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A New Type of Disorder Affecting the Dielectric Properties of Long-Chain Esters

ROBERT W. CROWE, JOHN D. HOFFMAN AND CHARLES P. SMYTH
General Electric Research Laboratory, Schenectady, New York, and Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

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The dielectric properties of a series of long-chain esters have been investigated in the solid state. Like other long-chain molecules containing 20 or more carbon atoms, most of the ester molecules showed evidence of hindered molecular rotation about their long axes in the crystal lattice. It was also found that higher dielectric constants resulted when the samples were rapidly frozen than when they were allowed to solidify gradually, the effect being more pronounced as the chain length was increased. In order to explain this behavior, it has been assumed that the esters may crystallize in an ordered lattice in which the dipoles are in a plane, or in a longitudinally disordered lattice in which some of the chains are reversed. In the latter case, the dipoles may or may not form two planes depending upon the position of the polar group in the chain. It has also been assumed that the degree of longitudinal disorder increases with increase in freezing rate. Once frozen in, however, it remains fixed until the sample is remelted.

The potential barrier hindering rotation has been assumed to be much higher in the ordered state than in the disordered state because separation of the dipoles should lower steric and dipole interaction in the latter. Since the rotational transition temperature is proportional to a potential energy difference V_0 related to the barrier against rotation, the transition temperature should increase with increase in longitudinal order. In a completely ordered ester or a nearly symmetrical disordered ester, the barrier may be sufficiently high to raise the transition point to a temperature near or above that of fusion. The experiments agree with these assumptions.

I. INTRODUCTION

SINCE the conclusion reached by Müller[1] in 1932 that long-chain hydrocarbon molecules may assume a state of hindered rotation about their long axes in the solid state, dielectric constant measurements have shown that this behavior persists even when a polar group is introduced at the end of the chain. These polar molecules include long-chain alcohols,[2,6] bromides[3,4] and ethyl esters.[5,6] Andrew[7] has recently confirmed Müller's original conclusion by nuclear resonance studies on crystalline *n*-octacosane (n-$C_{28}H_{58}$) and dicetyl (n-$C_{32}H_{66}$). It is now clearly understood that the chains do not rotate freely in the lattice and that rotational oscillation is a more accurate description. Inasmuch as the rotation of molecules in this sense appears to be a typical order-disorder phenomenon culminating in a first-order transition, we will refer to this effect as rotational disorder.

A recent investigation of the dielectric properties of a number of long-chain alkyl esters[8] has revealed that rotational disordering of chains is also possible when the polar group is introduced near the center of the molecule. During the course of this investigation, however, two unusual phenomena were observed: (1) a definite dependence of the dielectric constants and transition points of the solid esters upon rate of solidification, and (2) a striking dissimilarity in dielectric behavior depending upon the symmetry of the molecule in respect to the placement of the polar group. This paper is an attempt to explain, at least qualitatively, these phenomena in terms of permanent *longitudinal disorder* or reversal of chains in the crystals realized during solidification (Fig. 1).

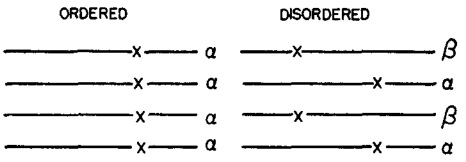

FIG. 1. Longitudinally ordered and disordered phases in crystalline long-chain esters.

II. EXPERIMENTAL

The esters investigated include *n*-decyl palmitate, *n*-dodecyl palmitate, *n*-tetradecyl palmitate, *n*-hexa-

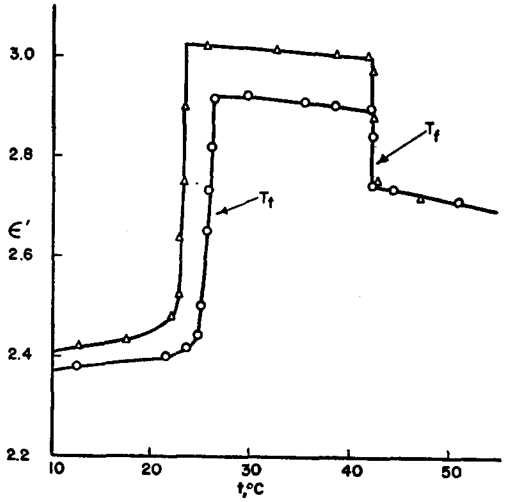

FIG. 2. Variation of the dielectric constant of *n*-dodecyl stearate with increasing temperature after freezing times of one-half hour Δ and two hours ○.

