phase II a low dielectric constant form, which seems probable.

The molar polarization of these materials likewise undergoes a change at the transition point and is a linear function of $1/T$ in the range between the transition and melting temperatures. This is in agreement with the prediction of the Debye dipole theory but nevertheless is of doubtful significance except as qualitative evidence that a dipole polarization is present in these solids. Qualitative evidence that dipole rotation is contributing to the dielectric constant is also given by the correlation between the magnitude of ϵ and the dipole moment. No values are available for the moment of camphoric anhydride but it is safe to predict that it is the highest of this group of materials, probably between 4 and 5 *D*. The moment of camphor, 2.7 *D*, is higher than either bornyl chloride or borneol, as is its dielectric constant.

Summary

A study of the dielectric properties of *d*-camphor, *dl*-camphor, *d*-camphoric anhydride, borneol, isoborneol and bornyl chloride has shown that these materials undergo solid–solid transitions. These transitions have not been previously reported in the literature, except for *d*-camphor. Above the transition the value of the dielectric constant of the solid is that normally expected of the polar material in the liquid state. Below the transition the dielectric constant has a low value, approximately equal to the square of the optical refractive index. This dielectric behavior is explained by the rotation of dipoles in the solid.

NEW YORK, N. Y.

RECEIVED JUNE 18, 1935

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, NEW YORK CITY]

Transitions in Camphor and Chemically Related Compounds. II. Vibration of Atomic Groups

BY ADDISON H. WHITE AND S. O. MORGAN

Introduction

In 1914 Wallerant[1] observed at −28° a transition of *d*-camphor from rhombohedral crystals of slight birefringence to similar crystals of pronounced birefringence, upon cooling. P. W. Bridgman[2] studied this transition at higher temperatures and pressures, and designated the solid phases stable above and below it as phase II and phase III, respectively.

Linus Pauling[3] has shown that some crystalline transitions accompanied by thermal phenomena may be explained by assuming that molecules or atomic groups begin to rotate at the transition when the crystal is heated. The possibility that a rise of molecular rotation is responsible for transitions occurring in crystals of complex organic molecules, as well as in the simple molecular lattices studied by Pauling, was the original subject of this investigation.[4] Activity was centered on the above-mentioned transition in *d*-camphor, at which dielectric constant undergoes a change similar to that predicted by Pauling for the transitions in crystals composed of simpler polar molecules.[5]

The molecule of *d*-camphor is so much more complex than that of hydrogen, which Pauling studied, that a mathematical discussion of the possibility of its rotation in the crystal would not be very informative. However, Pauling's theory suggests three lines of attack which should help to determine experimentally the mechanism responsible for the transition in *d*-camphor.

1. Heat capacity measurements through the transition should yield information as to any increase in mobility of units whose motion is restrained below the transition.
2. Specific volume and thermal expansion measurements should reveal any general loosening up of structure such as may accompany increased mobility of its units.
3. Dielectric measurements, interpreted in the light of the Debye[6] theory, should give some information as to the specific type of motion involved, and particularly as to whether the motion is rotational or translational.

---

[1] Wallerant, *Compt. rend.*, **158**, 597 (1914).

[2] P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **52**, 91 (1916).

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

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

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

[6] Debye, "Polar Molecules," Chemical Catalog Co., New York City, 1929.

Experimental Work

Thermal Measurements.—A modified Nernst vacuum calorimeter, modeled on that described by Southard and Andrews,[7] but greatly simplified, was used in this work. Measurements were made by the continuous heating method of Deese.[8] A large lag of temperature of the sample behind that of the container, to which the thermocouples were attached, undoubtedly resulted. Neither this error nor that of calibration of the container was important in work where the significant data are the increase of heat capacity at the transition and the heat of transition. However, the heat capacity of Schering-Kahlbaum calorimetric naphthalene as determined in this calorimeter at intervals between −180 and 0° was found to differ from the values of Southard and Andrews[7] by no more than 5%, being always lower than their more accurate measurements. The direction of the error agrees with that found by Deese.[8] It was concluded that despite its simplicity this calorimeter was capable of determining the increase of heat capacity and the heat of transition of *d*-camphor with the accuracy required.

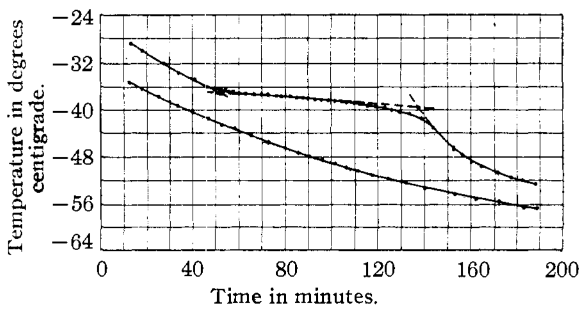

Fig. 1.—Cooling curve of *d*-camphor through the transition. The upper curve represents the temperature of the sample; the lower, that of the bath.

The *d*-camphor used in these measurements was purified as described by Yager and Morgan.[4]

Table I records the values of heat capacity found from the tangents of continuous heating curves taken at various temperatures and heating rates and for each phase of the *d*-camphor.

