two layers. The upper layer of 1-piperidinemethanol was separated and dried over anhydrous sodium sulfate.

Crude 1-piperidinemethanol (3 g.) was dissolved in dry ether (30 cc.) and treated with hydrogen selenide obtained from aluminum selenide (1 g.). A slow stream of nitrogen gas was passed through the apparatus during the reaction and continued until the ether had evaporated. The selenide remained as a white crystalline precipitate and was recrystallized by dissolving in ethyl acetate at room temperature and cooling to 0°. After drying *in vacuo* over sulfuric acid, 1.8 g. of glossy white plates, melting at 67°, were obtained.

Anal. Calcd. for $C_{12}H_{24}N_2Se$: N, 10.2; Se, 28.7. Found: N, 10.3; Se, 28.6.

bis-(1-Piperidylmethyl) selenide dissolved readily in the common organic solvents. It was only slightly soluble in water, decomposition occurring in this solvent as in the case of the morpholine analog.

Summary

1. *bis*-(4-Morpholylmethyl) and *bis*-(1-piperidylmethyl) selenides were prepared from hydrogen selenide, formaldehyde, and the corresponding secondary amines. Attempts to prepare stable selenides using dimethylamine and diethanolamine were unsuccessful.

2. Both selenides were found to be very sensitive to oxidizing agents and highly toxic when injected into rats.

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

Dielectric Evidence of Molecular Rotation in the Crystals of Certain Non-aromatic Compounds*

BY ADDISON H. WHITE AND W. S. BISHOP

A molecular crystal may be considered, as a first approximation, to be a collection of rigid molecules held in a regular arrangement by rather weak intermolecular forces. In 1930 thermal evidence led Pauling to suggest that certain molecules of small moment of inertia are able to rotate in the high-temperature forms of such crystals,[1] the center of gravity of each molecule remaining at or near a point of the appropriate space lattice. He predicted that when the molecule in question is polar the dielectric constant of the high-temperature phase of the crystal should behave like that of a pure polar liquid.[2] This prediction was confirmed by measurement of hydrogen chloride, hydrogen bromide, hydrogen iodide and hydrogen sulfide, whose dielectric constants were found to drop from the high values characteristic of rotating polar molecules at transitions from one solid phase to another, instead of at the freezing points.[3,4,5] By far the greatest number of molecular crystals are organic. Dielectric, volumetric, and thermal measurements of such crystals have more recently revealed similar evidence of the rotation of organic molecules of large moment of inertia, including certain polar derivatives of camphane, cyclohexane and ethane.[6,7,8,9] Dielectric measurements have now been extended to other compounds belonging to these three classes, and show as reported below that the molecules of a surprisingly large number of organic crystals engage in rotational motion nearly or quite as freely as in the corresponding liquids.

In this communication the term "molecular rotation" will be used in the sense in which it has been generally adopted to explain the dielectric behavior of pure polar liquids. Although recent work indicates that the rotation of molecules in liquids is not free,[10] there can be no doubt that its amplitude is far greater than in most solids; *e. g.*, the dielectric constant of nitrobenzene drops from 35.8 to about 3.2 upon freezing.[11] Such a value or lower is characteristic of ordinary organic crystals, in which to a first approximation the rotational motion of the molecules is considered to be an harmonic oscillation.[12]

(*) Published with the financial assistance of an anonymous donor.

[1] Pauling, *Phys. Rev.*, **36**, 430 (1930).

[2] Debye, "Polar Molecules," Chemical Catalog Co., New York, N. Y.

[3] Cone, Denison and Kemp, THIS JOURNAL, **53**, 1278 (1931).

[4] Smyth and Hitchcock, *ibid.*, **55**, 1830 (1933).

[5] Kemp and Denison, *ibid.*, **55**, 251 (1933).

[6] Morgan, Yager and White, *ibid.* **55**, 2171 (1933).

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

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

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

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

[11] Smyth and Hitchcock, THIS JOURNAL, **54**, 4631 (1932).

[12] For example, the lattice heat capacity calculated by Lord, Ahlberg and Andrews, *J. Chem. Phys.*, **5**, 649 (1937), for benzene approaches at room temperature the classical value of three translational and three rotational modes of harmonic motion for each molecule.

Preparation of Materials

The sources of compounds not prepared in these laboratories are indicated by the footnotes of the first column of Table I; the remainder of them were prepared as indicated by the references of the third and fifth columns. The thiocamphor prepared by Sen's method contained camphor as an impurity; 16.08% sulfur was found by analysis, as compared with a theoretical content of 19.05%. Among five samples sulfur content was found to decrease steadily with increasing melting point. The optical activity of *l*-camphor and *l*-borneol was checked with a polarimeter. Chlorocyclohexane, bromocyclohexane and camphoricimide were measured as received. Other materials obtained from outside sources were fractionally recrystallized or redistilled, several times when necessary. The purity of the samples measured is indicated in columns two to five of Table I by the comparison of their boiling and melting points with those of the literature. Where the melting point recorded in column four is below room temperature it designates the temperature at which the specimen was observed to solidify in the cell used for dielectric measurement, and is hence not very accurate. Sharp melting points and visible regularities of structure indicated that in the solid state these samples were crystalline rather than amorphous.

