[CONTRIBUTION FROM CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA]

The Dielectric Properties of Solid and Liquid *cis*- and *trans*-Decahydronaphthalene

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The measurement of the dielectric constant of *cis*- and *trans*-decahydronaphthalene over a temperature range constitutes another addition to a series of measurements made on these substances. Hydrocarbons have in the pure state a low dielectric constant and have either zero or a very low value for the dipole moment. Hence very slight polarity is to be expected in these bicyclic hydrocarbons and this polarity is possible only when the molecules exhibit some lack of symmetry. One would, therefore, expect the symmetrical *trans* isomer to have no dipole whereas the unsymmetrical *cis* isomer might have a small permanent dipole moment.

In the present investigation it was decided to measure the dielectric constant over a temperature range for both liquid and solid. Any difference in behavior might then throw some light on the spatial structures of these two compounds. The problem of the dielectrics of non-polar substances in solid form has only recently been considered and the theory is therefore limited. Considerable theory has been developed for long-chain ketones which, being polar, show a pronounced change of polarization when they become fixed in a crystal lattice.[1b] Such changes in the dielectric constant of non-polar compounds have been found to be relatively small. Thus Müller noticed that the dielectric constant of a long-chain hydrocarbon increased at the freezing point by 2 to 6% for different experiments.[2] His work, however, was directed toward the measurement of polar compounds and he considered the changes for the hydrocarbon to be negligible. Much experimental work has been done on measuring the dielectric constant change in passing through the melting point region but little in the reverse direction. Recently R. Giullien[3] reported discontinuities in the dielectric constant–temperature relationships near the fusion point.

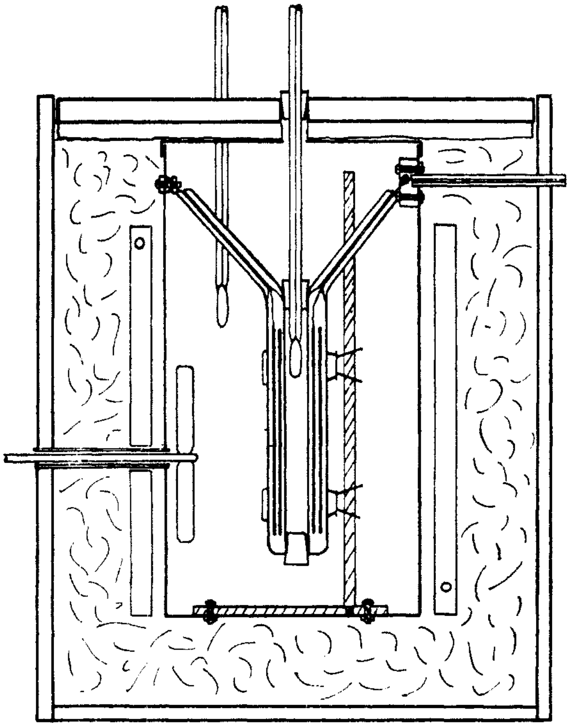

Fig. 1.—Test cell assembly.

The difficulties of measuring the dielectric constants with a cell suitable for both liquid and solid states is at once apparent. The dielectric constant change when the material in the cell crystallizes will depend somewhat upon the rate of crystallization, the type of crystals formed, the viscosity of the material, its latent heat and the temperature at which crystallization starts. All these factors will probably effect the nature of voids between the plates of the condenser. These voids will tend to lower the dielectric constant an indeterminate amount. As a result of these uncertainties it would be extremely difficult to obtain accurate values of the dielectric constant through the transition range from liquid to solid or the reverse. It should be possible, however, to get an indication of the nature of the change transpiring and a comparison of the behavior of the two isomers.

Procedure.—The dielectric constants were measured by using an electrical circuit designed by Alexander[4] and constructed here by Basil A. Dunell.[5] He, using a plate potential of 90 volts, had previously encountered troublesome drifts with the set-up which were, however, completely eliminated in the present case by raising the plate voltage to 160 volts. Also the open stainless steel cell used by him was replaced by one (Fig. 1) similar to that designed by Smyth[6] as evaporation losses were thus eliminated. Instead of three concentric cylinders as in the Smyth cell only two were used with an annular space of 0.09 cm. For shielding, the entire cell was placed in a grounded metal container. The cell held about 40 cc. of the test liquid.