TABLE I

	t, °C.	V	C_p(cal./°C./mole)
Phase III	−56	1.86	39
	−49	1.86	42
	−40	1.86	40
	−31	1.86	40
		Average	40
Phase II	−30	1.57	58
	−28	1.39	59
	−16	1.86	58
	−14	1.86	58
		Average	58

The rate of heat input is proportional to the square of the applied voltage, which is listed in the third column of the table. The data show an increase of molar heat capacity of about 18 calories per degree accompanying the transition from phase III to phase II. The possibility that the high values observed in phase II are merely due to a further contribution of the heat of transition to the apparent specific heat is reduced by two considerations.

1. The heat capacity of phase II is relatively independent of temperature between −30 and −14°.

2. The value at −30° was obtained after cooling the sample only to −32°, where because of temperature hysteresis[4] the transition had not yet started. The cooling curve of the same sample shows in Fig. 1 that the transition does not begin above −36°. These data were not subject to temperature lag inasmuch as they were obtained with the thermocouple embedded in the sample.

The heat of transition was determined from continuous heating curves such as that illustrated in Fig. 2, where heat was applied to a sample of 6.871 g. of camphor at the rate of 0.1549 watt. The heat of transition was found from the time AB to be 1780 calories per mole. Two other measurements yielded the respective values of 1850 and 1950 for this quantity, whose best value was therefore taken to be 1860 calories per mole.

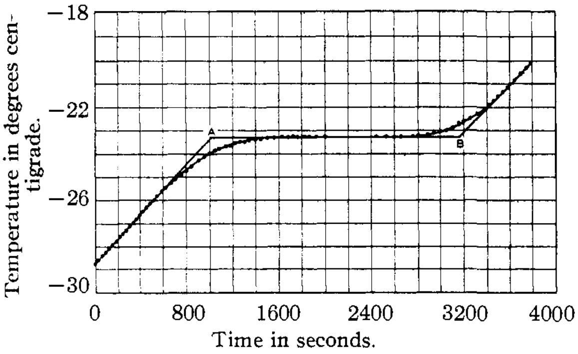

Fig. 2.—Calorimeter heating curve of *d*-camphor through the transition.

It will be noticed in Fig. 2 that the temperature of the transition as recorded thermally is about −23°, where Wallerant,[1] Bridgman,[2] and Yager and Morgan[4] place it between −28 and −40°. The difference is believed to be a rough measure of the temperature lag involved in making a continuous measurement in this calorimeter. Figure 3 shows, however, that the heat of transition thus determined falls on the same curve as those determined by the application of the Clapeyron-Clausius equation to Bridgman's data,[2] where the temperature of the transition is increased by the application of high pressures. This is regarded as evidence of the general accuracy of these thermal measurements.

Specific Volume.—A gas expansion volume meter similar in principle to that described by MacGee[9] was used to measure the specific volume of *d*-camphor through the transition. The apparatus differed from that of MacGee in that no mercury was allowed to enter the reference volumes, which were maintained at equal temperatures by means of a constant temperature bath. This modification was made necessary by the desirability of obtaining data below the freezing point of mercury. The random error of observation greatly exceeded errors from all other sources, being about ±0.5%.

---

(7) Southard and Andrews, *J. Franklin Inst.*, **209**, 349 (1930).

(8) Deese, THIS JOURNAL, **53**, 3676 (1931).

(9) MacGee, *J. Am. Ceram. Soc.*, **9**, 817 (1926).

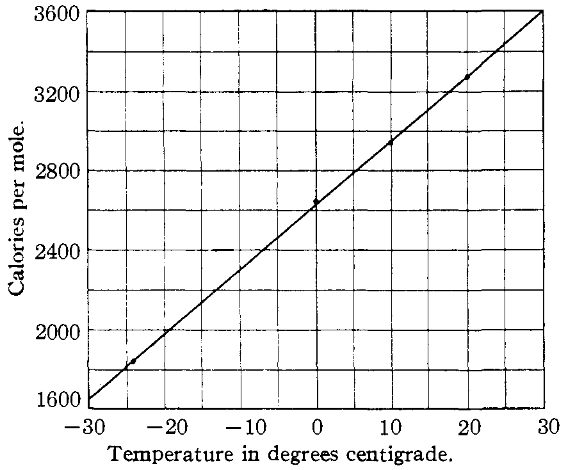

Fig. 3.—Heat of transition of *d*-camphor as a function of temperature.

The data thus obtained are represented in Fig. 4, and show a decrease of about 7% in the specific volume of *d*-camphor between −37 and −41°. The dielectric data are included for comparison. No temperature hysteresis of specific volume, analogous to those observed by thermal and dielectric measurements, could be detected. The discrepancy has not been satisfactorily explained, since equivalent precautions for obtaining thermal equilibrium were taken in the two series of measurements.

