Molecular Rotation in Crystalline Disubstituted Ethanes

Addison H. White and S. O. Morgan

Molecular Rotation in Crystalline Disubstituted Ethanes

ADDISON H. WHITE AND S. O. MORGAN
Bell Telephone Laboratories, New York, N. Y.
(Received May 5, 1937)

The dielectric constants and conductivities of ethylene chloride, ethylene bromide, ethylene cyanide, ethylene diamine and ethylene thiocyanate have been measured over a wide temperature range in the solid and liquid states and in the frequency band 1–100 kc. Thermal measurements have revealed hitherto unreported transitions in ethylene cyanide at $-38°$ to $-46°$ and in ethylene bromide at $-23°$ to $-25°$. The ethylene cyanide molecule rotates about all three axes in the crystal between the transition and melting temperatures. The internal rotational motion of atomic groups about the central $C-C$ bond, which is believed to characterize this molecule in the liquid state, is not observably restricted by solidification. This internal motion is believed to facilitate molecular rotation in the crystal by increasing the time-average symmetry of the molecule. An atomic polarization of about 17 cc below the transition is ascribed to the persistence of some degree of torsional vibration within the molecule even in the low temperature phase of the crystal. In none of the other crystals does the polar form of the molecule rotate below the freezing point nor is there evidence of unusual intramolecular motion except possibly in ethylene thiocyanate. It is probable, however, that the *trans* form of the ethylene bromide molecule rotates about its long axis between the transition and melting points.

THE existence of internal rotation about the $C-C$ bond in the ethane molecule[1] has led to a number of measurements of the dipole moments of its symmetrically disubstituted derivatives. This work has all been done in either dilute solution or the gaseous state. If such an internal motion persists in the solid phase, the resulting dielectric properties should be unusual. Relative mobility of the parts of the molecule might be expected to facilitate rotation of the whole molecule in the lattice in a manner similar to that suggested for the pliable cyclohexane derivatives.[2] This paper presents the results of dielectric measurements of a series of such compounds in the crystalline and incidentally the liquid states.

The consensus of the theoretical and experimental work on ethylene chloride (1,2-dichloroethane) and ethylene bromide (1,2-dibromoethane) is that at room temperature and in dilute solution or the vapor phase most of the molecules are in states which involve internal rotational oscillation of considerable amplitude.[3] Experimentally the dipole moments of these molecules increase with temperature, so it is quite clear that their configuration of minimum potential energy is the *trans* form, whose moment is zero. This is due to the predominance of the electrostatic repulsion which tends to force the two internal dipoles as far apart as possible.

Williams'[4] measurements of the dipole moments of three ethylene halides and ethylene cyanide (succinonitrile), all in dilute benzene solution at 25°C, are summarized in the fourth column of Table I. Using the observed moments

TABLE I.

	$\mu_{C_2H_5X}$	μ_{calc}	μ_{obs}	$\dfrac{\mu_{obs}}{\mu_{calc}}$
$C_2H_4Cl_2$	2.0D	2.7D	1.75D	0.65
$C_2H_4Br_2$	1.9	2.5	1.4	.56
$C_2H_4I_2$	1.7	2.3	1.3	.57
$C_2H_4(CN)_2$	3.45	4.6	3.8	.83

of the corresponding ethyl derivatives of the type C_2H_5X for the two component dipoles within each of these molecules, the resultant effective molecular moments, calculated for perfectly free internal rotation[4] with no distortion of carbon valence angles, are listed in the third

[1] Ebert, Leipziger Vortrage (1929), p. 44; Wagner, Zeits. f. physik. Chemie **14B**, 166 (1931); Eyring, J. Am. Chem. Soc. **54**, 3191 (1932); Eucken and Weigert, Zeits. f. physik. Chemie **23B**, 265 (1933); Bartholomé and Karweil, Naturwiss. **25**, 172 (1937); however, cf. Kemp and Pitzer, J. Chem. Phys. **4**, 749 (1936) and Howard, Phys. Rev. **51**, 53 (1937).

[2] White and Morgan, J. Am. Chem. Soc. **57**, 2078 (1935).