Temperatures between room temperature and −40° were obtained by circulating acetone through the jacket and a copper coil immersed in a Dry Ice–acetone-bath. Temperatures below this and down to −60° were obtained by adding Dry Ice directly to the cell container.

Above room temperature, the temperature was measured by a calibrated mercury thermometer placed in the air-bath. This thermometer could not be placed in the

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[1a] Holder of the Shell Oil of B. C., Fellowship for 1946–1947.

[1b] H. Fröhlich, *Proc. Roy. Soc.* (*London*), **A185**, 399 (1946).

[2] A. Müller, *Proc. Roy. Soc.* (*London*), **A158**, 403 (1937).

[3] R. Giullien, *J. phys. radium*, [8] **1**, 29 (1940).

[4] F. Alexander, Dielectric Constant Meter, Electronics, **18**, #4, p. 116 (1945).

[5] Basil A. Dunell, Master's Thesis, 1946 (holder of the Shell Oil of B. C. Fellowship, 1945–1946).

[6] Smyth and Morgan, THIS JOURNAL, **50**, 1547 (1928).

center of the cell because the mercury column would carry induced currents to the unshielded center plate. For measuring low temperatures a pentane thermometer was used. This was immersed in a liquid in the center cavity of the cell. Gasoline, being non-polar and having a low freezing point, was used as the liquid. This arrangement gave temperatures which at all times were very close to that of the liquid in the cell itself. With the mercury thermometer arrangement, however, considerable time was required for the liquid in the cell to come to the temperature indicated by the thermometer.

Materials.—The benzene used for calibrating the condenser was recrystallized "Merck thiophene-free benzene." Four crystallizations did not raise the freezing temperature, which remained constant over the entire freezing period. The freezing temperature as measured by a Leeds and Northrup platinum resistance thermometer was 5.38°. The sample was then taken as being pure.

The two isomers of decahydronaphthalene were samples taken from various lots of the material that had been prepared from time to time in this laboratory by methods previously described.[7] The *cis* form had freezing points lying between $-43.15°$ and $-43.24°$, while that of the *trans* form lay between $-30.64°$ and $-30.80°$. The cyclohexane was part of a sample specially prepared for spectroscopic work and had a freezing point of 6.5° and a refractive index of 1.4263 for the D line. All the hydrocarbons before use were dried by allowing them to stand for several days over metallic sodium.

Calibration of Cell.—The dielectric constant corresponding to the dial reading of the variable condenser was determined by observing the dial reading for resonance for benzene at a fixed temperature. The cell was filled with benzene and the two condensers (C_1 and C_2) were set so that the dial setting for circuit resonance was at the lower end of the dial for benzene at about 50°. With this setting the dielectric constants of both *cis*- and *trans*-decalin between 0° and 100° were in the dial range. The dial readings for benzene at other temperatures were also observed. From these results and from the known values of the dielectric constant of benzene a calibration curve could be drawn giving the dial readings in terms of the dielectric constant. Since the condenser had been found to vary linearly, the curve could be extrapolated to dial readings between 15 and 85.

The dielectric constants of benzene used in the calibration were taken from the results of Clay, Dekker and Hemelrijh[8] and were extrapolated to higher temperatures on the basis of the linear relation found by previous investigators.

Whenever it became necessary to change the setting of the condenser C_2 in order to measure dielectric constants in a different range, a known dielectric constant in the new range had to be measured and the calibration curve had to be shifted accordingly.

In order to find an unknown dielectric constant it was now only necessary to determine the dial reading for any fixed temperature. The dielectric constant could then be read off the calibration curve.