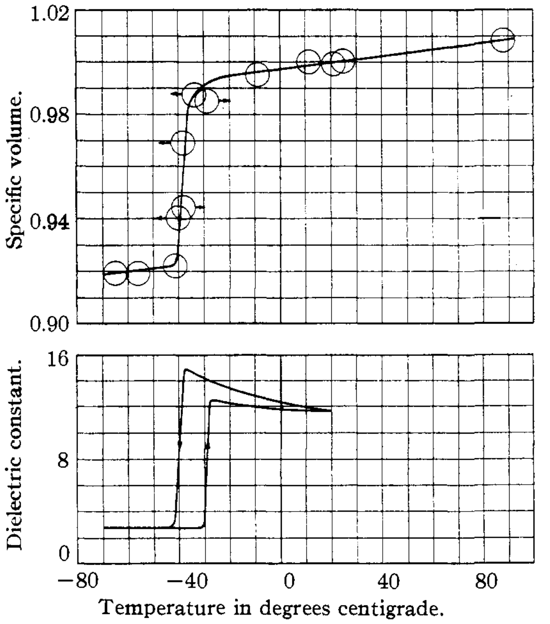

Fig. 4.—Specific volume of *d*-camphor compared with its dielectric constant.

Since dielectric measurements[4] had shown several closely related compounds to undergo dielectric transitions similar to that of *d*-camphor, the specific volume of these materials was measured in the hope of revealing a corresponding similarity in the behavior of this property. Figure 5 shows that a similar volume transition of about 4% is found in *dl*-camphor between −55 and −80°. Figures 6 and 7 portray data obtained for borneol and isoborneol by the much more sensitive method of observing the rise with temperature of a mercury meniscus in the calibrated capillary outlet of a dilatometer in whose bulb the sample had been solidified so as to be as free as possible from voids into which the mercury could not enter. Specific volume undergoes a small change at each of these transitions. The temperature hysteresis of dielectric constant observed in isoborneol[4] is reproduced by the specific volume data.

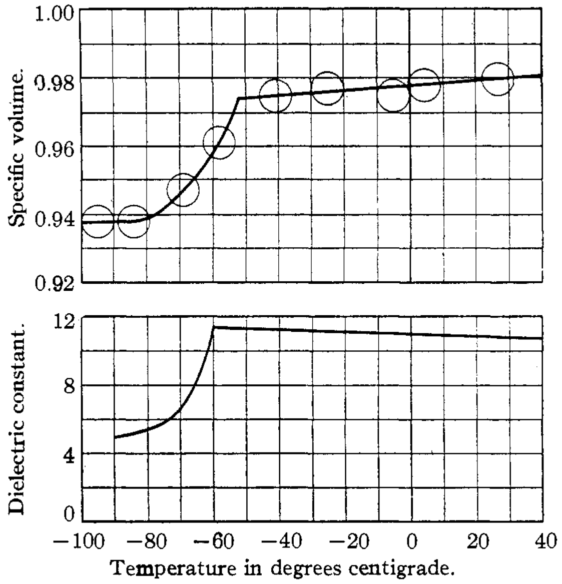

Fig. 5.—Comparison of specific volume and dielectric constant of *dl*-camphor.

Dielectric Measurements.—In seeking data on thermal transitions similar to that observed in *d*-camphor, it was found that in cyclohexanol there is a heat absorption of 1960 cal./mole and an increase of about five calories in C_p at a transition occurring at −10°.[10] Since these thermal data resemble those obtained for *d*-camphor, a corresponding similarity in dielectric properties was sought by measuring the variation of dielectric constant through this transition. Both cylindrical and parallel plate condensers were used to make grounded capacity measurements, which were in substantial agreement.

The results are shown for cyclohexanol in Fig. 8. Dielectric constant is, within the error of measurement, continuous through the melting point (+18°). It is possible to supercool phase I of the cyclohexanol far below the transition temperature;[10] below −25° an anomalous dispersion similar to that observed in supercooled liquids and involving nearly the whole polarization is observed. After the transformation to phase II, which occurred anywhere between −40 and −62°, heating failed to reverse the process until a temperature of about −25° was reached. Repeated distillation and drying of the cyclohexanol, which raised the melting point from 12 to 18°, and the boiling point to 161.0°, failed to change the upper temperature limit of this transition by any measurable amount. It is nevertheless thought to be essentially the

---

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

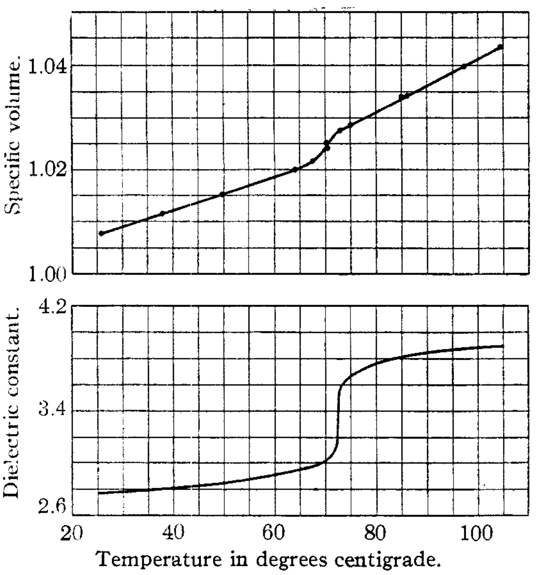

Fig. 6.—Specific volume and dielectric constant of borneol.

transition which Kelley[10] observed at −10°, especially considering the relative impurity of the samples as measured here; the melting point of the pure material is 24°, and its boiling point, 161.1°.

