phane derivatives and the tetramethylethylene halides indicates that they rotate about all three axes in the solid state. It has been suggested that internal motion of atoms unrestrained by valence forces may produce in ethylene cyanide[9] and the cyclohexane derivatives[8] sufficient time-average molecular symmetry to account for their rotation about three Cartesian axes in the crystal. Since this suggestion was made, there has been an accumulation of evidence that internal motion about the single carbon-to-carbon bond is not as free as was then supposed,[21] although no other explanation of the dipole moments of ethylene chloride[22] and ethylene cyanide[23] has yet appeared. Finbak and Hassel interpret their X-ray measurements of solid cyclohexane derivatives in terms of molecular rotation about only one axis, although the nearest distance of approach of methylene groups of neighboring molecules thus calculated is anomalously large.[24]

The authors are indebted to Dr. S. O. Morgan for his helpful advice in connection with this work; to Dr. B. S. Biggs for the preparation of cyclohexyl fluoroform; and to the Hercules Powder Company for the sample of camphoricimide which they kindly supplied us.

Summary

Dielectric evidence of the rotation of polar molecules has been observed in the crystals of two derivatives of ethane, one derivative of cyclopentane, five derivatives of cyclohexane, and thirteen derivatives of camphane. In most of these solids dielectric constant rises abruptly at a transition, as temperature is increased, to a value characteristic of polar liquids. A relatively symmetrical gravimetric and volumetric distribution of atoms around the center of gravity of the molecule evidently facilitates its rotation in the crystal.

NEW YORK, N. Y. RECEIVED AUGUST 24, 1939

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[21] See, *e. g.*, Kistiakowsky and Nazmi, *J. Chem. Phys.*, **6**, 18 (1938).

[22] See, *e. g.*, Lennard-Jones and Pike, *Trans. Faraday Soc.*, **30**, 830 (1934).

[23] Williams, *Z. physik. Chem.*, **138A**, 75 (1928).

[24] Finbak and Hassel, *Z. physik. Chem.*, **40B**, 391 (1938).

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, NEW YORK, N. Y.]

Dielectric Evidence of Molecular Rotation in the Crystals of Certain Benzene Derivatives*

BY ADDISON H. WHITE, B. S. BIGGS AND S. O. MORGAN

This paper presents dielectric measurements which show that molecular rotation may occur in the crystalline form of benzene derivatives as well as in aliphatic compounds, provided certain requirements of symmetry are met. The use of dielectric constant data as evidence of the existence of molecular rotation[1] is based on the fact, now well established, that a dielectric constant higher than the refraction value (that equal to the square of the optical refractive index) in a homogeneous, non-conducting organic material arises from the orientation or rotational motion of polar molecules or groups. Since the refractive index for organic compounds rarely exceeds 1.7, the excess of dielectric constant over about 3 is a good measure of the extent to which orientation of dipoles is contributing thereto. There is little tendency to question such a statement as it applies to the dielectric constant of organic liquids whose molecules have been shown by dipole moment measurements to be polar. It has become evident from the work of Smyth and his associates and from papers from this Laboratory that the same view can be carried over to organic solids having large molecules.

Baker and Smyth have presented evidence of rotation in rod-like molecules,[2] in comparatively spherical molecules,[3] and in intermediate "pear-shaped" molecules.[3] The earlier work from this Laboratory on camphor compounds[4,5] and ethane derivatives[6] has been extended to include other members of these series. The work reported in the present paper represents an extension of the ideas of the importance of symmetry gained from our earlier work to a new class of compounds, substi-

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* Published with the financial assistance of an anonymous donor.

[1] The term "molecular rotation" will be used in the sense in which it has been generally adopted to explain the dielectric behavior of polar liquids.

[2] Baker and Smyth, THIS JOURNAL, **60**, 1229 (1938).

[3] Baker and Smyth, *ibid.*, **61**, 2063, 2798 (1939).

[4] Yager and Morgan, *ibid.*, **57**, 2071 (1935).

[5] White and Morgan, *ibid.*, **57**, 2078 (1935).

[6] White and Morgan, *J. Chem. Phys.*, **5**, 655 (1937).

tuted benzenes, which are geometrically symmetrical about one axis, but electrically assymmetrical.

Experimental Methods

The apparatus and methods employed were similar to those described elsewhere.[7,8] Tin-foil electrodes were affixed to pressed sheets of each compound, using a very thin film of petrolatum as adhesive. Measurements of such solid sheets and of the corresponding liquids were made in the cells of Fig. 2 and Fig. 1, respectively, of a previous paper.[6] The density of the sheets at room temperature was determined roughly from their weights and dimensions. As an example of the accuracy of this procedure, the densities of hexamethylbenzene and hexachlorobenzene thus measured are 1.05 and 1.96, respectively; the corresponding densities calculated from X-ray data are 1.035 and 2.044.[9] Although such density measurements as the former are often in error because of voids in the sample, they determine the actual number of molecules per cc. of the specimen upon which dielectric measurements are made and are thus more appropriate than the true density for the calculation of molar polarization.

Preparation of Materials.—The substances marked E. K. in Table I were obtained from the Eastman Kodak Company. The liquids were fractionally distilled and a middle fraction taken for measurement. The solids were recrystallized from a non-polar solvent (usually petroleum ether, 30–60° range) before use. The other compounds were all prepared in this Laboratory. All are pure materials with the exception of the trichloro-*m*-xylene and trichloro-*o*-xylene, which were distillation fractions from chlorination products obtained by direct chlorination of the respective hydrocarbons.

3,4,5-Trichloro-*o*-xylene was obtained by chlorination of *o*-xylene and fractionation of the product. Of the two possible trichloro-*o*-xylenes the 3,4,6- melts at 48° and the 3,4,5- at 96°. The fraction boiling at 269–270° goes completely solid on being cooled and melts at 94–96°. It is therefore rather pure 3,4,5-trichloro-*o*-xylene.