The maximum variation of the dial reading for successive runs at constant temperature was two dial divisions, corresponding to 0.003 dielectric constant unit. All the results, however, depend upon the benzene calibration and any error in this will produce a proportionate error in all the results. The relationships between the dial readings and the dielectric constants for benzene and those of the two bicyclic compounds were linear. Two methods of measuring the dielectric constants were used, one in which the temperature was kept constant to within 0.1°, and the other in which the temperature was allowed to rise or fall at a steady rate and dial readings were made over small temperature intervals. The values of the dielectric constant at various temperatures for *cis*- and *trans*-decahydronaphthalene were plotted and gave straight lines over the entire temperature range above their fusion points. The equations for these lines by the method of least squares was found to be for the *cis* compound: $\epsilon_{cis} = 2.238 - 0.00103T$ and for the *trans* compound $\epsilon_{trans} = 2.205 - 0.00101T$ where ϵ is the dielectric constant and T the absolute temperature.

Discussion of Results.—Careful attention was directed to the measurements of the dielectric property of the *cis* hydrocarbon in the neighborhood of 50°, since some of the other physical properties of this compound appeared to behave in an irregular manner at this temperature. None were observed in this case although Dunell[5] had observed a pronounced peak in the dielectric constant-temperature curve at this temperature. To test the behavior of this compound still further, a series of readings were made with the temperature slowly rising and falling over a temperature range from 40 to 90° with readings at intervals of 1°. The results when plotted showed decidedly linear relationships.

In measuring the dielectric constant at the liquid–solid transition point several difficulties were encountered. First, these difficulties were due to the fact that the cell and the circuit were designed specifically for the measurement of liquid dielectric constants at and above room temperatures. Since it was difficult to control the temperature in this region readings were taken with the temperature slowly falling or rising and no attempt was made to reach an equilibrium state. Second, the design of the cell made it rather difficult to add a seed crystal; hence, supercooling was another difficulty. Particularly was this so with the *cis*-isomer.

A third difficulty was fluttering and uncertainty due to the large changes in the dielectric constant at the freezing point. As mentioned previously, the circuit was constructed specially for the accurate measurement of small regular dielectric changes. This required a large capacity and a small L/R ratio resulting in considerable instability when abrupt dielectric constant changes were encountered.

Numerous runs for different samples of both the *cis* and *trans* hydrocarbons through the freezing and melting points were made. Typical runs are shown in Fig. 2. The configuration of the *trans*-decalin was remarkedly reproducible, largely perhaps due to the almost complete absence of supercooling. The maximum value of the dielectric constant for eight runs lay between 2.29 and 2.30. Much difficulty was encountered when working with the *cis*-decalin because of supercooling, and here it was always necessary to add a seed crystal to bring about the freezing process. Unlike the *trans*-decalin, only the general behavior and not the exact curves were reproducible.

What is striking in this case is the marked difference in shape of the two areas enclosed by the freezing and melting curves. This is most clearly seen in Fig. 3 where the curves drawn represent averaged values. In the case of *cis*-decalin the dielectric constant of the liquid just above the

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[7] Seyer and Walker, THIS JOURNAL, **60**, 2125 (1938).

[8] Clay, Dekker and Hemelrijh, *Chem. Abst.*, **38**, 5120 (1946).

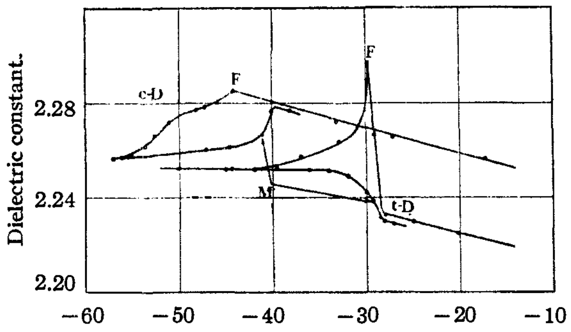

Fig. 2.—Typical run through freezing and melting points: *c*-D, *cis*-decalin; *t*-D, *trans*-decalin; M, melting point; F, freezing points.

freezing point is higher than that of the solid and the shape of the melting point curve is similar to that of many substances already examined, particularly glycerol. It is of course conceivable that if the freezing or melting processes were carried out infinitely slowly the area enclosed by the curves would vanish. In such a case freezing and melting would be a reversible process. It is obvious that the freezing process of the *trans*-decalin is quite different than that of the *cis*-isomer.