Experimental Methods

The equipment used in this work for measurement of the capacity, conductance and temperature of the condenser containing the test specimen, and for control of the temperature, was essentially that described by Morgan and Lowry.[13] The type of cell in which the dielectric properties of each of these compounds were measured is indicated in the last two columns of Table I. "A" specifies that grounded capacity measurements were made with a condenser consisting of three parallel plates of gold-plated brass, which was immersed in the liquid and, where the melting point was below room temperature, in the solid that was formed after sufficient cooling. This condenser is described and illustrated in more detail elsewhere.[9] "B" indicates that the cell illustrated in Fig. 1 was used; it was designed for use with small amounts of material and requires only 6 cc. The cell consists of two concentric gold-plated brass cylinders which are held in place with respect to each other by the shape of the glass container. There is a clearance of only about 0.08 mm. between brass and glass both inside and outside, allowing for differential thermal expansion. Leads consist of small gold-plated brass rods which are silver-soldered to the electrodes and which are rigid enough to permit their use for adjusting the electrodes into identical positions for successive measurements. Since only grounded capacity measurements can be made in this condenser and since the high potential electrode is in direct contact with the inner glass tube, the condenser was calibrated in place in the bath used for temperature control in subsequent measurements. The alterable capacity of this cell is 36.6 $\mu\mu$f, and was found to be reproducible to within about 3%. Although less accurate than a more rigid condenser, it was used for measurement of liquids or of solids freezing below room temperature when only small quantities were available. C indicates that rectangular sheets of the solid were pressed, using pressures as high as 14,000 lb./sq. in. (1000 atm.). These sheets measured 5.08 × 1.75 cm. and were about 1.2 mm. thick. Comparison of accurately measured densities with those calculated from the weight and dimensions of the pressed sheets indicated that not more than 4% of the volume of such sheets was occupied by voids; where the waxy high-temperature form of a compound existed at room temperature, the volume of voids was negligible. When the sheet was not waxy enough for the gold-plated brass facing plates used in the die to adhere strongly to it, tin-foil electrodes were affixed, using a very thin film of petrolatum as adhesive. These sheets were measured as previously described and illustrated.[9] Sheets of the tetramethylethylene halides sublimed so rapidly at higher temperatures that circular electrodes with a guard ring were provided in an arrangement otherwise similar in principle to the above. When direct capacitance measurements on a pressed disk were thus made, evaporation of that part of the sample covered by the guard ring had no effect on the observed dielectric constant. The use of this method is indicated by D in Table I.

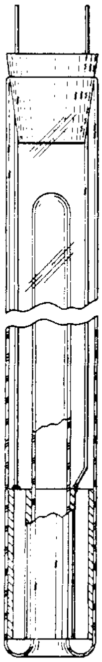

Fig. 1.—Condenser for measurement of small quantities of liquid.

Experimental Results

A summary of the experimental results is included in Table I, in which the compounds are listed more or less in the order of the complexity of their molecular structures. Under t°_{T} is given the temperature range in which the greater part of the increase of dielectric constant from its low-temperature to its high-temperature value occurs; such an abrupt change of dielectric constant will be designated in this paper as a transition, although the heating curves required to establish isothermal absorption of heat have not been run.[14] The word "none" indicates that no such transition was observed in the solid state. Columns seven and eight, under $\Delta\epsilon_{\mathrm{T}}$, list the dielectric constants observed at the lower and upper limits, respectively, of the transition temperature range t°_{T}. These values were observed at a frequency of 30 or 100 kc. except in cyclopentanol, where because of anomalous dispersion the 1 kc. value is more representative of the static polarizability due to the rotational motion of the dipoles. Under $\Delta\epsilon_{\mathrm{MP}}$ columns nine and ten of Table I record the 100-kc. dielectric constant at the melting point for

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

(14) Isothermal absorption of heat and abrupt change of density have been observed at the temperature of the discontinuity of dielectric constant in a number of similar crystals (see references 3–9).