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[1] A. Müller, Proc. Roy. Soc. (London) A138, 514 (1932).

[2] J. D. Hoffman and C. P. Smyth, J. Am. Chem. Soc. 71, 431 (1949).

[3] J. D. Hoffman and C. P. Smyth, see ref. 2, 72, 171 (1950).

[4] J. D. Hoffman, J. Chem. Phys. 20, 541 (1952).

[5] R. Buckingham, Trans. Faraday Soc. 30, 377 (1934).

[6] W. O. Baker and C. P. Smyth, J. Am. Chem. Soc. 60, 1229 (1938).

[7] E. R. Andrew, J. Chem. Phys. 18, 607 (1950).

[8] R. W. Crowe and C. P. Smyth, J. Am. Chem. Soc. 73, 5401 (1951).

decyl palmitate, *n*-dodecyl stearate, *n*-tetradecyl stearate, *n*-octadecyl stearate, and *n*-octadecy acetate. The methods of preparation, purification, and measurement of dielectric properties have been described in an earlier publication.[8] Approximately eight grams of sample were required to fill the measuring cell. The measurements were made for the most part at five kilocycles, and in some cases at a lower frequency to insure that the *static* dielectric constant was always obtained. Dielectric relaxation phenomena will not be considered here. In order to make the picture more complete, data taken from the literature for ethyl stearate[6] ($C_{17}H_{35}COOC_2H_5$) and ethyl behenate[5] ($C_{21}H_{43}COOC_2H_5$) have been included in the discussion.

III. DISCUSSION

Dielectric evidence for hindered molecular rotation or rotational disorder of polar molecules in the crystal lattice consists in the solid having a dielectric constant similar to that of the liquid, i.e., one considerably larger than n^2, the square of the refractive index. This effect should not be confused with subtransitional dielectric phenomena, which often cause the dielectric constant to be slightly above n^2. Normally, molecules containing 20 or more carbon atoms in the chain show evidence of molecular rotation between the freezing point and a first-order rotational transition point. In the shorter molecules, the rotational transitions are normally monotropic because of an irreversible transformation to a third crystalline form with a higher melting point.[3] Above 24 carbon atoms, however, the transitions are completely reversible and the higher melting form usually can be realized only by crystallization from solvent.

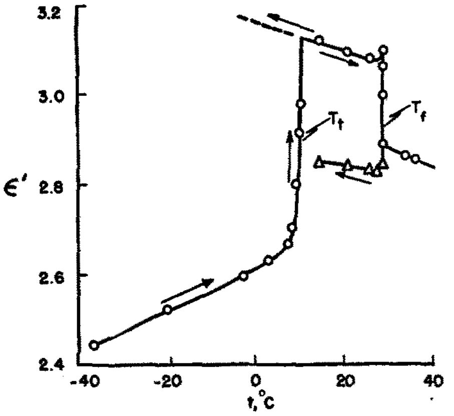

FIG. 3. Temperature dependence of the dielectric constant of *n*-decyl palmitate after freezing times of one-half hour ○ and two hours Δ.

Contrary to expectation, certain of the esters showed little or no evidence of rotational disorder in the solid state even though the chain length was much longer than is usually necessary to induce rotation (Fig. 6), while closely related members of the series showed the expected behavior (Figs. 2–5). Furthermore, the absolute values of the dielectric constants of the rotator phases of the latter depended strongly and uniquely upon the rate of solidification. We wish to advance the following hypothesis to explain these phenomena.

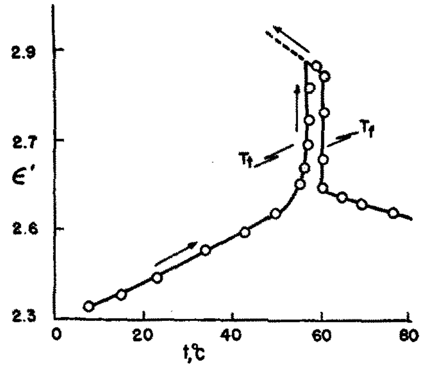

FIG. 4. Temperature dependence of the dielectric constant of *n*-octadecyl stearate. Little dependence upon rate of freezing.