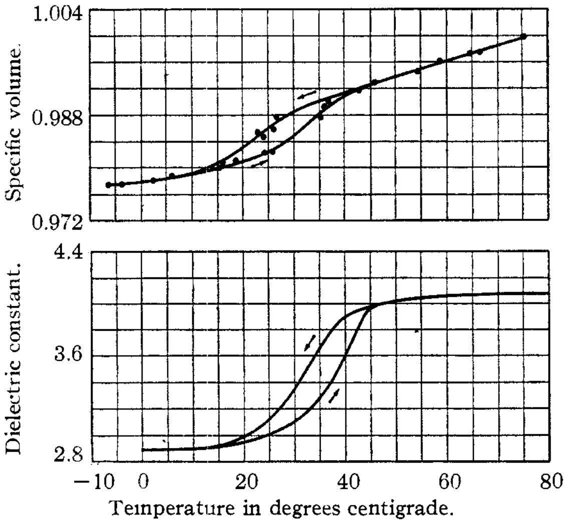

Fig. 7.—Specific volume and dielectric constant of isoborneol.

Measurements were also made on dilute solutions of the same sample of *d*-camphor in purified petroleum hexane, in order to calculate the dipole moment and atomic polarization of the *d*-camphor molecule according to the Debye theory.[6] Dielectric constant, density, and refractive index of each solution were measured by the method and with the equipment described by Morgan and Lowry.[11] Extrapolation of the refractive index measurements to low frequencies with respect to the optical showed the *d*-camphor to have as expected a molar refraction of 44.4 cc.

Density and dielectric constant data interpolated at 10° intervals from the experimental curves are plotted against concentration in Figs. 9 and 10. It is obvious that both variables are linear functions of concentration within the error of measurement. Thus it is possible accurately to calculate molar polarization of *d*-camphor at infinite dilution by the method of Hedestrand.[12] Such a calculation yields the curve of molar polarization against the reciprocal of absolute temperature shown in Fig. 11.

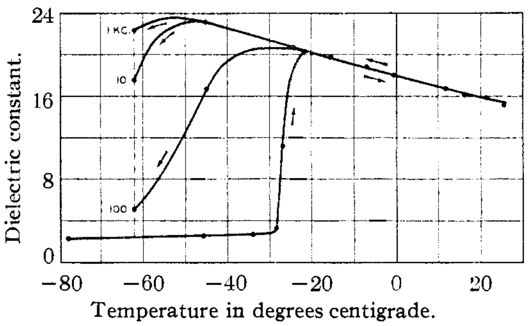

Fig. 8.—Dielectric constant of cyclohexanol as a function of temperature and frequency. The melting point of this sample is 18°.

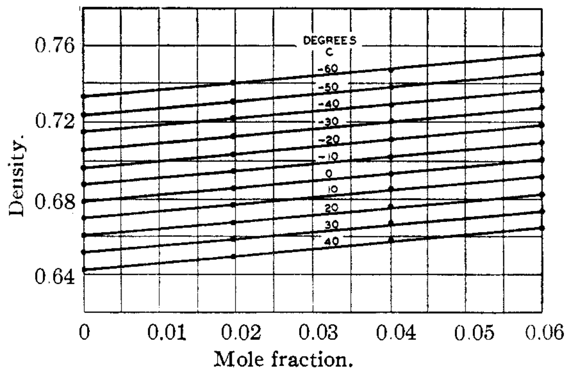

Fig. 9.—Density of solutions of *d*-camphor in petroleum hexane at various concentrations and temperatures.

Discussion of Results

From the theoretical point of view the significant increase of heat capacity at the transition in *d*-camphor is that at constant volume rather than the value experimentally determined at constant pressure. There are no compressibility data available for making the correction from C_p to C_v for the two phases of *d*-camphor. Andrews[13] has proposed the following approximation for this correction for organic lattices

$$C_p - C_v = 0.0214(T/T_M)\, C^2 \text{ (Molecule)}$$

where $C_p - C_v$ is expressed in calories per mole, C (Molecule) is the heat capacity at constant volume due only to translational and rotational

---

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

(12) Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

(13) Andrews, *Chem. Rev.*, **5**, 533 (1928).

oscillations of the unit molecules, T_M is the melting point of the crystal, and T is its absolute temperature. Assuming C (Molecule) as calculated by Andrews[13] for benzene to be roughly typical of all organic lattices whose molecules are of similar complexity, this quantity should reach its classical value of about 12 calories in the crystal of *d*-camphor at some temperature between −170 and −120°. If then T_M is the same in both phases of *d*-camphor, $C_p - C_v$ does not increase at the transition, and the change of C_v should essentially correspond with that of C_p, being about 18 calories.

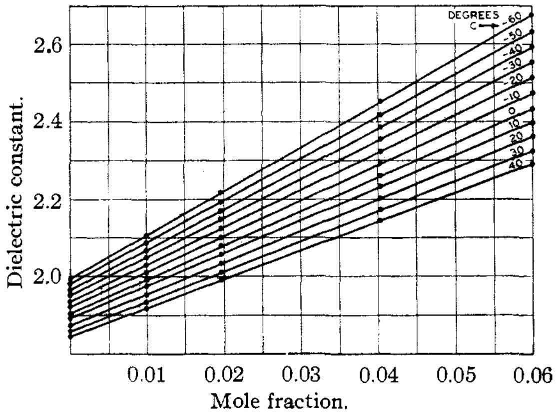

Fig. 10.—Dielectric constant of solutions of *d*-camphor in petroleum hexane at various concentrations and temperatures.