TABLE I

	B. p., °C.		M. p., °C.		t°_{T}	$\Delta\epsilon_{\mathrm{T}}$		$\Delta\epsilon_{\mathrm{MP}}$		Method	
	Obsd.	Lit.	Obsd.	Lit.		From	To	Solid	Liquid	Solid	Liquid
Tetramethylethylene chloride[a]	...	...	159 to 160	159 to 160[e]	−10 to +4	3.3	4.7	...	...	D	..
Tetramethylethylene bromide[a]	...	...	...	decomp.[e]	+75 to 110	2.9	3.9	...	...	D	..
Cyclopentanol	140.1	141[f,i]	−20	...	−72 to −70	2.87	34.2	27.1	25.5	A, B	A, B
1-Methylcyclopentanol-1	...	...	+34.6	35 to 37[j]	None	..	...	3.06	6.97	A	A
Cyclopentanone[b]	130.7–130.8	130.6[f]	−51	...	None	..	...	2.84	16.3	A	A
1,3-Cyclohexadiene	80.5	80.5[f,k]	−89	−98[f]	−114 to −109	2.66	2.75	2.68	2.66	A	A
Cyclohexene[b]	82.1–82.2	83[f]	−105	−103.7[f]	...	..	...	2.52	2.60	A	A
Methylcyclohexane[b]	100.4	100.8[f]	−129	−126.4[f]	None	..	...	2.28	2.26	A	A
Chlorocyclohexane[b]	...	...	−47	−43.9[g]	−68 to −60[v]	3.0	10.0	10.5	10.9	A	A
l-*α*-Menthol[b]	...	...	+42.2	+42.5[f]	None	..	...	2.48	3.95	A	A
Cyclohexanone[b]	155.7	155.7[h]	−40	−45[g], −26[h]	−62 to −53	5.1	21.6	20.2	19.9	A	A
2-Methylcyclohexanone-1[b]	164.8–165.2	164.8–165.0[l]	−20 to −15	...	None	..	...	3.66	16.4	A	A
3-Methylcyclohexanone-1[b]	169.3–169.8	168.6–168.9[l]	−89	...	None	..	...	3.53	18.2	A	A
4-Methylcyclohexanone-1[b]	171.3–171.6	171.4–171.5[l]	−41	...	None	..	...	3.29	15.7	A	A
1,4-Cyclohexadione	...	...	+78	+78[m]	+48 to 51	2.81	3.13	...	4.40	C	A
Cyclohexanone oxime[b]	...	...	+89	+89.5 to 90.5[e]	None	..	...	2.74	3.04	A	A
Cyclohexyl fluoroform	107.0	107.0[f]	−85	< −78[n]	−109 to −106	2.86	8.95	9.44	11.9	A	A
α-Hexachlorocyclohexane[b]	...	...	+156	+157[f]	None	..	...	2.91	4.77	A	A
Bromocyclohexane[b]	...	...	−70 to −65	...	None	..	...	2.82	11.0	A	A
Cyclohexylamine[a]	134.1–134.3	134[e]	−21	...	None	..	...	2.63	5.37	A	A
Cyclohexane carboxylic acid[b]	...	...	+31.2	+31[f]	None	..	...	2.50	2.67	B	B
Cyclohexyl adipate[b]	...	...	+35.2 to 35.5	...	None	..	...	2.81	4.84	A	A
o-Cyclohexylphenol[b]	...	...	+54.5 to 55	...	None	..	...	3.09	3.97	A	A
p-Cyclohexylphenol[b]	...	...	+130.6	+132 to 133	None	..	...	2.62	4.42	A	A
d-Camphene[b]	...	...	+39.5 to 41.5	+42.7[f]	−124 to −118	2.14	2.70	2.36	2.33	A	A
l-Camphor	...	...	+180.0	+178.6[e]	−31 to −30	2.91	12.2	...	...	C	..
l-Borneol[c]	...	...	...	...	+71 to 75	2.90	3.54	...	...	C	..
dl-2,3-Camphanedione	...	...	+203	+198 to 202[o]	+45 to 55	2.69	17.7	12.4	16.3	C	A
3-Oxymethylene-*d*-camphor	...	...	74.9 to 75.1	+80 to 81[p]	None	..	...	3.02	13.7	C	B
dl-Bornyl bromide	...	...	+94.6 to 94.8	+91[e,w]	−68 to −61	3.91	9.16	4.91	5.21	C	A
α-Chloro-*α*′-nitro-*dl*-camphor	...	...	+95.8	+95[e,w]	+45 to 76	5.0	34	31.5	27.7	C	A
3-Cyanocamphor	...	...	+129.3 to 129.5	+127 to 128[q]	+110 to 116	4.0	25	(23)	23	B, C	B
Camphoricimide[d]	...	...	+249	...	+92 to 94	2.91	5.46	5.7	5.5	C	A
dl-Thiocamphor	...	...	138.6 to 139.0	+145[r]	−30 to −10	4.6	11.0	8.8	(8.5)	C	B
3-Nitro-*d*-camphor	...	...	+102.3 to 102.9	+102[s]	+40 to 49	3.2	18.2	...	...	C	..
3-Nitro-*dl*-camphor	...	...	+102.1 to 102.3	+102[s,w]	?	..	21.3	...	...	C	..
3,x-Dichloro-*dl*-camphor	...	...	+71.5 to 71.8	+70 to 77[e,t,w]	?	..	18.0	16.6	14.3	C	A
dl-Thioborneol	...	...	+116 to 117	+120[u]	?	..	4.58	...	...	C	..