It is believed that the long molecules may arrange themselves in a more or less ordered or disordered array in the crystal lattice, depending upon the rate of solidification. A simplified picture of this type of behavior is shown in Fig. 1.

A. Longitudinal Disorder and Rate of Solidification

Whenever, in the present investigation, rotational disorder was evident in the solid esters, the dielectric constants were found to be dependent upon rate of solidification, higher values being obtained after rapid freezing as shown in Figs. 2, 3, and 5. Once the samples

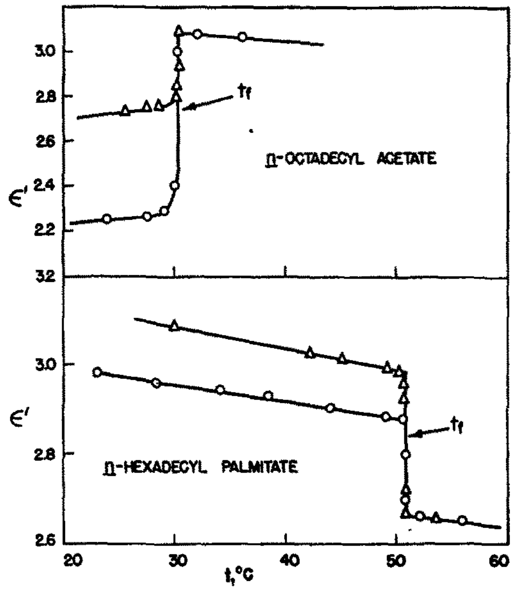

FIG. 5. Variation of the dielectric constants of *n*-octadecyl acetate and *n*-hexadecyl palmitate with decreasing temperature after freezing times of one-half hour Δ and two hours ○.

were frozen, their dielectric constants assumed time-independent values for any given temperature below the freezing point.* If the longitudinal disordering of chains does exist in these compounds, it is obvious that the degree of disorder will be promoted by rapid freezing. It is also logical that the dipoles do not form a continuous plane in the disordered state as they do in the ordered, providing the polar group is not in the center of the molecule. It has been found that pure symmetrical ketones, in which longitudinal disorder is impossible, do not show rotational disorder in the solid.[9,10] This would lead us to expect that hindered molecular rotation would be difficult in the ordered state of esters because of similar steric or dipole interaction effects. The dielectric constants of the longitudinally ordered esters should therefore be comparable to those of symmetrical ketones. In a region of longitudinal disorder, however, polar groups in adjacent chains may be sufficiently separated from one another that their interaction is no longer so important and the chains may rotate. Variations in the degree of longitudinal disorder that can be frozen into the samples can thus result in corresponding variations in orientation polarization as has been observed. *An important characteristic of longitudinal disorder is that, once frozen in, it remains unchanged until the sample is remelted.*

It can be seen in Figs. 2, 3, and 5 that the dielectric constant and thus the degree of longitudinal disorder increases not only with increase in freezing rate, but also with increase in total chain length for a given freezing rate. An extreme example of this behavior is illustrated in Fig. 5. The relatively short *n*-octadecyl acetate exhibited a dielectric constant near n^2 after gradual solidification, while even rapid freezing yielded a value far below that of the liquid. The much longer *n*-hexadecyl palmitate, on the other hand, invariably yielded a solid dielectric constant significantly above that of the liquid,† with much less dependence upon freezing rate. With *n*-octadecyl stearate (Fig. 4), the chain length was apparently long enough that nearly complete longitudinal disorder was realized when the sample was solidified gradually. Such a trend is to be expected since a more severe rearrangement is undoubtedly required for very long molecules to form an ordered configuration in going from the disordered liquid to the longitudinally ordered solid.

Contrary to what one might expect from the foregoing statements concerning the unsymmetrical esters, it has been reported that unsymmetrical ketones do not rotate in the solid state.[10] The possible reason for this is that molecules of sufficient chain length have not been investigated with the techniques employed here, i.e., variation in freezing rate.

Buckingham[5] concluded from a dielectric investigation of ethyl behenate that variations in dielectric constant with rate of solidification were the result of variations in the manner in which the crystallites aligned themselves between the plates of the measuring condenser. Although such behavior could lead to differences in the value of the dielectric constant because of the anisotropic nature of the crystals, it seems unlikely that such slight variations in solidification rate could have such a profound effect upon crystal alignment. Further evidence against Buckingham's hypothesis will be mentioned later.