The trichloro-*m*-xylene studied was that obtained by fractionally distilling the product of chlorination of *m*-xylene. The fraction boiling between 250 and 260° was recrystallized from alcohol and then from cold petroleum ether. The compound separates in long, glistening waxy needles melting at 95°.

3-Nitro-4,5-dichloro-*o*-xylene and 5-nitro-3,4-dichloro-*o*-xylene were prepared from the corresponding dichloro-*o*-xylenes by the method of Hinkel.[10] The 4,5-dichloro compound could not be obtained completely free of isomers and the resulting nitro compound melted at 82° rather than at 78°, its recorded melting point. This 5-nitro compound probably contained a small amount of the higher melting 3-nitro-4,5-dichloro-*o*-xylene in solid solution.

Pentachloroethylbenzene was prepared by chlorination of ethylbenzene in carbon tetrachloride solution with antimony pentachloride as catalyst. It was fractionally distilled, the 300° fraction being recrystallized from alcohol several times and finally crystallized from heptane. The melting point recorded in Beilstein is in error. The value consistently obtained here was 56° and this is in agreement with that reported by E. I. du Pont de Nemours & Company.[11] Because of the wide discrepancy between the recorded melting points the material was analyzed.

Anal. Calcd. for $C_8H_5Cl_5$: C, 34.53; H, 1.78. Found: C, 34.28; H, 1.87.

Pentaethylacetophenone is apparently a new compound. It was prepared from pentaethylbenzene and acetyl chloride by the Friedel–Crafts reaction, heptane being used as the reaction medium. The aluminum chloride addition compound was decomposed in the usual manner and sufficient benzene was added to keep the crystalline product in solution. The benzene solution was washed with dilute hydrochloric acid, with sodium carbonate solution, and finally with water. The solvent was then allowed to evaporate from an open dish. The crystalline residue was recrystallized twice from alcohol and finally from heptane. It crystallizes in thick, colorless needles which melt at 141°.

Anal. Calcd. for $C_{18}H_{28}O$: C, 83.00; H, 10.84. Found: C, 83.15; H, 10.74.

Pentamethylnitrobenzene and *o*-dinitrotetramethylbenzene were prepared by the methods of Smith and Taylor, and Smith and Harris, respectively.[12,13]

Experimental Results

A summary of the dielectric properties of some of the benzene derivatives which were measured is provided in Table I. A (+) in the third column indicates that rotation of the molecule is observed in the crystalline solid and a (−) that it is not. The last column gives data on the circumstances attending the cessation of molecular rotation, *i. e.*, whether it ceases at the melting point (m. p.), at a transition point (t. p.) or with anomalous dispersion (a. d.).[14] The measurements on compounds which show evidence of molecular rotation in the solid are represented in Figs. 1 to 13. When anomalous dispersion appeared measurements were made at the frequencies of 1, 3, 10, 30, 100 kc. The dielectric loss in regions of anomalous dispersion is represented in terms of the imaginary part ϵ'' of the complex dielectric constant,[15] which is equal to the product of real dielectric constant ϵ by the tangent of the loss angle. The generally negligible d. c. conductivity was not subtracted from the total a. c. conductivity in calculating ϵ''.

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

(8) White and Morgan, *J. Chem. Phys.*, **5**, 655 (1937).

(9) Lonsdale, *Proc. Roy. Soc.* (London), **123**, 494 (1929); **133**, 536 (1931).

(10) Hinkel, Ayling and Bevan, *J. Chem. Soc.*, 1874 (1928).

(11) French Patent 814,479.

(12) Smith and Taylor, THIS JOURNAL, **57**, 2400 (1935).

(13) Smith and Harris, *ibid.*, **57**, 1289 (1935).

(14) The temperature given in connection with those materials having anomalous dispersion is that at which the relaxation time τ is 10^{-6} second.

(15) Debye, "Polar Molecules," The Chemical Catalog Co., New York, N. Y., 1929, pp. 92–94.

Discussion of Results

The data supply two kinds of evidence of molecular rotation in the crystal: (1) the dielectric constant of the solid behaves like that of the corresponding liquid, and (2) among these solids, ϵ may be correlated with dipole moment of the molecule.

The figures show that with one exception the dielectric constant of the solid at the highest temperature measured is higher than that of the liquid in those cases where the latter has been observed. As among non-aromatic compounds,[4,5,6] this is taken to be evidence that the molecules rotate with much the same freedom in the solid as in the liquid.

Since no determination of the corresponding dipole moments has been found in literature, the fifth column of Table I lists values estimated by vectorial addition for some of these compounds, assuming the moment of the methyl radical to be $+0.4\ D$ and of the chlorine atom $-1.5\ D$.[16] In 3,4,5-trichloro-*o*-xylene the presence of an unsubstituted hydrogen atom probably leads to a considerably lower dipole moment than that estimated as above. The dielectric constant of 1,2,3-trimethyl-4,5,6-trichlorobenzene will be shown below to suffer an unusually large reduction due probably to intermolecular action. Otherwise the correlation between dielectric constant and calculated dipole moment is good in spite of the tendency of density and intermolecular action to mask it. Since a permanent dipole cannot affect the dielectric constant except through rotational motion, this correlation is convincing evidence that the molecules of all of these solids engage in such motion.

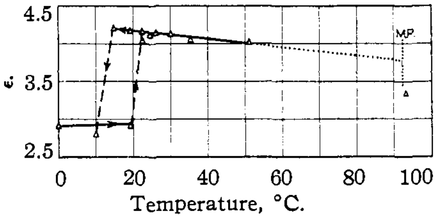

Fig. 1.—Dielectric constant of trichloro-*m*-xylene at 100 kc.