[a] Supplied by Fraenkel–Landau. [b] Supplied by Eastman Kodak Co. [c] Supplied by the British Drug Houses. [d] Supplied by Hercules Powder Co. [e] "Beilstein," 4th ed. [f] "International Critical Tables." [g] Handbook of Chemistry and Physics, 12th ed. [h] Supplement Beilstein, 4th ed. [i] Nenitzescu and Ionescu, *C. A.*, **27,** 1329 (1933). [j] Zelinsky and Namjetkin, *Ber.*, **35,** 2683 (1902). [k] "Org. Syn.," Vol. XII, p. 26; Crossley, *J. Chem. Soc.*, **85,** 1416 (1904). [l] Signaigo and Kramer, THIS JOURNAL, **55,** 3326 (1933). [m] Herman, *Ber.*, **16,** 33 (1883). [n] Swarts, *Bull. acad. roy. Belg.*, 399 (1920). [o] Allard, *C. A.*, **28,** 7255 (1934). [p] Bishop, Claisen, and Sinclair, *Ann.*, **281,** 1414 (1894). [q] Lapworth, *J. Chem. Soc.*, **77,** 1058 (1900). [r] Sen, *J. Indian Chem. Soc.*, **12,** 647 (1935). [s] Lowry, *J. Chem. Soc.*, **107,** 1038 (1915). [t] Cazeneuve, *Compt. rend.*, **94,** 731 (1882). [u] Sen, *J. Indian Chem. Soc.*, 12, 651 (1935). [v] With temperature falling. [w] For an optical isomer.

the solid and liquid states, respectively, as measured in the immediate neighborhood of this temperature, or as determined by extrapolation in cases such as those illustrated in Fig. 11.

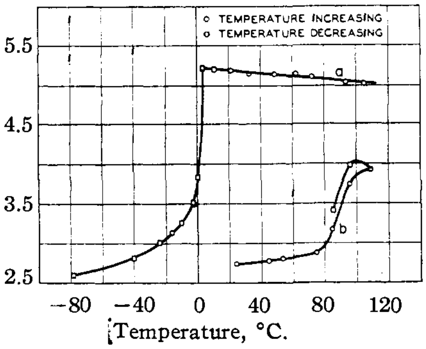

Fig. 2.—Dielectric constant of (a) tetramethylethylene chloride and (b) tetramethylethylene bromide at 100 kc.

Figures 2–13 provide a more complete record of those measurements which constitute evidence that molecular rotation occurs in the crystal. A considerable frequency range, usually 1–100 kc., was covered in this work. Only one measurement is recorded for each temperature except where anomalous dispersion appears, or the spurious effects of electrode polarization capacity are found at low frequency. Total a. c. conductivity also was measured but is reported only where anomalous dispersion and the accompanying dielectric loss are found. The observed conductivities are then used to calculate loss in terms of imaginary dielectric constant ε″, which is equal to the product of the ordinary dielectric constant ε′ by the tangent of the loss angle.

Experimental points in the figures represent temperature equilibrium in the sense that each temperature was held constant within 0.1° until the dielectric properties of the sample ceased to change with time. Apparently discontinuous changes of dielectric constant are indicated in the figures by broken lines whose horizontal components measure the interval between successive constant temperatures of measurement. More exact determination of such temperatures of transition is best made with cooling and heating curves.

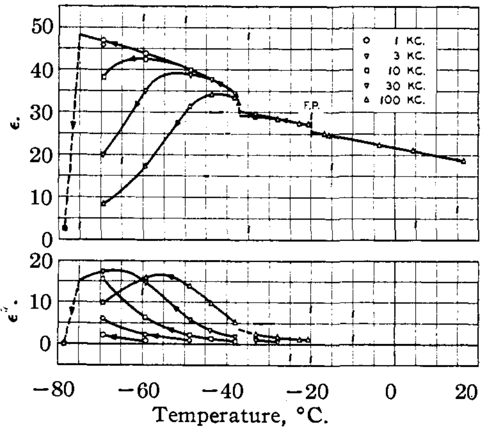

Fig. 3.—Dielectric properties of cyclopentanol as functions of declining temperature.

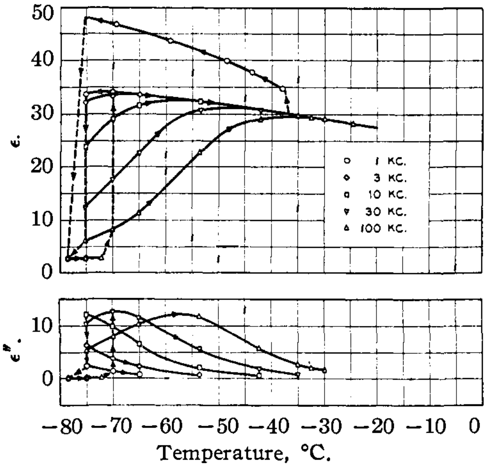

Fig. 4.—Dielectric properties of cyclopentanol as functions of rising temperature.