B. Rotational Transitions in Longitudinally Disordered Phases of Esters

The rotational transitions in the long-chain esters were, in some cases, difficult to find because of the tendency of their rotationally disordered phases to super-cool. The rotator phase of *n*-dodecyl stearate could be super-cooled as much as 17° before the transition took place, while the transition in *n*-decyl palmitate could be found only on warming. Because of this uncertainty, transition temperatures are reported only as observed during warming. In only two members of the series, *n*-octadecyl acetate and *n*-hexadecyl plamitate, was it impossible with the techniques employed to locate the transition temperature. Since *n*-dodecyl stearate was examined more completely in the region of its transition point than the other esters in the present work, its behavior will be used as an example in the following discussion.

n-Dodecyl stearate exhibited a first-order and reversible rotational transition (Fig. 2) similar in nature to those found in long-chain bromides,[4] alcohols,[2] and paraffins.[1,4] The temperature of this transition was found, however, to shift to lower values with increase in degree of longitudinal disorder, but remained sharp. Such a shift cannot be accounted for by Buckingham's conclusion. Apparently, almost any degree of longitudinal disorder may be frozen into a sample, and the rotational transition temperature then depends uniquely on the degree of this disorder.

The shift in transition temperature T_t with degree of longitudinal disorder may be understood in terms of a recent treatment[4] of hindered molecular rotation in long-chain compounds, in which the potential energy difference V_0 associated with rotation is assumed to be as shown in Fig. 7(b). A consequence of this treatment is that T_t is proportional to V_0.

If longitudinal disorder is present, the average value of V_0 should be different than that observed for the ordered state. Let $V_0(\sigma)$ be the value of V_0 averaged over a lattice whose long-range longitudinal order is

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* In some of the shorter alcohols,[2] different rates of freezing led to different dielectric constants in the solid state, but the dielectric data were time-dependent. The effects in alcohols were due to an irreversible vertical-tilted transformation in the rotator phase. Such a transformation does not take place in long esters.

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

[10] V. Daniel and K. H. Stark, Trans. Faraday Soc. 47, 149 (1951).

† The increase in dielectric constant at the freezing point is due to the normal increase in density accompanying solidification.

TABLE I.

Ester		Chain length (m_1+m_2+1)	Symmetry (m_1-m_2)	Rotation	T_f	T_t
Name	Formula					
(1) Ethyl behenate	$C_{21}H_{43}COOC_2H_5$	25	18	yes	47.8	43
(2) *n*-Octadecyl acetate	$CH_3COOC_{18}H_{37}$	21	18	yes	30.1	?
(3) Ethyl stearate	$C_{17}H_{35}COOC_2H_5$	21	14	yes	30.5	23.6
(4) *n*-Decyl palmitate	$C_{15}H_{31}COOC_{10}H_{21}$	27	4	yes	29.0	10
(5) *n*-Dodecyl stearate	$C_{17}H_{35}COOC_{12}H_{25}$	31	4	yes	42.0	23
(6) *n*-Hexadecyl palmitate	$C_{15}H_{31}COOC_{16}H_{33}$	33 Type *A*	2	yes	51.0	?
(7) *n*-Octadecyl stearate	$C_{17}H_{35}COOC_{18}H_{37}$	37	2	yes	60.0	57
(8) *n*-Dodecyl palmitate	$C_{15}H_{31}COOC_{12}H_{25}$	29 Type *B*	2	no	38.5	None
(9) *n*-Tetradecyl stearate	$C_{17}H_{35}COOC_{14}H_{29}$	33	2	no	50.1	None
(10) *n*-Tetradecyl palmitate	$C_{15}H_{31}COOC_{14}H_{29}$	31	0	no	47.0	None

specified by an order parameter σ,

$$\sigma=(n_\alpha-n_\beta)/(n_\alpha+n_\beta),\quad 0\leqslant\sigma\leqslant 1. \tag{1}$$

Here n_α is the number of molecules whose long axes are oriented in a specified direction, and n_β is the number oriented in the opposite direction (see Fig. 1).