The abrupt rise of ϵ with temperature between 19 and 22° exhibited in Fig. 1 by trichloro-*m*-xylene is typical of a transition marking the onset of molecular rotation. As among the non-aromatic transition compounds, the solid is brittle below the transition temperature and quite waxy above it. Above 50° the specimen sheets became so waxy as to deform in the condenser, and hence could not be measured accurately. Extrapolation of the observed curve to the melting point indicates that ϵ is at least as high after solidification as before and hence that molecular rotation is about as extensive in the solid as in the liquid.

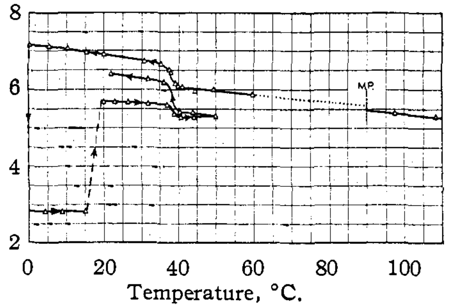

Fig. 2.—Dielectric constant of 3,4,5-trichloro-*o*-xylene at 100 kc.

Figure 2 portrays the complicated behavior of 3,4,5-trichloro-*o*-xylene. Waxiness again prevented measurement of sheets above 60°, but extrapolation indicates that ϵ does not change much at the freezing point and hence that the molecules of the crystal are rotating. Upon cooling through a declining sequence of constant temperatures, a transition appears between 40 and 36°, at which ϵ rises by about 0.5. With further cooling the transition to the brittle non-rotating form of the crystal had occurred after the sample had been left at $-0.2°$ for one hour. The corresponding rise of ϵ with heating occurs between 15 and 20°; the value of ϵ at which the rise ceases is, however, much lower than expected. Figure 2 shows that after heating to 50°, ϵ returned at 25° much more nearly to its original value. This behavior may be explained by the formation of voids upon transformation to the low temperature form; such voids would be at least partially eliminated at temperatures where the material is very waxy.

The dielectric constant of 3.4 found in 5-nitro-3,4-dichloro-*o*-xylene at 0° as shown in Fig. 3 is enough higher than the refraction value to indicate some molecular rotation even at this low temperature. The dielectric constant rises progressively as temperature increases, particularly between 50 and 64°. Above the latter temperature the specimen became so waxy that no further measurement of sheets could be made. After measuring the liquid the material was therefore allowed to solidify with the condenser for liquids immersed in

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[16] Smyth, "Dielectric Constant and Molecular Structure," Chem. Catalog Co., New York, N. Y., 1930, pp. 106–114.

it. Although such measurements are accurate only for temperatures near the melting point of the solid, the essential continuity of the ε curves for liquid and solid indicates that the freedom of molecular rotation is approximately the same in the solid and liquid phases. In this condenser the reverse transition to the low temperature form had not occurred after the temperature of the sample had remained in the neighborhood of 30° for several days.

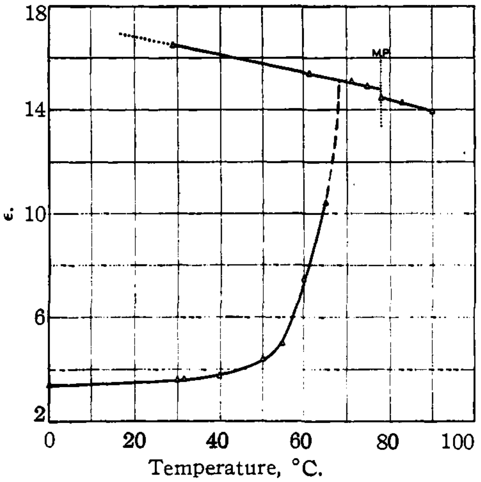

Fig. 3.—Dielectric constant of 5-nitro-3,4-dichloro-*o*-xylene at 100 kc.

The behavior of the isomer of this compound, 3-nitro-4,5-dichloro-*o*-xylene, is striking by contrast; at 111°, only six degrees below its melting point, ε is 3.02, which is evidence of no molecular rotation in the crystal. Its nitro group lies between chlorine and methyl radicals, while in the isomer the adjacent methyl is replaced with a hydrogen atom.

Figure 4 shows the gradual rise of the dielectric constant of *o*-dinitrotetramethylbenzene. The abrupt completion of this rise at 154° leaves the dielectric constant of the solid as extrapolated to the melting point much lower than that of the liquid. The behavior of this compound is consistent with the onset of a considerable degree of rotational motion between 100 and 154°, but it is evident that there is a further increase of such motion at the melting point. There was no great degree of waxiness to be observed above 154°; electrode polarization capacity prevented measurement at temperatures higher than 165°.

The behavior illustrated in Figs. 1 to 3 and to some extent in Fig. 4 is very similar to that usually observed in the many non-aromatic compounds in which there is molecular rotation below the freezing point. Dielectric constant rises more or less sharply at what appears to be a transition of the solid from one crystalline form to another. With cooling, the corresponding fall of ε often occurs at a lower temperature, producing a temperature hysteresis loop. The dielectric constant is independent of frequency through the range measured except for electrode polarization effects such as in Fig. 4 at 164°. There are no dielectric loss maxima. Above the transition temperature these materials are waxy; pressed sheets or solidified melts are very translucent. Below the transition temperature the same materials are brittle; the progress of the transformation to the low temperature form often may be observed as a growth of opaque regions in the translucent matrix of the high temperature form. There is evidence of a considerable change of density at such transitions. The molar volume estimated from the weight and dimensions of sheets of 3,4,5-trichloro-*o*-xylene pressed below the transition temperature was 136 cc.; when the sheets were pressed above the transition temperature, the molar volume was 143 cc. The actual difference in molar volume of the rotating and non-rotating forms is undoubtedly even greater since the apparent molar volume of the low temperature form is the more likely to be enhanced by voids in the sheet.