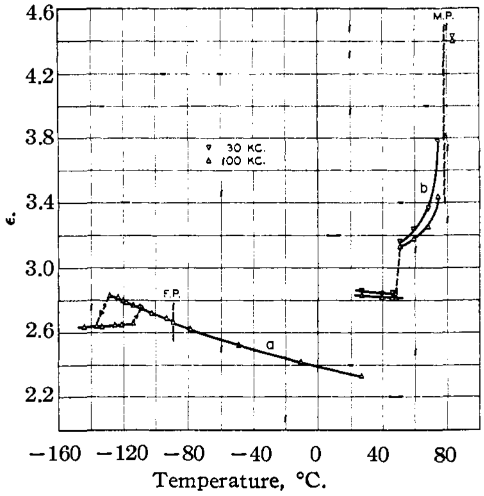

Fig. 5.—Dielectric constant of (a) 1,3-cyclohexadiene and (b) 1,4-cyclohexadione.

Lack of space forbids detailed discussion of the individual experiments except where the figures are not adequately self-explanatory. Inspection of these figures shows, however, that in most cases where measurements of the liquid were obtained, any discontinuity of the dielectric constant curve at the freezing point is so small as to indicate that the polar molecules are able to rotate about as freely in the crystalline as in the liquid state. Only in 1,4-cyclohexadione (Fig. 5b) and cyclohexyl fluoroform (Fig. 7b) is there an extensive drop of dielectric constant upon freezing; any molecular rotation in these crystals must be considerably restricted as compared with the corresponding liquids.

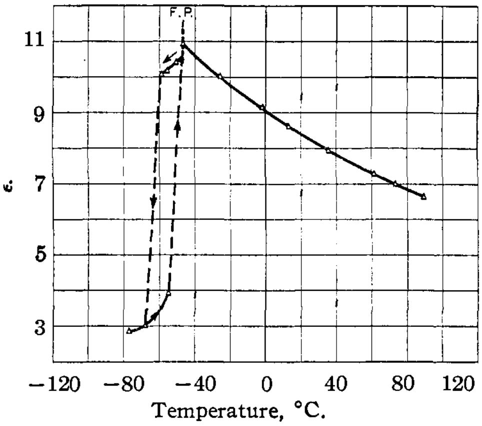

Fig. 6.—Dielectric constant of chlorocyclohexane.

When solid cyclopentanol is cooled through a sequence of constant temperatures, a transition occurs between −36.7 and −37.4°. After cooling to −40.4°, the same transition is observed with rising temperature. The results of only one run are represented in Figs. 3 and 4 by experimental points because the absolute values observed after successive solidifications differed by 5%, due probably to variability in the formation of voids. The data obtained in other runs were used to define the temperature range of each of the transitions more accurately than indicated by the points of Figs. 3 and 4. Immediately below the transition at −37° the dielectric constant at frequencies lower than 30 kc. was found to have risen from about 30 to about 34, and $-d\epsilon/\epsilon dt^\circ$ to have increased from 0.006 to 0.015. No change in the translucent, camphor-like appearance of the solid was visible. To assume that density increases at this transition does not explain the large increase in the negative temperature coefficient of dielectric constant nor the increase of its absolute value, as measured under circumstances where the total number of molecules between the plates of the condenser does not change.

Below −37° an anomalous dispersion involving all or nearly all of the rotational polarization affects dielectric measurements made at frequencies between 1 and 100 kc., as in the supercooled high-temperature form of cyclohexanol.[8] This is evidence that at these temperatures the frequency of rotational motion of the cyclopentanol molecules in the crystal ranges in the neighborhood of 10^6 c. p. s. At −75.2° the frequency of maximum loss is 11.5 kc. and the relaxation time τ calculated according to Debye[2] is 1.30×10^{-6} second.

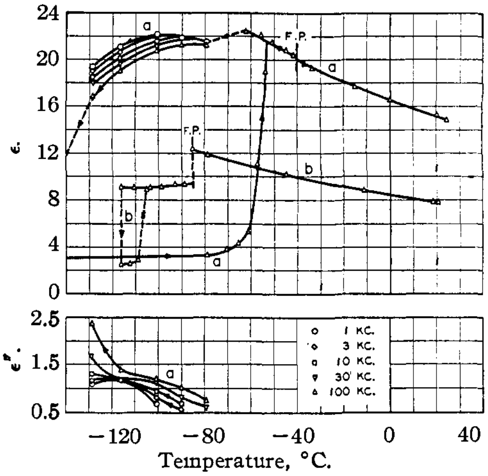

Fig. 7.—Dielectric properties of (a) cyclohexanone and (b) cyclohexyl fluoroform.