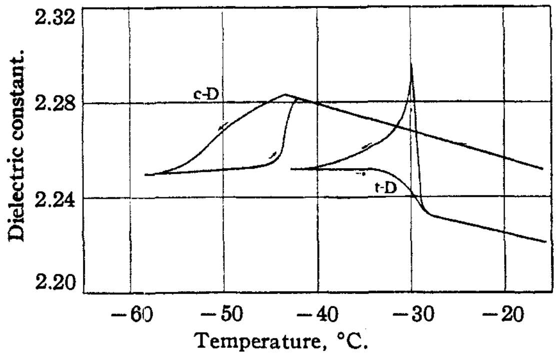

Fig. 3.—Averaged dielectric constant curves through freezing and melting points: *c*-D, *cis*-decalin; *t*-D, *trans*-decalin.

Here the dielectric constant of the liquid just above the freezing point is lower than that of the solid. During the freezing process the dielectric constant not only rises to meet that of the solid but rises considerably above it. Upon melting this path is not followed but the dielectric constant falls slowly to that of the liquid. As mentioned before, if little supercooling was allowed the curves were reproducible with considerable accuracy for the different runs. To investigate this matter further, the hydrocarbon cyclohexane was examined. Recent work on this compound indicates that at room temperatures this substance exists almost entirely in the *trans* state. The behavior of this compound is shown in Fig. 4 and its similarity to that of *trans*-decahydronaphthalene is noteworthy. In the case of cyclohexane the increase in the dielectric constant became so large during the freezing process that the reading was completely off the dial scale. Again, the dielectric constant of the liquid just above the freezing point is lower than that of the solid. Whether or not this sudden augmentation of the dielectric properties during the freezing or solidification process is characteristic of the *trans* state cannot be decided until further observations are made. However, in the case of these two compounds it must be assumed that some deepseated change in the geometrical structure of the molecule must take place, which would involve the loosening of some of the bonds during solidification. Figure 3 shows further that within the limits of experimental error the dielectric constant of solid *cis*- and *trans*-decahydronaphthalene is the same. This would lead one to suspect that the crystal structure of the two solids would be very similar. It would appear that in the *trans* system crystallization and melting are not, at least mechanically speaking, strictly reversible processes. Unlike the case of the *cis* isomer where crystallization and melting are merely the coagulation in an orderly manner and dispersion of the molecules, here some molecular change must precede crystallization.

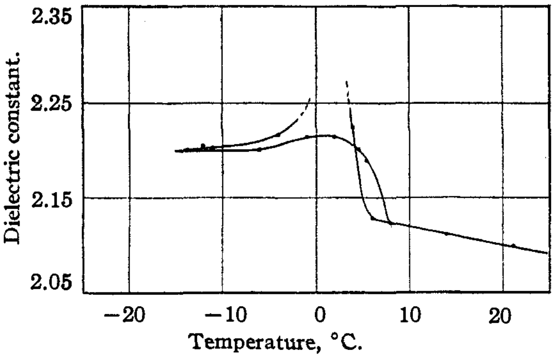

Fig. 4.—Dielectric constant of cyclohexane through freezing and melting points.

The molar polarizations (P) for *cis*- and *trans*-decahydronaphthalene have been calculated for a few temperatures up to 100° and are shown in Table I. The densities were those found previously in this laboratory.[9]

TABLE I

MOLAR POLARIZATION DATA FOR *cis*- AND *trans*-DECALIN

Temp., °C.	Density	Dielectric constant	*P*
	cis-Decalin		
20	0.897	2.219	44.4
50	.874	2.188	44.8
80	.852	2.156	45.1
100	.836	2.136	45.4
	trans-Decalin		
20	0.870	2.184	44.9
50	.848	2.150	45.2
80	.825	2.123	45.6
100	.810	2.103	45.8

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[9] Seyer and Davenport, THIS JOURNAL, **63**, 2426 (1941).

The slightly larger value of P for the *trans*-isomer than for the *cis*-isomer is to be expected in view of the less compact structure of the former compound. At 20° this difference is close to 0.45. This is small but greater than the limits of error in the measurement of the dielectric constant. The polarizabilities (α) have been calculated in the usual manner and compared with those of benzene in Table II.