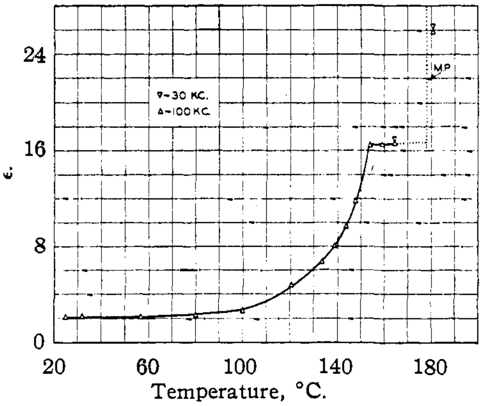

Fig. 4.—Dielectric constant of *o*-dinitrotetramethylbenzene at 30 and 100 kc.

Although the evidence of molecular rotation below the freezing point as exhibited in Figs. 5 to 13 is equally good, the behavior of these solids is otherwise strikingly different from that of the compounds discussed above. Dielectric constant rises gradually from its low temperature value, and through a different temperature range for each frequency of measurement. There is no tem-

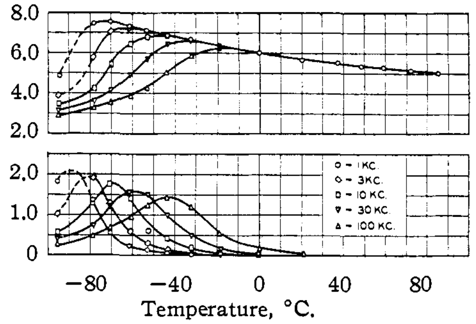

Fig. 5.—Dielectric properties of pentamethylchlorobenzene.

perature hysteresis. For any given frequency the rise of dielectric constant is accompanied by a maximum of dielectric loss as a function of temperature. This temperature behavior of ε and ε″ is, of course, typical of anomalous dispersion. Although the dielectric constants of these materials are high at room temperature, the solids are so brittle that they can be powdered easily, and the pressed sheets are opaque.

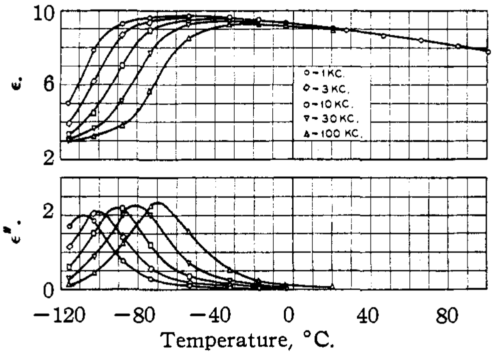

Fig. 6.—Dielectric properties of 1,2,3,4-tetramethyl-5,6-dichlorobenzene.

In Fig. 8 the static dielectric constant of 1,2,3-trimethyl-4,5,6-trichlorobenzene falls gradually over a temperature range of fully 120°, but the behavior of this compound does not otherwise resemble that of the solids which show sharp transitions; its pressed sheets are brittle, opaque, and their density is 1.48, agreeing with the value 1.49 in the isomer, 1,2,4-trimethyl-3,5,6-trichlorobenzene. Furthermore, these two isomers exhibit in Figs. 7 and 8 the same general temperature range of anomalous dispersion.

Several derivatives of camphane, 3-nitro-*dl*-camphor for example, have also exhibited no transition of the static dielectric constant,[17] the rotational polarization disappearing with anomalous dispersion as temperature is reduced. In each such case, however, the waxiness and translucence of the material clearly indicate that it belongs to the same class as the high temperature forms of the transition dielectrics; there was some evidence that the failure of the transition to appear was due to the presence of solid solutions of optical isomers or to the existence of the high temperature form in a metastable state at temperatures below that of its presumed transition. If the compounds of Figs. 5 to 13 are existing in a metastable state at any temperature, not the slightest evidence of such behavior has been found.

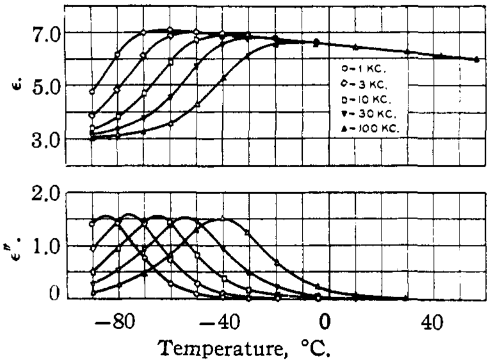

Fig. 7.—Dielectric properties of 1,2,4-trimethyl-3,5,6-trichlorobenzene as measured by W. A. Yager.

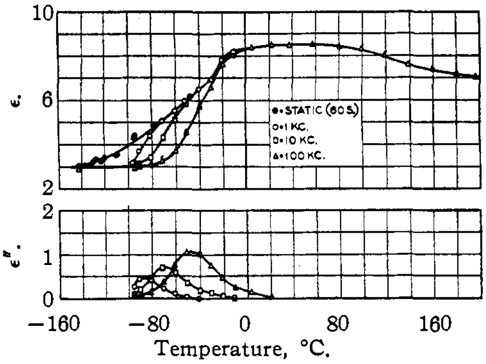

Fig. 8.—Dielectric properties of 1,2,3-trimethyl-4,5,6-trichlorobenzene.

