2$	0	0	180

These values may be compared with the results to be expected on the basis of the better known space formulas which have been proposed from time to time. Although some of these formulas have been abandoned because of failure to explain the observed chemical behavior, those representing types of spatial arrangement markedly different from one another will be briefly considered. In the structure according to Baeyer's formula[8] (Fig. 1), the axes of the doublets would point upward, making only such angles with one another as would be caused by mutual repulsion of the chlorine atoms. As the doublets would thus reinforce one another, the moments of the dichloro compounds would all be greater than that of monochlorobenzene instead of showing the variation observed. The formula of Koerner[9] (Fig. 1), later supported by Vaubel[10] and others, and treated recently by Huggins[11] from the electronic point of view, may be regarded as a highly puckered ring. In this structure two doublets in the *ortho* position would point in opposite directions, thus opposing and practically canceling each other, while in the *meta* position they would point in the same direction, thus giving a moment double that of monochlorobenzene. Ladenburg's[12] prism formula also fails to give relations between the moments remotely approximating those observed here.



Baeyer's model



Körner's model

Fig. 1.—Models of the benzene molecule.

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

[9] Koerner, *Gazz. chim. ital.*, **4**, 444 (1874).

[10] Vaubel, *J. prakt. Chem.*, [2] **44**, 137 (1891); **49**, 308 (1894); **50**, 58 (1894).

[11] Huggins, THIS JOURNAL, **44**, 1607 (1922); **45**, 264 (1923).

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

The conventional hexagonal arrangement with the carbon and hydrogen atoms all in one plane is the structure employed in the long used Kekulé formula, the modern electronic formulas of Stark and Pauly,[13] and the theory recently proposed by Pauling,[14] who reverts to the diagonal formula of Claus, abandons the tetrahedral carbon atom and explains the benzene ring in terms of orbital electrons in a manner consistent with the hexagonal arrangement in graphite indicated by the more recent x-ray investigations. If two hydrogens were replaced by chlorine atoms to form *o*-dichlorobenzene, as shown in Fig. 2, in which the small circles represent chlorine nuclei and the heavy black arrows the approximate locations, size, and directions of the doublets thus formed, the angle between the directions of the axes of the doublets would be 60° if the structure were not distorted by substitution. Similarly, in the *meta* compound the angle would be 120°, and in the *para* 180°. The resultant moments of the molecules should then have the values shown in Col. 3 of Table I. The values of the moments of the *para* and *meta* compounds show close conformation to these theoretical angles. The nearest carbon atoms in graphite are 1.42 Å. apart, which is taken by Pauling as approximately the carbon-to-carbon distance around the benzene hexagon. As this distance differs little from the radius of the chlorine atom, it appears probable that two chlorine atoms on adjacent carbon atoms would repel each other somewhat as do the chlorine atoms in the chloromethanes, the moments of which have been determined by Sänger.[15] In methane and carbon tetrachloride, the atoms attached to the carbon atom are commonly supposed to be arranged at the apices of a regular tetrahedron. If this symmetrical arrangement were maintained in methyl chloride, dichloromethane and chloroform, the doublet produced by the replacement of a methane hydrogen by a chlorine to form methyl chloride should have the same moment as the resultant of the doublets in chloroform, while the dichloromethane molecule should have a moment 1.15 times as great as either.[16] Mutual repulsion of the chlorine atoms attached to the same carbon atom would increase the angle between the axes of the doublets, thus decreasing the resultant moment. The result is that dichloromethane has a smaller instead of a larger moment than methyl chloride, and chloroform, in which the effect of repulsion should be greater because of the pressure of the

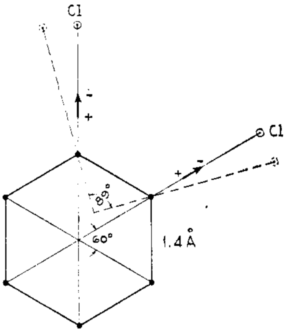

Fig. 2.—Plane hexagonal model of *o*-dichlorobenzene.

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[13] Henrich, "Theories of Organic Chemistry," translated by Johnson and Hahn, John Wiley and Sons, New York, 1922, p. 208.

[14] Pauling, This Journal, 48, 1132 (1926).

[15] Sänger, *Physik. Z.*, 27, 556 (1926).

[16] Compare Ref. 1, p. 541.

three chlorine atoms, has a moment less than half that of methyl chloride. In *o*-dichlorobenzene the repulsive effect should be smaller because the chlorine atoms are not attached to the same carbon atom, but they are sufficiently close to warrant the expectation of a not inconsiderable mutual repulsion, which would increase the angle between the axes of the two doublets, as shown by the dotted lines in Fig. 2, and decrease the resultant moment.[17]

The chlorine atoms, in forcing each other apart, might be expected to increase the distance between the carbon atoms to which they are attached, thus slightly distorting the benzene hexagon. An increase of the angle between the axes of the doublets from 60° to 89° probably involves only a small increase in the angle between the lines joining the carbon atoms to the center of the hexagon, because the large chlorine atoms with their mobile electrons can readily shift enough to bring about this increase in the angle between the doublets. As the distortion is not necessarily wholly in the plane of the original hexagon, repeated substitution might produce a more or less puckered ring.

We have considered briefly the effect of attaching two positive groups to the benzene ring, the doublets thus produced being too small for accurate treatment, and we have discussed in detail the moments arising from the attachment of two strongly negative radicals. The moments of molecules containing one positive and one negative group attached to the ring may be studied in the values in Table II, which have been calculated by the methods used for the chlorobenzenes from the measurements of Philip and Haynes[18] upon solutions.