Between −75.2 and −78.5° the dielectric constant of cyclopentanol drops abruptly at all frequencies alike to about 2.7. Figure 4 shows that with increasing temperature the solid goes back to a form in which there is again rotational motion of the molecules, the transition occurring between −72 and −70°. At all frequencies, however, the values of ϵ' and ϵ'' are much lower than when −70° was approached from higher temperatures. Upon cooling immediately to −75.2° the transition was not reversed; a complete frequency run at this temperature showed the frequency of maximum loss to be 16 kc., yielding a relaxation time of 1.31×10^{-6} second, about the same as when ϵ' as observed at 1 kc. and −75.2° was 48 instead of 34. Further cooling again produced the transition to the non-rotational form of the solid between −75.2 and −78.5°. From this point temperature was increased regularly, until it became evident as in Fig. 4 that the dielectric constant curve is continuous with that originally observed above −37°, and that with temperature rising from below −75° there is no dielectric evidence of the transition at −37°.

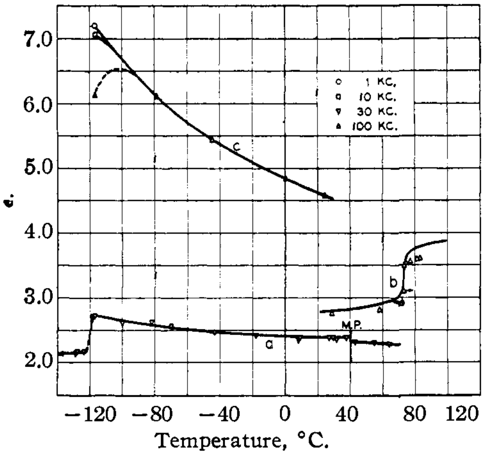

Fig. 8.—Dielectric constant of (a) *d*-camphene, (b) *l*-borneol and (c) *dl*-thioborneol.

l-Borneol and *l*-camphor were measured in order to compare their dielectric behavior with that of the corresponding dextrorotatory compounds. To this end the curves drawn in Figs. 8b and 9b are reproductions of those reported for the *d* compounds by Yager and Morgan,[7] while the points represent experimental values obtained from the *l* isomers. An arrow attached to an experimental point represents the direction of temperature change before and after its observation. The similarity of dielectric constant and transition temperature exhibited by the *d* and *l* forms of each of these two compounds shows as expected that the forces acting between molecules are of identical symmetry and magnitude in crystals of optically active isomers.

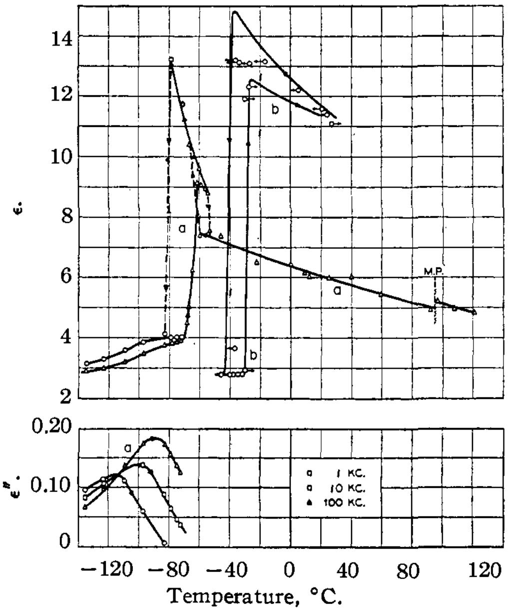

Fig. 9.—Dielectric properties of (a) *dl*-bornyl bromide and (b) *l*-camphor.

Since the behavior of *dl*-bornyl bromide is very complicated, the temperature range in which the transitions occur is illustrated in Fig. 10 on a larger scale than in Fig. 9a. With falling temperature the first transition, from what will be called Phase I to Phase II, occurred between −60.1 and −66.5°. Dielectric constant and its negative temperature coefficient increased greatly, much as in cyclopentanol. When the temperature was increased before converting to the non-rotating form, hysteresis appeared and the transition from Phase II to Phase I was found between −54.5 and −53.7°. Upon cooling again, dielectric constant fell on the curve of Phase II as indicated by points at −71.1 and −79.1°. The transformation to Phase III was characterized by an abrupt fall of dielectric constant from 13 to about 4 between −79.1 and −83.0°. Evidence of a residual molecular rotation in Phase III was found in the high value of its dielectric constant and the anomalous dispersion which caused the high-frequency dielectric constant to drop to 2.9 at −135°. After reversing the direction of temperature change, dielectric constant rose rapidly but with a measurable temperature coefficient between −70 and −61°. The value to which it rose was 9.16, showing that this transition was from Phase III to Phase II rather than to Phase I.