If the molecules of *d*-camphor are subject to a rotational oscillation capable, as inferred from Andrews' calculation for benzene, of absorbing heat above −120° at the classical rate of about six calories per degree per mole, the transition of this oscillation alone to free rotation should involve a decrease of specific heat, because of the loss of potential energy degrees of freedom. Even the transitions at much lower temperatures which are specified by Pauling[3] as involving molecular rotation are found to be characterized by only a very small increase of heat capacity. For example, the thermal transitions occurring at −174.6° in hydrogen chloride,[14] at −183.2° in hydrogen bromide,[15] at −207° in hydrogen iodide,[16] and −169° in hydrogen sulfide[17] all show a net increase of heat capacity of less than 1.5 calories per mole. Frenkel and his colleagues[18] have calculated that in hydrogen chloride the heat capacity should decline 1.32 calories per mole at the transition after correcting the observed values to constant volume. Each of the above-mentioned transitions involves so great an increase of dielectric constant over that normally observed in crystals that the rise of simple molecular rotation seems to be the best explanation.[19,20,21] It is therefore concluded that if C_v for *d*-camphor increases at the transition similarly to C_p, as has been assumed, the magnitude of this increase indicates that some change other than a simple rise of molecular rotation is occurring.

The observed heat of transition, 1860 calories per mole, also appears to be rather too large to be explained by the rise of molecular rotation alone. It is true that a three-dimensional molecule rotating in the crystal with so low an energy that its average potential and kinetic energy terms were nearly equal would have in the classical theory a total energy of $3RT$, which would be about 1500 calories per mole in *d*-camphor at 250 Å. However, all of this energy would have to be absorbed at the transition to explain the observed absorption of heat. This in turn would imply that below the transition temperature the rotational oscillation of the molecule is almost completely restrained. There is no reason to believe that this is true; Andrews' work[13] referred to above indicates that in the benzene crystal energy is absorbed by the degrees of freedom of rotational oscillation at the classical rate at tem-

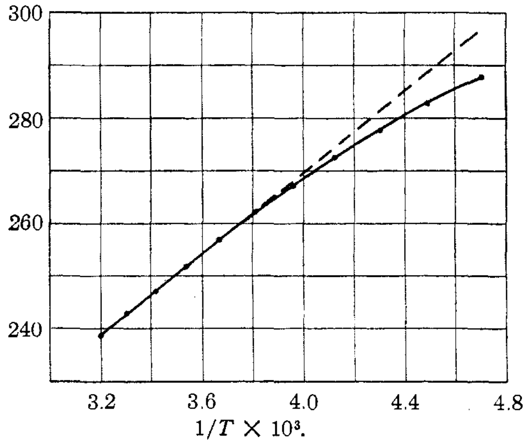

Fig. 11.—Molar polarization of *d*-camphor at infinite dilution as a function of reciprocal temperature (uncorrected).

---

(14) Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

(15) Giauque and Wiebe, *ibid.*, **50**, 2193 (1928).

(16) Giauque and Wiebe, *ibid.*, **51**, 1441 (1929).

(17) Clusius, *Z. Elektrochem.*, **39**, 598 (1933).

(18) Frenkel, Tode and Ismailow, *Acta Phys. U. R. S. S.*, **1**, 97 (1934).

(19) Cone, Denison and Kemp, THIS JOURNAL, **53**, 1278 (1931).

(20) Smyth and Hitchcock, *ibid.*, **55**, 1830 (1933).

(21) Kemp and Denison, *ibid.*, **55**, 251 (1933).

peratures far below 250 Å. It therefore seems unlikely that the heat of transition can be completely accounted for by a rise of rotation of rigid molecules.

In terms of the current theory there is reason to believe that the rotation of so large and polar a molecule as *d*-camphor would not ordinarily be expected. Pauling's theory[3] shows that molecular rotation is unlikely where potential energy of restraint of molecular orientation and molecular moment of inertia are large. For a polar molecule Frenkel and his co-workers[18] state the potential energy to be

$$V = \mu E(1 - \cos \vartheta)$$

where μ is the dipole moment, at angle ϑ with the field E due to surrounding molecules. While nothing is known about E in the camphor crystal, μ is sufficiently large (at least 2.7 D) to indicate that the maximum value of V is not unusually small. On the other hand, the moments of inertia of the *d*-camphor molecule are far larger than those of the molecules which Pauling found able to rotate in the crystal. Mr. L. A. MacColl of these Laboratories has calculated the three moments of inertia of the camphor molecule from the accepted three-dimensional model, and finds the values 690, 600 and 510, all multiplied by 10^{-40} g. sq. cm. The moment of inertia of camphor about any axis of rotation is thus about 250 times as great as that of hydrogen chloride; molecular rotation in the crystal should therefore be considerably more difficult for the rigid *d*-camphor molecule than for hydrogen chloride, as far as the theory goes.