TABLE II

COMPARISON OF THE MOLAR POLARIZATIONS AND POLARIZABILITIES FROM RESULTS AT 20°

	P	α_{20}
Benzene	26.71	1.05×10^{-25}
cis-Decalin	44.4	1.75×10^{-25}
trans-Decalin	44.9	1.77×10^{-25}

Again it appears that the polarizability of the *trans*- is slightly greater than that of *cis*-isomer.

A comparison of the dielectric constants and the squares of the refractive index for the D line of sodium is made in Table III for benzene, cyclohexane and the two bicyclic hydrocarbons.

TABLE III

COMPARISON OF THE DIELECTRIC CONSTANT WITH THE SQUARE OF THE REFRACTIVE INDEX

	n_{20}	$(n_{20})^2$	ϵ_{20}	$\epsilon_{20} - n_{20}^2$
Benzene	1.50142	2.254	2.289	0.035
Cyclohexane	1.42635	2.033	2.052	.019
cis-Decalin	1.48113	2.194	2.219	.025
trans-Decalin	1.46968	2.160	2.184	.024

It is seen that even for the simple theory which is not directly applicable to liquids the agreement is quite satisfactory. All results indicate a zero or a very small dipole moment for both isomers.

Summary

1. The dielectric constant of *cis*-decalin has been measured at 3.5 megacycles and 20° and has been found to be 2.219±0.003. The temperature coefficient between the freezing point and 100° is 0.0010 per °C. No anomalous behavior in any of the samples tested was observed between −40 and 100°.

2. Under the same conditions, *trans*-decalin has been found to have the values 2.184±0.003. The temperature coefficient between the freezing point and 100° is also 0.0010 per °C. As in the *cis*-isomer no anomalous behavior was observed.

3. The dielectric constant has been measured through the freezing point and to the solid phase. A marked difference in the behavior of the two isomers was observed. Furthermore, the curves for heating and cooling for both the decahydronaphthalene isomers and cyclohexane are quite different. Both *trans*-decalin and cyclohexane show a pronounced and unexplained maximum at the freezing point.

4. The molar polarizations of *cis*- and *trans*-decalin have been calculated at a number of temperatures and the variation with temperature has been found to be the same as the variation of the polarization of liquid benzene with temperature. Furthermore, the squares of the refractive indices are in close agreement with the dielectric constants.

5. The molar polarization of the *trans*-isomer is slightly larger than that of the *cis*-isomer. This indicates a looser or less compact molecular structure for the *trans*-isomer.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Electric Moments of Hydrogen Fluoride, Hydrogen Chloride and Hydrogen Bromide in Several Non-polar Solvents[1]

BY A. J. WEITH, JR.,[1a] MARCUS E. HOBBS AND PAUL M. GROSS

Introduction

The electric moments of hydrogen fluoride, hydrogen chloride and hydrogen bromide in dilute solutions of non-polar solvents are of particular interest since measurements[2] by Fairbrother on some of the hydrogen halides in a limited number of solvents indicated that hydrogen chloride, hydrogen bromide and hydrogen iodide all exhibit a positive solvent effect. Hydrogen fluoride was not measured by Fairbrother; in fact, only recently has a value for the electric moment for this molecule been reported[3] and this was for the gas state. The present measurements were undertaken to establish the magnitude of the solvent effect for these solutes in a more extended series of solvents, to determine the value of the electric moment of hydrogen fluoride in solution and finally to establish the effect of bonding of these acid molecules to acceptor solvent molecules by measuring the electric polarization of the solutes in solutions of dioxane. It was hoped that, because of the relative simplicity of the halides, the data obtained would be useful in future attempts toward elucidation of the origin and mode of action of the solvent effect in electric moment measurements and that some insight might be gained into

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[1] Part of a Thesis of A. J. Weith, Jr., submitted in partial fulfillment of the requirements of the Ph.D. degree in Chemistry at Duke University, June, 1947.

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[2] F. Fairbrother, *Trans. Faraday Soc.*, **30**, 862 (1934).

[3] Hannay and Smyth, THIS JOURNAL, **68**, 171 (1946).