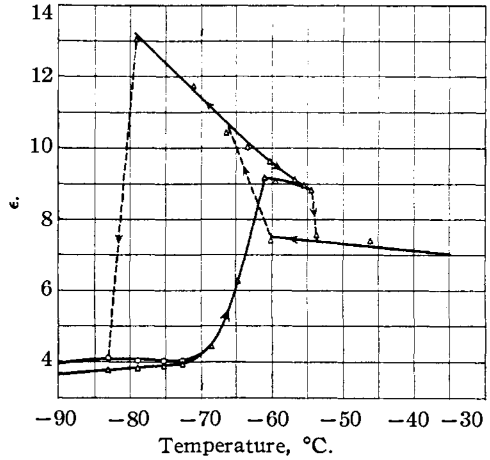

Fig. 10.—Dielectric constant of *dl*-bornyl bromide in region of transitions.

The failure of the dielectric constant of *dl*-thiocamphor to return to its original value with rising temperature, as shown in Fig. 11a, is not a

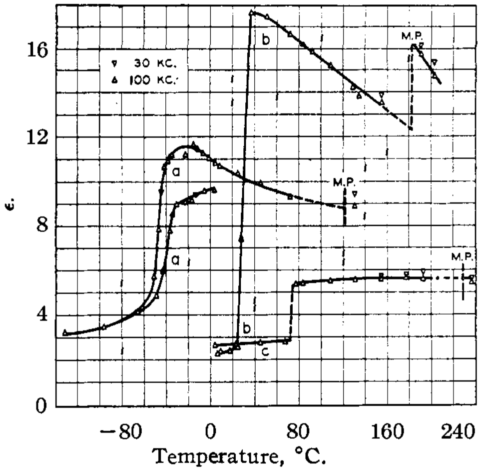

Fig. 11.—Dielectric constant of (a) *dl*-thiocamphor, (b) *dl*-2,3-camphanedione and (c) camphoric imide.

real effect. It was found that the waxy sheets originally pressed had been shattered by the embrittlement and the presumably large density change which occurred when the sample went over to the low-temperature form, leaving voids which were not eliminated when the transition was reversed, because of the lack of constraint along the edge of the sheets. When the specimens which had been through this temperature cycle were pressed again, dielectric constant returned to its original value of 11.0.

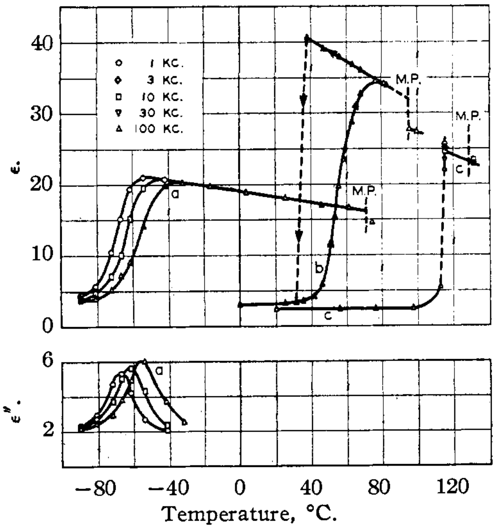

Fig. 12.—Dielectric properties of (a) 3,x-dichloro-*dl*-camphor, (b) α-chloro-α'-nitro-*dl*-camphor and (c) 3-cyanocamphor.

The dielectric constant of 3-nitro-*dl*-camphor at room temperature is not very different from that of the 3-nitro-*d*-camphor in the high-temperature form, as may be seen in Fig. 13. Upon cooling to low temperature there was no transition at which dielectric constant fell at all frequencies alike to a low value indicative of no molecular rotation. Anomalous dispersion appeared instead, eliminating at −98.7° practically all effect of molecular rotation on the dielectric constant at frequencies as low as 1 kc. This presumably means only that the relaxation time of the rotational motion of the molecules is much longer than 10^{-3} second at this temperature. Two other crystalline compounds in which dielectric constant similarly falls off with anomalous dispersion rather than at a transition are 3,x-dichloro-*dl*-camphor (Fig. 12a) and *dl*-thioborneol (Fig. 8c).

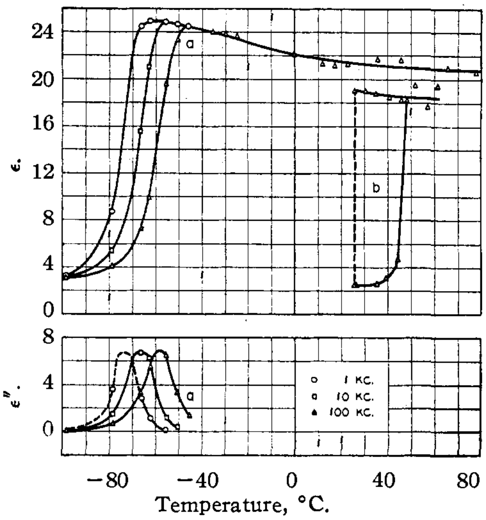

Fig. 13.—Dielectric properties of (a) 3-nitro-*dl*-camphor and (b) 3-nitro-*d*-camphor.