In general, any increase of C_v, at temperatures above 150 Å. and in crystals whose units are complex organic molecules, is due to atomic or group vibration within the molecule. When the heat capacity of such a crystal increases by about 50% it seems reasonable to ascribe most of that change to an abrupt increase of vibration of atoms or atomic groups. This should be particularly true when the molecule involved is completely saturated at all carbon to carbon bonds. Raman data show that vibration is more easily excited about single than about double bonds.[22] It is therefore proposed that unusually vigorous vibration of atoms or atomic groups arises in the molecule of crystalline *d*-camphor at the transition temperature.

If an increase of intramolecular vibration were the only significant mechanical feature of the transition in the *d*-camphor crystal, a certain increase of dielectric constant due to atomic polarization might be expected at the transition temperature, and a further large increase of dielectric constant due to free rotation of polar *d*-camphor molecules would be expected at the melting point of the crystal. Furthermore, the value of the atomic polarization would not in general be expected to decrease with increasing temperature.

Reference to the experimentally determined dielectric constant data for solid *d*-camphor[4] shows that neither of the above conditions is met. Dielectric constant rises sharply at the transition, subsequently declines rapidly with increasing temperature, and proves to be larger 20° below the melting point than immediately above it. These data lead Yager and Morgan to the conclusion that the dielectric properties of *d*-camphor in phase II are best explained by the assumption that the molecules rotate in the crystal lattice to much the same extent that they do in the liquid. Similarly, the dielectric constant of cyclohexanol, whose transition also seems to involve the rise of atomic vibration, changes so little at the melting point as to suggest that the rotation of polar molecules which is known to typify its liquid phase must continue below the freezing point.

The thermal data, dielectric measurements and Pauling's theory of molecular rotation in crystals may be reconciled by the following picture. As the crystal of *d*-camphor is heated through −30° the very marked increase of atomic vibration against reduced restoring forces suggested by the thermal data occurs rather generally throughout the crystal at the transition temperature. The accompanying reduction of the directional forces within the crystal should be large, as evidenced by a heat of transition larger than that of the fusion of *dl*-camphor[23] and by the 8% increase of specific volume. This reduction of internal forces together with the increased molecular pliability which should accompany the increased vibrational freedom would greatly reduce the magnitude of Pauling's potential hump $2V_0$, and permit the complex camphor molecules to rotate in the manner suggested by Pauling where molecules of more rigid structure might not be able to do so. This is of course only a rough

---

(22) See, *e. g.*, Andrews, *Phys. Rev.*, **36**, 531, 545 (1930).

(23) Frandsen, *Bur. Standards J. Research*, **7**, 477 (1931).

working hypothesis, as a detailed mathematical consideration of such a picture would become extremely involved. It seems to be useful, however, when the solution measurements are examined in the light of its implications.

Figure 11 shows that the measured molar polarization of *d*-camphor in dilute solution varies with temperature above $-10°$ ($(1/T) \times 10^3 = 3.81$) as predicted by the Debye theory, according to which

$$P = P_e + P_a + B/T$$

P_e the electronic polarization or molar refraction and P_a the atomic polarization are assumed to be independent of temperature, while the polarization of the rotating dipoles is a linear function of the reciprocal temperature, with tangent B related to the dipole moment μ by the expression

$$\mu = 0.0127\sqrt{B} \text{ Debye units}$$

From the tangent observed above $-10°$ the dipole moment is found to be 2.51 Debye units and from the intercept at $T = \infty$ the sum of P_e and P_a is found to be 113.3 cc. Since P_e is 44.4 cc., the value of P_a in the temperature range -10 to $+40°$ turns out to be 69 cc.

Jenkins[24] has recently shown that dilute solution measurements yield spuriously high values of atomic polarization unless the effect of temperature on the dielectric constant of the solvent is taken into account. At any given temperature the polarization of *d*-camphor calculated from the data of Figs. 10 and 11 is found to obey a modified form of Müller's[25] empirical formula for its variation with dielectric constant of the medium

$$P = A - B(\epsilon - 1)^2$$

where P is observed total polarization of *d*-camphor in solution and ϵ is dielectric constant of the solution. The constant A is taken to be the value of the solute polarization after correcting for all effect of the solvent. Within experimental error B was found to be independent of temperature in the case of *d*-camphor, having the mean value 20.78. Using this value of B, the accurately determined polarizations of Fig. 11 were then corrected for the effect of the dielectric constant of the solvent by finding the respective values of A in equation (2). The results thus obtained are shown in the second column of Table II; the nature of the P *vs.* $1/T$ curve is unchanged, although the part above $-10°$ which is linear shows a dipole moment of 2.69 D and an atomic polarization of about 69.6 cc. for the *d*-camphor molecule.

TABLE II

T, Å.	P	$P_0 = 43{,}600/T$	P_e	$P_a = P - P_0 - P_e$
313	253.3	139.3	44.5	69.5
303	258.2	143.9		69.8
293	262.8	148.8		69.5
283	268.3	154.1		69.7
273	273.9	159.7		69.7
263	279.9	165.8		69.6
253	285.5	172.3		68.7
243	291.5	179.4		67.6
233	297.1	187.1		65.5
223	302.7	195.5		62.7
213	308.5	204.7		59.3

This atomic polarization is very much higher than any reported in the reliable literature,[26] and would be regarded with extreme suspicion if there were no corollary evidence of unusual atomic vibration in the camphor molecule. The hypothesis proposed above for the mechanism of the crystalline transition, however, would require even freer atomic group vibration in the molecule when in the liquid state than when in the crystal lattice, since the restraints of the crystal forces on this vibration are eliminated in the former case. Van Vleck[27] has concluded that atomic polarization is negligible in stable diatomic molecules, but not necessarily so in those which are polyatomic. For a diatomic molecule he finds the contributions of atomic polarization to the total dielectric constant to be inversely proportional to the square of the natural frequency of the vibration involved. Applying this relation to the polyatomic camphor molecule, it is evident that an unusually large atomic polarization is required by our hypothesis that the intramolecular vibration is opposed by small restoring forces and therefore has an unusually low natural frequency.