It may then be shown that (see Appendix I)

$$V_0(\sigma)=V_0(1)-(1-\sigma^2)\Delta V:\quad \Delta V=V_0(1)-V_0(0). \tag{2}$$

In the present application, ΔV is positive‡ because of the interactions of carbonyl groups of neighboring pairs of α-type or β-type molecules. Therefore, the transition temperature is lowered by disordering according to the relation,

$$T_t(\sigma)\propto V_0(1)-(1-\sigma^2)\Delta V. \tag{3}$$

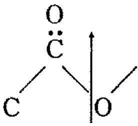
If ΔV is large enough, one may observe a transition in a disordered phase of a substance whose ordered phase possesses only a virtual transition above its ordinary melting point.

If a sample were cooled at an extremely nonuniform rate, it should be possible to obtain microphases with rather wide fluctuations in σ. This would lead to variations in T_t which would broaden the transition points. No such experiments are at hand.

It is very curious that, in certain of these esters, one can permanently freeze in practically any desired degree of longitudinal order (σ), and that this in turn affects the first-order transition temperature associated with a cooperative change in *rotational* order.

C. Calculation of the Dielectric Constant of *n*-Dodecyl Stearate

In order to estimate the static dielectric constant ϵ_0 of long-chain compounds it is necessary to know μ, the dipole moment perpendicular to the chain axis, and the degree of rotational order x. The latter is essentially the fraction of molecules frozen in deep wells (Fig. 7(b)) as opposed to those of higher energy. In the present case μ may be estimated by assuming that the keto and ether group moments are opposed. For long ketones $\mu=2.75$, and for ethers $\mu=1.15$, so that a



C moment should be roughly 1.60. The Kirkwood equation[11] is

$$4\pi N\mu^2 g/9kT=\frac{M}{d}\cdot\frac{(\epsilon-n^2)(2\epsilon+n^2)}{\epsilon(n^2+2)^2}, \tag{4}$$

where the constants have their usual significance. In the present case it seems reasonable to assume that $g=1-x^2$ as was shown to be the case for the *n*-bromides.[4] Details of the calculation of x from T have been given previously.[4] For *n*-dodecyl stearate $T_t=296$°K, $M=428$, $d=0.97$ and $\epsilon_\infty\cong n^2\cong 2.30$. In the rotationally melted phase which has virtually no rotational order, $g\cong 1$ and the calculated dielectric constant is 3.11. This is slightly higher than the observed value of 3.02 for the rapidly frozen sample. The calculated value just below T_t where $x\cong 0.85$ is 2.53 in good agreement with the observed value of 2.50. In the latter calculation Ω, the degeneracy of the upper states, was assumed to be 12 as was found for other long-chain molecules.

D. Longitudinal Disorder and Molecular Symmetry

In Table I are summarized the significant structural, symmetry, and orientational disorder data for the esters under consideration. In this table, m_1 and m_2 represent the chain length on either side of the polar carbonyl group.§ m_1 always refers to the longer of the two. As can be seen, rotation does not disappear until the carbonyl group approaches the center of the chain. If $m_1-m_2=0$, ΔV is certainly very small, while if $m_1-m_2=2$, it may still be so small that $T_t(\sigma)$ is above the ordinary melting point for all σ (Fig. 6).

However, it may be seen from Table I that certain compounds for which $m_1-m_2=2$ do show the rotational transition for at least some values of σ. This may be because of the following circumstance. In compounds

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‡ It should be noted that ΔV will always be small since the interactions of the carbonyl groups furnish only a small part of the total barrier to rotation. Large changes in T_t will therefore never be expected.

[11] J. G. Kirkwood, J. Chem. Phys. 7, 911 (1939); H. Fröhlich, *Theory of Dielectrics*, Oxford University Press, London (1949), p. 52.

§ The total chain length m, counting the carbonyl group, is m_1+m_2+1.

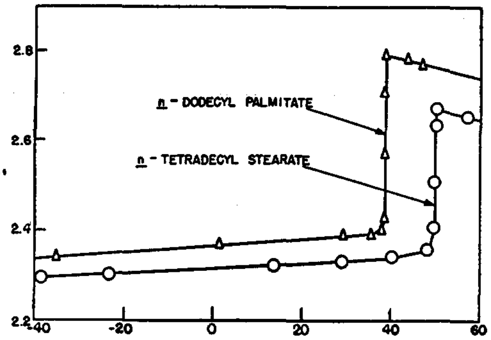


FIG. 6. Temperature dependence of the dielectric constant of *n*-dodecyl palmitate Δ and *n*-tetradecyl stearate ○. No dependence upon rate of freezing.

of type *A*, e.g., *n*-octadecyl stearate, the chain oxygen atom of the upper chain lies between the two carbonyl dipoles and should show a small dipole repulsion effect between it and the lower carbonyl (Fig. 7a). This would serve to lower V_0, and therefore T_t in compounds of type *A*. No such repulsion occurs in type *B* where the chain oxygens do not intervene.