TABLE II

MOMENTS OF MOLECULES HAVING 1 POSITIVE AND 1 NEGATIVE GROUP

			Moment $\times 10^{18}$, e.s.u.		
Substance	Moment $\times 10^{18}$, e.s.u., obs.	Substance	Obs.	Calcd. ($CH_3 = 0.40$, $OH = 1.73$)	Calcd. ($CH_3 = 0.20$, $OH = 1.63$)
$C_6H_5CH_3$	0.40	C_6H_5OH	1.73	...	...
o-$C_6H_4(CH_3)_2$	.58	*o*-$CH_3C_6H_4OH$	1.54	1.57	1.54
m-$C_6H_4(CH_3)_2$	.46	*m*-$CH_3C_6H_4OH$	1.76	1.97	1.74
p-$C_6H_4(CH_3)_2$	.23	*p*-$CH_3C_6H_4OH$	1.81	2.13	1.83

The doublet obtained on replacing a hydrogen atom by an hydroxyl radical given by the moment of the phenol molecule, 1.73×10^{-18}, and that arising from the presence of the methyl group, 0.40×10^{-18}, combine in very different fashion from the doublets previously considered, for in *o*-cresol

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[17] Strong support of this hypothesis is given by the results of Errera just published (Ref. 7), which show that the ratio of the moment of the *ortho* to that of the *meta* compound decreases on passing from the chloro through the bromo to the iodo compounds, as would result from a widening of the angle between the two doublets in the *ortho* compounds caused by the increasing repulsion with increasing size of the halogen atoms.

[18] Philip and Haynes, *Trans. Chem. Soc.*, **87**, 998 (1905).

they partially oppose one another, while in the *para* compound they should act in the same direction. The relative error in the value of the methyl doublet is too large to make significant the calculation of the exact angle between the two doublets, but it is of interest to compare the observed values for the cresols with those calculated on the assumption of the hexagonal structure which fitted the moments of the chlorobenzenes so well, the axes of the doublets being supposed to make angles of 60°, 120° and 180° with one another in the *ortho, meta* and *para* compounds, respectively. The calculated value for the *ortho* compound is close to the observed, but those for the *meta* and *para* compounds are higher than the observed, although changing in the same direction. In order to ascertain whether these differences were due to incorrectness in the assumption of the hexagonal structure or might arise from errors in the observed results, different values within the range of the probable error in the observed values of the moments of the methyl and the hydroxyl doublets were tried in the calculations. When a value of 1.63×10^{-18} was used for the moment of the hydroxyl doublet and 0.20×10^{-18} for that of the methyl doublet, both values well within the range of the probable error, the values given in the last column of Table II were obtained, showing very close agreement with the observed values for the cresols. These calculations indicate that the results are consistent with the hypothesis of the regular hexagonal structure which explains so satisfactorily the moments of the molecules of the chlorobenzenes. It appears that in *o*-cresol the positive methyl group and the negative hydroxyl group do not repel each other as do the two negative chlorine atoms in *o*-dichlorobenzene.

The electric moments of these different substituted benzenes point to a definite physical foundation for the positive or negative character attributed, sometimes rather vaguely, to organic radicals as a result of their chemical behavior and may provide a means of determining this character on a quantitative basis.

In explaining these results no account has been taken of the electronic shifts in the ring which are discussed so much in attempts to explain orientating influences. It has been found by one of the authors in previous studies that while electronic shifts induced along a carbon chain apparently affect the moment of the molecule somewhat, such effects are usually much smaller than the effects of atomic shifts of the type which has been discussed. Consequently, although these electronic shifts may make some small contribution to the observed differences in the moments, they do not materially affect the validity of the conclusions.

While this paper was being written, a note was published by Höjendahl,[19] giving the values of moments determined for a number of substituted benzene molecules. His value for chlorobenzene, 1.58×10^{-18}, agrees

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

well with the value 1.61×10^{-18} obtained in the present investigation, and its closeness to the value for bromobenzene, 1.56×10^{-18}, is interesting when compared to the moments 1.42×10^{-18} for chlorobenzene and 1.39×10^{-18} for bromobenzene, obtained some years ago by one of the authors[2,3] by a different method which might be expected to give a somewhat lower result. Although the other compounds studied by Höjendahl are different from those here investigated, the values which he obtains for the moments appear to be in complete accord with the results of the present work.

It is evident then that the values obtained for the moments of the mono and dichloro substitution products of benzene eliminate from consideration all of the more generally discussed structures of the benzene ring which differ greatly from a hexagon with all six carbon atoms in one plane, and that the moments of the cresols are consistent with this hexagonal structure. It appears logical, then, to suppose that the benzene molecule 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. We thus have a new line of evidence indicating a definite physical foundation for the old and generally accepted formula of benzene and providing a basis for the establishment of the positive or negative character of organic radicals.

Summary

The densities and dielectric constants of solutions in benzene and in hexane of the mono and dichloro substitution products of benzene have been measured at 0°, 25° and 50°, and from these data, together with the molecular refractions, the electric moments of the molecules have been calculated. Similar calculations have been made for phenol and the cresols.

A definite physical basis is provided for the determination of the positive or negative character of the benzene substituents. In conformity with the indications of previous calculations on aromatic hydrocarbons, the results show that the structure of the benzene molecule is best represented by 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.

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