In the following discussion the dielectric constant observed at frequencies so low that the rotational polarization is unaffected by anomalous dispersion will be designated the static dielectric constant ϵ_s. Figure 5 shows the curve of ϵ_s *vs.* $t°$ for pentamethylchlorobenzene to be concave upward, as in most polar liquids and in many solids in which dipole rotation is contributing to the dielectric constant. In 1,2,3,4-tetramethyl-5,6-

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(17) White and Bishop, THIS JOURNAL, **62**, 8 (1940).

dichlorobenzene and 1,2,4-trimethyl-3,5,6-trichlorobenzene the corresponding curves are shown in Figs. 6 and 7 to be concave downward through the measured temperature range. In Fig. 8 this trend reaches its logical conclusion with the most unsymmetrical of the hexasubstituted methylchlorobenzenes when ϵ_s, after becoming almost independent of temperature from +70 to +20°, starts to decline with falling temperature. At −70° anomalous dispersion begins to affect the measurements at frequencies as low as 1 kc.; below this temperature ϵ was measured ballistically, using a charging time of sixty seconds.[18] The results are recorded in Fig. 8 with filled circles and probably represent ϵ_s down to about −100°, below which even the sixty-second ballistic measurements may be affected by anomalous dispersion.

The behavior of the maxima of curves of ϵ'' is consistent with the course of ϵ_s in the several isomers. This maximum should be proportional to the difference between the static and refraction values of the dielectric constant ($\epsilon_s - \epsilon_\infty$). Since ϵ_∞ changes only very slightly with temperature, the height of the maxima of ϵ'' should increase or decrease with ϵ_s. Figure 5 shows a pronounced increase of ϵ'' maxima with declining temperature, while Fig. 8 shows an even more striking decrease.

A reasonable explanation of the reduction of the rotational polarizability of a condensed phase below that of the corresponding gas is found in Debye's theory of hindered rotation, in which this reduction is ascribed to the restraining force of intermolecular action.[19] The sinusoidal potential function which he chooses to represent the effect of this interaction on a given molecule is inadequate for the explanation of the behavior of 1,2,3-trimethyl-4,5,6-trichlorobenzene, however, since it leads to a static polarizability which continually increases with declining temperature, and since without added assumptions it does not account for anomalous dispersion. These difficulties are eliminated by a model recently proposed,[20] in which the rotational motion is from one to another of two equilibrium orientations of different potential energy, with the frequency and temperature range of anomalous dispersion determined by the height of the intervening potential hill.[21,22] The potential function of Fig. 9 is an example showing how such an hypothesis can account for the observed dielectric properties of 1,2,3-trimethyl-4,5,6-trichlorobenzene. After inferring from the shape of this molecule that the rotation is about only one axis, the curve of Fig. 9 represents an assumed angular variation of the potential energy of interaction of a given molecule with all of its neighbors. This interaction is taken to be independent of both temperature and time. As actually drawn the equilibrium orientations are represented as minima in parabolic potential valleys. The polarization due to harmonic torsional vibration of the dipole in either of these valleys is independent of temperature and, at frequencies below about 10^{11} cps., of frequency. In a mass of randomly oriented microcrystals and with an estimated dipole of 3.8 D, the molar polarization due to this motion would amount to about 4.5 cc. At −195° (78°K.) practically all of a statistical assemblage of such molecules lie in the valley centered at $\theta = 72°$ and there is no additional contribution to the polarization due to rotational motion from one to the other of the valleys. As the temperature rises, statistical equilibrium permits increasing numbers of molecules to occupy the potential valley centered at 0°; application of an external field modifies this distribution and thus produces a static rotational polarization P_r in accordance with[20]

$$P_r = \frac{2\pi N\mu^2 (1 - \cos\beta)}{9kT \cosh^2 (E/2kT)} \qquad (1)$$

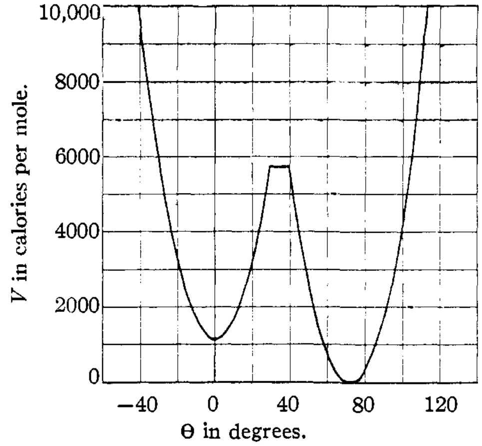

Fig. 9.—Potential function assumed for rotational motion of 1,2,3-trimethyl-4,5,6-trichlorobenzene molecule.

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[18] E. J. Murphy, *Trans. Electrochem. Soc.*, **45**, 133 (1934).

[19] Debye, *Physik. Z.*, **36**, 100 (1935); *Chem. Rev.*, **19**, 171 (1936).

[20] White, *J. Chem. Phys.*, **7**, 58 (1939).

[21] Frank, *Trans. Faraday Soc.*, **32**, 1634 (1936); Eyring, *J. Chem. Phys.*, **4**, 283 (1936).

[22] Mueller, Report of the Committee on Electrical Insulation of the Division of Engineering and Industrial Research of the National Research Council, 1935, p. 11.

N is Avogadro's number; μ is the dipole moment of 3.8 D; β is the angle of 72° between equilibrium orientations; and E is the difference between the energies of the two equilibrium orientations, in this case 7.8×10^{-14} erg per molecule or 1130 cal. per mole.

At temperatures above −100° the total molar polarization was derived from the observed values of static dielectric constant, employing at all temperatures the molar volume of 151 cc. observed in the sheets at 25°; in this method of measurement the number of molecules between the electrodes of the condenser is independent of temperature. After subtracting the entire polarization of 58.5 cc. observed at −195° and 100 kc., the remainder is represented as rotational polarization P_r by the circles in Fig. 10. P_r as calculated by equation (1) is shown by the smooth curve. Despite the use of two adjustable parameters in the calculation, the similarity of the temperature variation of the observed and theoretical curves over a 300° range is significant in exhibiting the ability of the model to account qualitatively for the behavior of ϵ_s in 1,2,3-trimethyl-4,5,6-trichlorobenzene. In passing it may be noted that 72° is not altogether an arbitrary choice for β, since the interval between potential valleys for a truly hexagonal molecule should be 60°.