E. An Alternative Model of Longitudinal Disorder

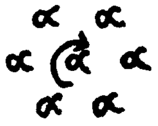
In the foregoing discussion it has been assumed that the dipoles in the longitudinally disordered phase in esters are staggered while the end groups remain in a plane (Fig. 1). A closely related but different picture of longitudinal disorder may be obtained by allowing the dipoles to remain in a plane while the end groups are staggered (not shown). In this new scheme the shift of T_t with σ could be ascribed to the difference in end-group forces instead of differences in polar forces. It is not obvious that the end-group forces will be very different when the end groups are staggered, but it is clear that dipole-dipole forces will diminish as $\sim\mu^2/(m_1-m_2)^3$ for the model where longitudinal disorder is as shown on Fig. 1. If the dipoles were always in the same plane, it would be more difficult to explain the variation of the dielectric constant with cooling rate. Neither of the above arguments permits rejection of the alternative model of longitudinal disorder, however. A somewhat better indication that the model of the disordered state shown in Fig. 1 is the better one may be had by consideration of the esters where $m_1-m_2=2$. If the alternative model of reversal of chains were employed, it would be found that both the dipolar and end-group forces were very nearly identical for all four cases, so that the observed differences in dielectric behavior could not be explained.¶ There is no reason to believe that the alternative arrangement may not appear in other compounds, however.

A direct determination of the structure of the disordered phases in long-chain compounds by x-ray methods aimed at differentiating the two models of the disordered state would probably be difficult unless longitudinal disorder could be found in a system where the polar group had a high atomic weight.

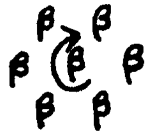
APPENDIX I

Calculation of the Average Value of V_0 as a Function of the Order Parameter σ

Let V_1= the value of V_0 for a chain which is completely surrounded by chains longitudinally oriented in the same direction, *viz.*,

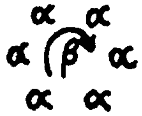


or



Let V_2= the value of V_0 for a chain completely surrounded by chains longitudinally oriented in the opposite direction, *viz.*,

or



The average value of V_0 experienced by an α-type molecule in the disordered lattice is

$$V_{0\alpha}=(n_\alpha V_1/N)+(n_\beta V_2/N) \qquad (1)$$

and for a β-type molecule,

$$V_{0\beta}=(n_\beta V_1/N)+(n_\alpha V_2/N). \qquad (2)$$

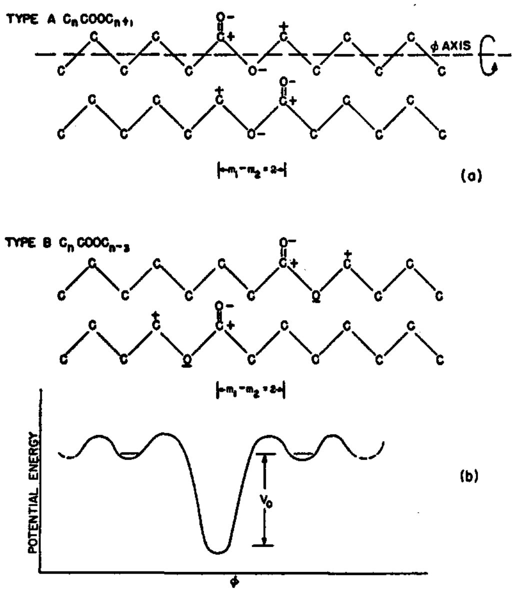


FIG. 7. (a) The two types of longitudinal disorder in esters where $m_1-m_2=2$. (b) Assumed potential energy function for rotation about ϕ axis.

¶ A. Bondi and L. B. Scott [Nature **167**, 486 (1951)] have found that certain pairs of long-chain esters form a continuous series of solid solutions, and interpret this to mean the dipoles do not form a single sheet. This is in accord with the picture of disorder presented in this paper.