Discussion of Results

Taken all together these measurements and those previously reported[6,7,8,9] constitute convincing evidence that extensive rotational motion of large organic molecules is much more commonly found in crystals than has been suspected. It is also evident that this ability of the molecule to rotate in the crystal lattice is much more frequently found among the derivatives of cyclic polymethylenes than among the generality of organic compounds, whose polarizations have normally been found to be so low in the solid state as to be ascribed to distortional effects only. Inspection of Table I indicates that among the cyclic polymethylene derivatives the attachment of a large substituent to the ring inhibits molecular rotation, as in cyclohexyl adipate, the cyclohexylphenols, and cyclohexane carboxylic acid. Even the substitution of one methyl group for a hydrogen atom has the same effect in such cases as the methylcyclohexanones and 1-methylcyclopentanol-1. There is no satisfactory correlation of ability to rotate or of transition temperature with either the dipole moment or the moment of inertia of the molecule.

Among the compounds of Table I molecular rotation in the crystal is much more noticeably correlated with the gross physical properties of the crystal than with the chemical structure of the molecule. Crystals in which there is no molecular rotation at room temperature are relatively hard and brittle; those in which the molecules rotate at room temperature are soft and waxy. When one of these compounds is solidified from the melt in a test-tube, the formation of a semi-transparent mass having an appearance similar to that of camphor is characteristic of molecular rotation; the transition to the form in which there is no such rotation is marked by the rise of opacity, possibly because of shattering due to change of density. Perhaps the most significant physical characteristic of the crystals in which we have found molecular rotation is their low heat of fusion, as roughly observed by the rapidity with which a large sample is able to freeze at a temperature only a few degrees below its melting point. Since the crystal does not "freeze" with respect to rotational motion until the transition temperature is reached, a low heat of fusion is to be expected, as has been pointed out by Clusius.[15]

Pirsch[16] reports that molecules of approximately spherical shape are found to produce crystals of much lower heats of fusion than molecules of roughly circular or linear shape. He suggests that this may result from the small ratio of surface to volume in a sphere, which means that the effectiveness of interatomic forces in producing intermolecular forces is low, relative to the number of atoms, in molecules of roughly spherical shape. Among such compounds cited by Pirsch for their large cryoscopic constants and correspondingly low heats of fusion are camphorquinone (2,3-camphanedione), camphor, borneol, bornyl chloride, bornyl bromide, and camphene, all of which we have found to exhibit molecular rotation immediately below the melting point. In these cases at least Pirsch's explanation of low heat of fusion may be modified by saying that at the melting point the crystal freezes with respect to translational motion of the molecules only; the intermolecular forces are so small, or, at least, so symmetrical, that the crystal does not "freeze" with respect to rotational motion until the transition temperature is reached. Hence the change of entropy which ordinarily would occur at the freezing point alone is divided between the freezing point and the transition temperature.

The other camphane derivatives and the tetramethylethylene halides in which we have observed molecular rotation are spherical in the sense in which Pirsch uses the term. However, cyclopentanol, ethylene cyanide and the many cyclohexane derivatives which exhibit a similar freedom of molecular rotation in the crystal, are not even approximately spherical. Pirsch[17] has noted that certain cyclohexane and cyclopentane derivatives exhibit much lower heats of fusion than do other circular compounds. The heat of fusion of 406 calories per mole observed in cyclohexanol[18] and that of 940 calories per mole reported for ethylene cyanide[19] fall on the curve of heat of fusion against temperature which Pirsch characterizes as that of spherical molecules.[19] On the other hand, such a spherical molecule as *t*-butyl alcohol shows no dielectric evidence of molecular rotation in the crystal,[20] while its heat of fusion of about 1600 cal./mole[19] is fully twice as high as that indicated by Pirsch's curve for spherical molecules without rings. Pirsch cites other spherical molecules of anomalously large heat of fusion.[17] It appears likely that among these non-aromatic compounds very low heat of fusion is more immediately associated with the ability of a molecule to rotate in the crystal lattice than with its spherical shape. For rotation in the crystal to be possible, however, a certain degree of either spherical or circular geometrical symmetry obviously is required of the molecule, and its center of figure should not be displaced too far from its center of gravity. The approximately spherical symmetry of the molecules of the cam-

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[15] Clusius, *Z. Elektrochem.*, **39**, 598 (1933).

[16] Pirsch, *Angew. Chem.*, **51**, 73 (1938).

[17] Reference 16, footnote 14.

[18] Kelley, THIS JOURNAL, **51**, 1400 (1929).

[19] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y.

[20] Smyth and McNeight, THIS JOURNAL, **58**, 1597 (1936).

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.

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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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[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).