Below $-10°$ this interpretation of the polarization data agrees with our picture in that the total polarization begins to decline below the value to be expected if the number of atomic groups engaged in unusual vibrations, and hence total atomic polarization, remained constant. The rate of decline of atomic polarization with temperature may be estimated by assuming that in this temperature range dipole moment remains

---

(24) Jenkins, *Trans. Faraday Soc.*, **30**, 739 (1934).

(25) Müller, *ibid.*, **30**, 729 (1934).

(26) Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, 1931, pp. 163–168.

(27) Van Vleck, "Electric and Magnetic Susceptibilities," Oxford Press, 1932, p. 51.

constant, as seems reasonable, since in the *d*-camphor molecule the effect of any atomic vibration on the time mean square of dipole moment would presumably be of the second order. Table II shows that the rate of decline of atomic polarization thus calculated is, as would be expected, less than that of the transition in the crystal, and seems to indicate that the maximum rate of this decline will occur below −100°. In a similar way the transition of *d*-camphor in *dl*-camphor[4] occurs at a lower temperature and over a broader range of temperatures than in pure *d*-camphor.

Donle and Volkert[28] and Wolf[29] agree in calculating a dipole moment of about 2.95 Debye units for camphor; the former investigators find a total polarization at 22° of about 234 cc. At 22° Fig. 11 shows a total polarization of 248 cc. for *d*-camphor. These values are in fairly good agreement, and the discrepancy between the accepted value of 2.95 Debye units for the dipole moment of camphor and the value of 2.69 presented here for *d*-camphor is mainly due to the large value calculated for P_a in the latter case. The older data were all obtained at single temperatures, no attempt being made to measure atomic polarization.

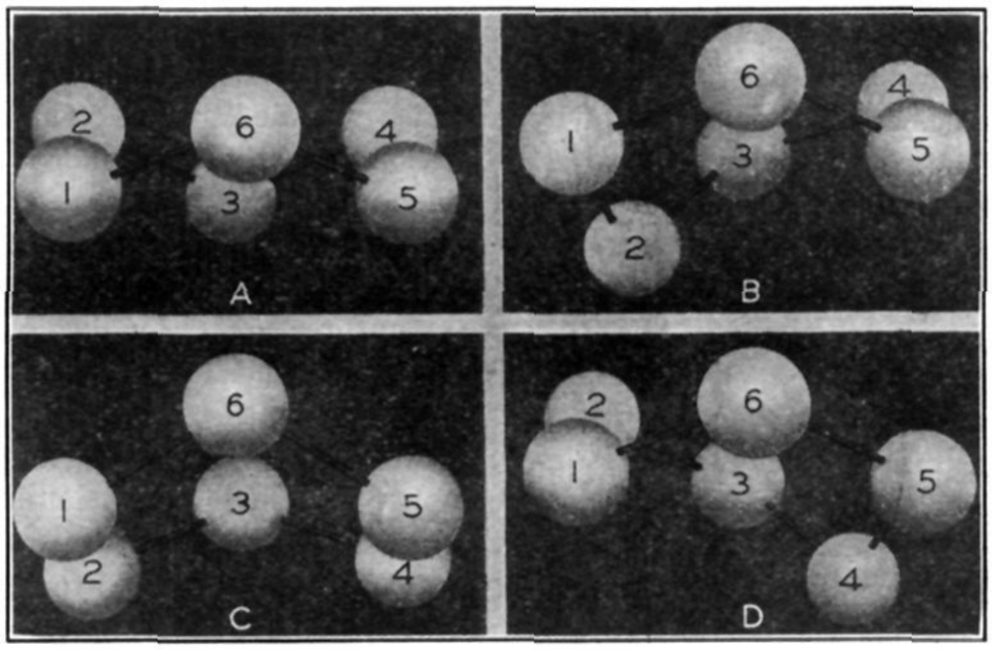

Fig. 12.—Strainless forms of the cyclohexane ring: A, the relatively rigid *trans* form; B, the pliable *cis* form obtained from A when atomic group No. 2 assimilates sufficient energy to change its position as indicated; C and D, further examples of the infinite series of equally probable configurations of the *cis* form.

It is obvious that without independent evidence of great atomic vibration in *d*-camphor, the above interpretation of the polarization data would not be necessary, and that even with the corollary evidence it should be accepted with considerable caution until verified by measurements of the temperature variation of polarization of other compounds undergoing a similar crystalline transition, such as borneol,[4] isoborneol,[4] cyclohexanol and cyclohexanone.