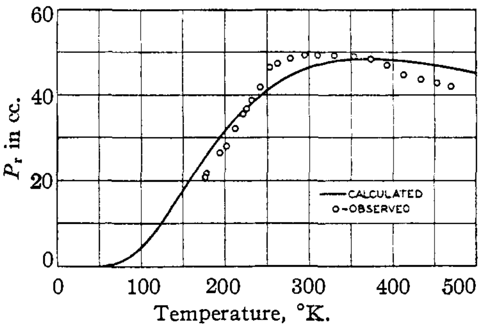

Fig. 10.—Rotational polarization of 1,2,3-trimethyl-4,5,6-trichlorobenzene.

The height of the potential hill in Fig. 9 determines the time required to establish an equilibrium distribution of molecular orientations between the two potential valleys, and hence may be estimated from the observed principal relaxation time τ where

$$\tau = \frac{\epsilon_\infty + 2}{\epsilon_s + 2} \frac{1}{2\pi f_m} \qquad (2)$$

ϵ_∞ being the dielectric constant at frequencies too high (or temperatures too low) for any rotational contribution, and f_m being at any given temperature the frequency at which $\epsilon = (1/2)(\epsilon_s + \epsilon_\infty)$. According to the Eyring–Frank theory of anomalous dispersion[21]

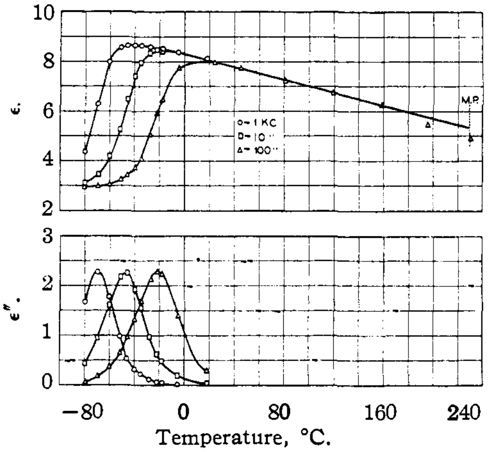

Fig. 11.—Dielectric properties of tetrachloro-*o*-xylene.

$$\frac{1}{\tau} = 5 \times 10^{11} e^{-V_0/kT} \qquad (3)$$

where V_0 is the height of the potential hill (above $V = 0$) and the factor 5×10^{11} is the frequency of torsional vibration in either potential valley, estimating the molecular moment of inertia to be 2.5×10^{-37} g.-cm.^{2}. Hence a potential hill V_0 of 3.97×10^{-13} erg per molecule or 5740 cal. per mole accounts for the observed relaxation time of 10^{-6} second at −52.5°. The value thus calculated for V_0 is undoubtedly artificial, for the model of Fig. 9 is analogous to chemical activation in one degree of freedom, while as Frank points out[21] there should be activation in many degrees of freedom in a crystal or liquid. Using $V_0 = 3.97 \times 10^{-13}$ erg, the relaxation time calculated from equation (3) is therefore not as sensitive to temperature as that observed in Fig. 8.

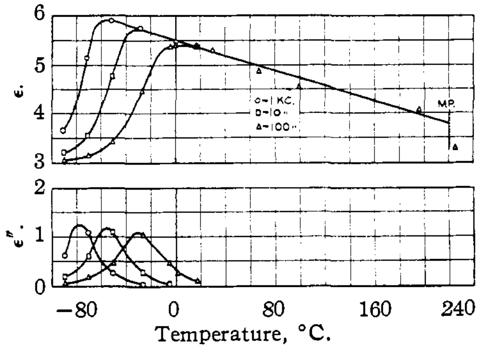

Fig. 12.—Dielectric properties of tetrachloro-*m*-xylene.

Potential functions similar to that of Fig. 9, but with the ratio V_0/E so large that the region of positive $d\epsilon_s/dt$ could not be observed at frequencies as high as 1 kc., are capable of accounting for both the reduction factors and the anomalous dispersion of the other compounds illustrated in Figs. 5 to 13. Once the idea of two or more potential minima is admitted to account for anomalous dispersion, it is difficult to avoid the conclusion that the energies of these minima should in general differ in crystals composed of polar molecules.

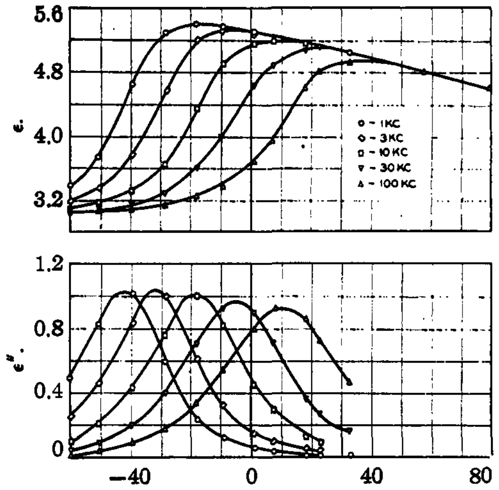

Fig. 13.—Dielectric properties of methylpentachlorobenzene.