If V_0 is then averaged over the entire lattice, it is found that

$$V_0 = V_1 - [2n_\alpha n_\beta/N^2](V_1 - V_2). \qquad (3)$$

The order parameter is defined as

$$\sigma = (n_\alpha - n_\beta)/N, \qquad (4)$$

which, when substituted in Eq. (3), gives

$$V_0(\sigma) = V_1 - (1-\sigma^2)(V_1/2 - V_2/2). \qquad (5)$$

Although V_1 is the energy difference of a molecule in the ordered state, $V_0(1)$, it must be remarked that complete disorder results in a molecule having on the average three α and three β nearest neighbors. For this disordered state, then, $V_0(0) = \frac{1}{2}(V_1 + V_2)$. Defining ΔV as $V_0(1) - V_0(0)$, Eq. (5) becomes

$$V_0(\sigma) = V_0(1) - (1-\sigma^2)\Delta V, \qquad (6)$$

which is the required form.

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The Molecular Structure of 1,2-Dichloropropane

William W. Wood* and Verner Schomaker
Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California†

(Received July 16, 1951)

Under the assumption of $V(\varphi) = V_0[1-\cos(\varphi-\varphi_0)]/2$ for the potential hindering internal rotation, visual interpretation of the electron-diffraction pattern leads to the results (best values and estimated limits of error): C−Cl, 1.79±0.035A; C···Cl, 2.715±0.025A; C−C, 1.56A (range: 1.49–1.60A); ∠C−C−Cl, 108±4°; $|\varphi_0| \leqslant 30°$ (i.e., essentially *trans* in the chlorine atoms), with a small positive value of φ_0 (increasing $CH_3\cdots Cl_{primary}$) most likely; $V_0 \geqslant 4$ kcal/mole. The best value for V_0 ranges from 10 kcal/mole for $\varphi_0 = 0°$ to 30–40 kcal/mole for $\varphi_0 = 25°$. The diffraction pattern is almost indifferently compatible with fractions ranging up to 50 percent of a *skew*-isomer with $\varphi_0 \sim 120°$ and a sufficiently low value of V_0, but consideration of dipole moment data provides some further evidence on its structure while showing the fraction present to be about 20 percent with an upper limit of about 30 percent.

The present investigation of propylene chloride was undertaken primarily to obtain structural information needed for an application[1] of Kirkwood's theory of optical activity,[2] which in this case predicts a strong dependence of the optical activity upon internal rotation quite different from that of the conspicuous aspects of the diffraction pattern. Our electron-diffraction data alone were accordingly inadequate, but dipole moment data were fortunately made available which made possible a fairly complete structure determination.

In an x-ray diffraction study of the gas Berger found satisfactory agreement[3] on the assumption of reasonable values for the bond distances, tetrahedral bond angles, and the potential function $V(\varphi) = V_0(1-\cos\varphi)/2$, with $V_0 = 0.88$ kcal/mole, for the dihedral angle of displacement φ of the $Cl-C_1-C_2$ and C_1-C_2-Cl planes from the *trans*-orientation. The structure of the related molecule, 1,2-dibromopropane, has been investigated by electron diffraction by Schomaker and Stevenson,[4] who reported normal values for the bond distances and bond angles and a root-mean-square torsional vibration of ±20° around the *trans*-position, again with no indication of the possible occurrence of other internal-rotation isomers.

THE ELECTRON DIFFRACTION INVESTIGATION

Experimental

Two sets of photographs were prepared, the first at the 11-cm camera distance from some of the commercial Paragon product that had been distilled through a 40-cm column packed with glass helices (n_D^{25} 1.4367, b.p. on redistillation through a similar 60-cm column 95.6–96.4°) and the second, partly at 11 cm and partly at 20 cm, from an independent sample prepared from propylene glycol by Dr. H. K. Garner (b.p. 96.2–96.5°, n_D^{25} 1.4368; see lit.[5]: b.p. 96.2°, n_D^{25} 1.43638), in the apparatus described by Brockway.[6] For the photographs actually used the sample temperature was about 25°.

The Photographs

Curve V_1 was drawn from the appearance and measurements of the photographs of the first set, the shape and height of the central maximum being guessed from past experience, while V_2, which was drawn after

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* Present address: Los Alamos Scientific Laboratories, Los Alamos, New Mexico.

† Contribution No. 1595.

[1] Wood, Fickett, and Kirkwood, J. Chem. Phys. **20**, 561 (1951).

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