The thermal and dielectric data indicate that the transition observed in cyclohexanol is due to the same mechanism as is the transition in *d*-camphor. Data to be published in the near future show similar dielectric transitions occurring in solid cyclohexene, cyclohexanone and chlorocylohexane. Now it is well known that there is possible in the cyclohexane ring a type of atomic group vibration which involves large amplitudes and large energy absorption, and which furthermore cannot occur in the benzene ring. Mohr's[30] modification of Sachse's[31] theory of strainless carbon rings predicted that the *cis*-form of the basic cyclohexane ring should be pliable and subject to large linear and rotational vibration of the methylene groups, while the *trans* form should be rigid. The possible amplitude of vibration of groups 2, 4 and 6 with respect to the plane of groups 1, 3 and 5 in the *cis* form of the ring is illustrated in Fig. 12. Henriquez[32] has shown mathematically that these vibrations may occur without bending or stretching any carbon valences which are directed away from each other at tetrahedral angles. It would therefore be expected that such a vibration would be possible in polar cyclohexane derivatives of the *cis* form, and would involve immensely greater displacements than would vibrations of equal energy but opposed by the elastic restoring forces of the valence bonds. A pliable polar molecule of this type should be unusually subject to deformation in an electric field, and hence should exhibit a large atomic polarization independent of temperature. This vibration would apparently account for part of the value of 1.6 found by O. Hassel[33] for the moment of 1,4-cyclohexadione.

---

[28] Donle and Volkert, *Z. physik. Chem.*, [B] **8**, 60 (1930).

[29] Wolf, *Physik. Z.*, **31**, 227 (1930).

[30] Mohr, *J. prakt. Chem.*, [II] **98**, 315 (1918).

[31] Sachse, *Ber.*, **23**, 1363 (1890).

[32] Henriquez, *Kon. Akad. Weten. Amst.*, **37**, 532 (1934).

[33] O. Hassel, *Trans. Faraday Soc.*, **30**, 874 (1934).

The appearance of this vibration only above a transition in the cyclohexane derivatives would be explained if at low temperatures the *trans* form (Fig. 12) of the cyclohexane ring were the more stable. With rising temperature vibration of increasing amplitude might be expected to attain sufficient energy to carry some carbon over the potential hump between it and the pliable *cis* position. The difficulty of exciting atomic group vibrations should then decrease abruptly by a large factor, in line with the reduction of the Einstein parameter Θ. Absorption of energy and increased heat capacity would result. In a crystal the effect might spread from one molecule to another very rapidly, in the manner suggested by Pauling[3] for rotational transitions, because of the relaxation of crystal forces which might be expected to accompany a great reduction of the rigidity of the molecule, and an expansion of its "average volume." The same reduction of crystal forces should greatly facilitate the molecular rotation which is also believed to rise at the transition temperature.

An alternative possibility is that, even if the *cis* form were stable at the lowest temperatures, dipole forces, London forces and steric hindrance might prevent pliable rotation and vibration until a transition temperature was reached.

The accepted model of the *d*-camphor molecule is not pliable in the same sense as the cyclohexane ring, and hence gives very little indication of being subject to the type of extremely low frequency vibration required by our hypothesis. It is possible that the mechanical model does not reveal all types of vibration actually present in the molecule. However, the model does show that camphor contains a cyclohexane *cis* ring, whose tendency to pliable vibration would be elastically opposed only by the two bonds in the "bridge" of the molecule.

Summary

1. A rise of about 18 cal./°C./mole in the specific heat of *d*-camphor at the transition at −30° is observed and is explained by assuming that unusually energetic intramolecular vibration arises at the transition temperature.

2. The rise of molecular rotation at the transition which is evidenced by the dielectric data of Morgan and Yager is qualitatively explained in terms of Pauling's theory of molecular rotation in crystals, by assuming that the forces opposing this rotation are greatly diminished by a transition which reduces the rigidity of the molecules.

3. The behavior of total polarization of *d*-camphor in dilute solution is explained by assuming that at room temperature dipole moment is smaller and atomic polarization much larger than formerly supposed, and that the latter polarization begins to decline with temperature below −10° when the transition to the more rigid molecules begins.

4. Transitions very similar to that occurring in *d*-camphor are observed in crystals of derivatives of cyclohexane, whose carbon ring is supposed to be very pliable in the *cis* form and relatively rigid in the *trans* form. These transitions appear to be due to transformations from the rigid to the pliable forms of the molecules of which the crystals are composed.

New York, N. Y. Received June 18, 1935

[Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 488]

A Quantum Mechanical Discussion of Orientation of Substituents in Aromatic Molecules

By G. W. Wheland and Linus Pauling

Introduction

When a substituent is introduced directly into an aromatic molecule, it may enter into certain of the available positions more readily than into others. This phenomenon of *orientation* has been exhaustively studied, and empirical rules have been found which describe the experimental results fairly satisfactorily. In a monosubstituted benzene C_6H_5R, for example, the introduction of a second substituent is governed by the nature of the atom or group, R, already present. Thus, for R = F, Cl, Br, I, OH, NH_2, and so on, the further substitution takes place largely in the ortho and para positions, while for R = COOH, CHO, NO_2, $(CH_3)_3N^+$, SO_3H, and so on, the substitution takes place largely in the meta position. Most ortho–para directing substituents, with the exception of fluorine, chlorine and bromine, acti-