With the exception of 1,2,3,5-tetramethyl-4,6-dichlorobenzene, Figs. 5 to 13 include dielectric measurements on all possible polar hexasubstituted methylchlorobenzenes. Since the rotational polarization of each of these compounds is subject to anomalous dispersion, it is of interest to correlate molecular structure with some temperature characterizing the rise of the dispersion. To this end the temperature t_1 at which $\tau = 10^{-6}$ second was obtained by interpolation from the dielectric data for each of these compounds. The results are listed in the sixth column of Table I. They appear to exclude dipole interaction as a determining factor; t_1 declines if anything with increasing dipole moment. Figure 14 shows, however, that considerable regularity appears when t_1 is plotted against the number of chlorine atoms in the molecule, indicating in terms of the theory[21] that the height of the potential hill between equilibrium orientations is increased by replacing a methyl radical in a molecule with a chlorine. The points fall within 7° of the straight line of Fig. 14 for each case except that of pentamethylchlorobenzene, whose point lies 53° above the line. A clue to the cause of its anomalous behavior is found in its crystal habit; it crystallizes from alcohol in plates, while all other members of this series crystallize in fine needles. Hexamethylbenzene, whose system is triclinic,[9] crystallizes from alcohol in plates; while hexachlorobenzene, whose system is monoclinic,[9]

TABLE I

Compound	M. p., °C.	Rotation in solid	Dielectric constant of solid at 20° and calcd. dipole moment		Temp. below which rotation ceases, °C.	
Methylpentachlorobenzene	+224	+	5.2	1.9	+11	a. d.
Tetrachloro-*m*-xylene	+223	+	5.3	1.9	−29	a. d.
Tetrachloro-*o*-xylene	+228	+	8.0	3.3	−26	a. d.
1,2,3-Trimethyl-4,5,6-trichlorobenzene	+225	+	8.5	3.8	−52	a. d.
1,2,4-Trimethyl-3,5,6-trichlorobenzene	+210	+	6.3	1.9	−44	a. d.
1,2,3,4-Tetramethyl-5,6-dichlorobenzene	+193	+	9.1	3.3	−74	a. d.
1,2,3,5-Tetramethyl-4,6-dichlorobenzene	+190	+	6.5			a. d.
Pentamethylchlorobenzene	+154	+	5.7	1.9	−47	a. d.
Trichloro-*m*-xylene	+ 94–95	+	4.1 (30°)	1.8	20–22	t. p.
3,4,5-Trichloro-*o*-xylene	+ 94–96	+	6.9 (30°)	3.6	15–20	t. p.
Pentamethylnitrobenzene	+154	−	3.2			m. p.
2,4,6-Trimethylnitrobenzene, E. K.	+ 44	−	3.0			m. p.
1,2,3,4-Tetramethyl-5,6-dinitrobenzene	+178	+	3.0 (16.5 at +160°)		+150	t. p.
2,4,6-Trimethyldinitrobenzene, E. K.	+ 85	−	3.0_5			m. p.
5-Nitro-3,4-dichloro-*o*-xylene	+ 82	+	3.6 (15.0 at +70°)			
3-Nitro-4,5-dichloro-*o*-xylene	+117	−	3.0			
Ethylpentachlorobenzene	+ 56	−	2.8_5			m. p.
Pentaethylacetophenone	+141	−	2.6_5			m. p.
1,2,3,4-Tetraethyl-5,6-dinitrobenzene	+116	−	2.7			m. p.
1,2,3,4-Tetrachlorobenzene, E. K.	+ 45	−	3.2			m. p.
4,5-Dichloro-*o*-xylene	+ 76	−	2.9_4			m. p.
o-Dinitrobenzene, E. K.	+117	−	3.5			m. p.

crystallizes in fine needles. Although attempts to grow large single crystals for goniometric measurement have failed, it is reasonable to suppose that all compounds represented in Fig. 14 crystallize in the monoclinic system except pentamethylchlorobenzene, whose crystal is triclinic. Any regularity of behavior of t_1 would certainly be destroyed by such a change of crystal system.

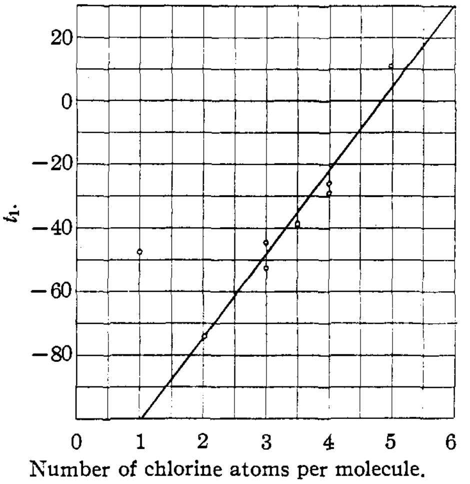

Fig. 14.—Temperature t at which $\tau = 10^{-6}$ seconds *vs.* number of chlorine atoms in hexasubstituted methylchlorobenzenes.

One striking feature of these results is the regular behavior of the relaxation time of 1,2,3-trimethyl-4,5,6-trichlorobenzene in the face of the very large reduction of ϵ_s. This argues in favor of a model in which the reduction factor and t_1 are determined by intrinsically independent features of the potential function, as in Fig. 9.

As a further test of the relation exhibited by Fig. 14, an equimolecular solid solution of methyl pentachlorobenzene and 1,2,3,4-tetramethyl-5,6-dichlorobenzene was prepared. This mixture was first melted and then cooled very slowly through the freezing range, in order to produce as far as possible an equilibrium distribution of the two molecular species throughout the specimen. The dielectric properties of pressed sheets of this solid solution are represented in Fig. 15. The value of t_1 thus observed is −38°, which as represented by the square in Fig. 14 is about what would be expected of a hexasubstituted methylchlorobenzene crystal each of whose molecules contained 3.5 chlorine atoms. Furthermore, the distribution of relaxation times about the principal value is not noticeably broader in the mixture than in the pure crystals, as may be seen by comparing the ratios $\epsilon''_m/(\epsilon_s - \epsilon_\infty)$, where ϵ''_m is the maximum value of ϵ'' at the temperature in question.[23] In the ideal case of a dielectric all of whose molecules have the same relaxation time, this ratio is 0.50; the observed values are 0.42 in methylpentachlorobenzene, 0.35 in 1,2,3,4-tetramethyl-5,6-dichlorobenzene, and 0.34 in the mixture. If any property of the individual molecule, such as moment of inertia, were of controlling importance in determining the frequency with which rotational motion could occur, a broadening of the distribution of relaxation times or possibly two separate principal relaxation times would have been expected in this solid solution. The absence of any such detectable inertia effect is, on the other hand, to be expected if these molecules pass over the potential hill classically as suggested by Frank[21] instead of passing through it in the quantum-mechanical tunnel effect as suggested by Mueller.[22]

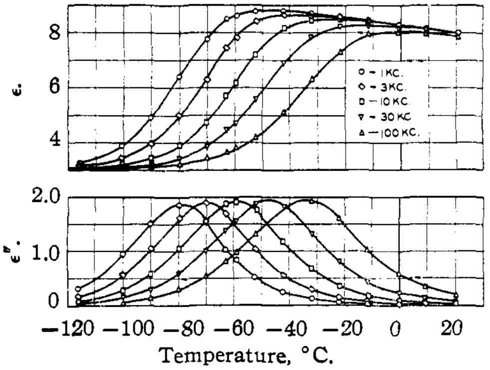

Fig. 15.—Dielectric properties of equimolecular mixture of 1,2,3,4-tetramethyl-5,6-dichlorobenzene and methylpentachlorobenzene.

Among the compounds of Figs. 1 to 4, in whose crystals molecular rotation sets in at a transition, only *o*-dinitrotetramethylbenzene is completely substituted. Among the compounds of Figs. 5 to 13, where there is molecular rotation but no transition, all are completely substituted. Diagrams of these molecules have been drawn to scale.[24] While it is difficult to evaluate the volumetric symmetry about the molecular center of gravity from such a drawing, the hexasubstituted compounds are in general much more symmetrical than the pentasubstituted, with 1,2,3-trimethyl-4,5,6-trichlorobenzene and *o*-dinitrotetramethylbenzene falling close to the dividing line. The

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[23] Yager, *Physics*, **7**, 434 (1936).

[24] The procedure was similar to that employed by Smyth in his diagram of o-dichlorobenzene, reference 16, p. 111.

appearance of transitions in pentasubstituted benzenes and the derivatives of camphane, cyclohexane and ethane may be pictured in terms of the reduction of rotational energy with declining temperature, which eventually permits the crystal to collapse into a dense form in which "interlocking" of molecules eliminates their rotation without changing the closest distance of approach of the peripheral atoms of nearest neighbors. The more symmetrical hexasubstituted benzene molecules appear to require about the same amount of space in the crystal whether they rotate or not. Hence when the energy (or frequency) of molecular rotation is reduced with the temperature, there is little or no tendency for the crystal to collapse into a denser form. At room temperature the molar volume of tetrachloro-*o*-xylene is about 145 cc., while that of the high-temperature form of 3,4,5-trichloro-*o*-xylene is 143 cc., indicating that when rotating the volume required by corresponding hexa- and pentasubstituted molecules is about the same. At almost the same temperature but in the absence of rotation, the molecules of 3,4,5-trichloro-*o*-xylene require a molar volume of only about 136 cc.

The above explanation of the absence of transitions in certain crystals whose molecules rotate is obviously incomplete. Anomalous dispersion in the 1–100 kc. frequency range has been observed in a number of derivatives of camphane and cyclohexane,[5,6] although usually a transition is also found or there is reason to suspect that the state is one of metastable equilibrium.

Further evidence of the influence of symmetry in determining the ability of molecules to rotate is supplied by the negative results for other compounds in Table I. For example, pentamethylnitrobenzene differs from pentamethylchlorobenzene in that the nitro group is larger than chlorine and in that it projects out of the plane of the flat hexagonal ring. These factors apparently result in a sufficient distortion of the symmetry of the molecule or in sufficient interference between nitro groups of neighboring molecules to prevent rotation. The table shows that ethylpentachlorobenzene also is not sufficiently symmetrical to permit rotation. Consideration of models indicates that the ethyl group projects out of the plane of the ring more than the nitro group and thus that rotation is less likely. Pentaethylacetophenone also illustrates the requirement that the symmetry be in the plane of the ring. The decrease in symmetry in going to the tetrasubstituted compounds is so great that no rotation is to be expected among them. For the 1,2,3,4-tetrachlorobenzene, the most asymmetrical, and for the 4,5-dichloro-*o*-xylene, the most symmetrical tetra-substituted compound, there is no molecular rotation.

The authors are indebted to Mr. W. A. Yager for making his measurements of 1,2,4-trimethyl-3,5,6-trichlorobenzene available to them.

Summary

The dielectric data supply two kinds of evidence of molecular rotation in certain aromatic crystals: (1) the dielectric constant of the solid behaves like that of the corresponding liquid, and (2) among these solids, ϵ may be correlated with the dipole moment of the molecule. Although each of the molecules involved possesses considerable volumetric symmetry about one axis through its center of gravity, the less symmetrical of them cease rotating abruptly at transitions, while the more symmetrical exhibit reduced frequency of rotation but no transitions as temperature declines. Among the symmetrical hexasubstituted methylchlorobenzenes, the temperature at which the relaxation time reaches a given value depends with one exception on the number of chlorine atoms per molecule. A function recently proposed by one of the authors to describe the interaction of a molecule with its neighbors is used to explain the peculiar temperature variation of the static polarization of 1,2,3-trimethyl-4,5,6-trichlorobenzene.

NEW YORK, N. Y. RECEIVED AUGUST 24, 1939