[3] Smyth, J. Am. Chem. Soc. **46**, 2151 (1924); L. Meyer, Zeits. f. physik. Chemie **8B**, 27 (1930); Smyth, Dornte and Wilson, J. Am. Chem. Soc. **53**, 4242 (1931); Zahn, Phys. Rev. **38**, 521 (1931); Phys. Rev. **40** 291 (1932); Greene and Williams, Phys. Rev. **42**, 119 (1932); Smyth and Kamerling, J. Am. Chem. Soc. **53**, 2988 (1932); Lennard-Jones and Pike, Trans. Faraday Soc. **30**, 830 (1934).

[4] Williams, Zeits. f. physik. Chemie **138A**, 75 (1928).

column of the table. Such values should be valid for purposes of comparison. It is obvious that the agreement between observation and calculation is best in ethylene cyanide (succinonitrile), and that it would only be improved by allowing in the calculation for distortion of the carbon valence angles due to dipole repulsion. It may fairly be concluded that of these molecules ethylene cyanide possesses much the greatest freedom of internal rotational motion. This conclusion is not significantly affected by the fact that the absence of measurements of the effect of temperature on this dipole leaves doubt as to whether the *trans* or the *cis* configuration of the molecule is the more stable. Weissberger[5] has suggested that if the quantum-mechanical exchange interaction were sufficiently large in such a compound, the potential energy of the *cis* form would be less than that of the *trans*.

The situation is more complicated in ethylene diamine because the molecule has three possible degrees of internal rotational freedom. Zahn's[6] measurement of the dipole moment yielded him no definite information as to the degree of internal motion about the $C-C$ bond, although he believed the polar NH_2 groups to be freely rotating.

Regarding the persistence of intramolecular rotation in the crystal, Mizushima[7] and his collaborators interpret their Raman spectra data for ethylene chloride and bromide to mean that these molecules are almost all in the *trans* configuration in the solid, although both the *cis* and the *trans* states are found in the liquid. X-ray measurements made by Klug[8] have definitely located the iodine atoms in the crystal of ethylene iodide, showing that there is little internal motion of this molecule in the crystal at room temperature. According to the hypothesis, then, none of these halides should be unusually likely to show end-over-end rotation of the unit molecule in the solid state.

No evidence has been found, as far as we know, regarding the internal motion of the ethylene cyanide, ethylene diamine, or ethylene thiocyanate molecules when they are in the

crystal. The dielectric properties of these crystals were measured with the hope that they might supply information on this point. Measurement of the halides was expected to confirm the results of the Raman measurements.

PURIFICATION OF MATERIALS

Ethylene chloride

Material from Eastman Kodak Company was dried for several days over anhydrous calcium sulfate and twice fractionally distilled; b. p. 83.8±0.05°.

Ethylene bromide

Eastman's product was dried over anhydrous calcium sulfate for several weeks and fractionally distilled; b. p. 131.6±0.05°.

Ethylene cyanide

Two samples were obtained from Eastman Kodak Company. That used in the dielectric measurements was twice fractionally crystallized from acetone, employing a narrow temperature range. After removing the acetone by evacuation the m. p. was 54.2°. The material used for the thermal measurement was found to melt at 54.2 as received, and was not further purified.

Ethylene diamine

Material from Eastman was thrice distilled from sodium. The second and third middle fractions boiled at the same temperature, 116.7°, after correction of the thermometer used by comparison with one calibrated by the National Bureau of Standards. The density of the best fraction was found to be 0.8970 g/cm at 19.9°. Although the above b. p. is 0.5° higher than the latest reported in the literature, this density agrees well with that reported by the same author,[9] 0.8978 g/cm at 20.0°. Since density is much more sensitive than b. p. to the presence of the hydrated compound, it is concluded that the latter was absent in the material as purified.

Ethylene thiocyanate

The Eastman product was twice fractionally crystallized from absolute alcohol; m. p. 89.8°.

[5] Weissberger, Trans. Faraday Soc. **30**, 852 (1934).
[6] Zahn, Physik. Zeits. **33**, 525 (1932).
[7] Mizushima, Morino and Noziri, Nature **137**, 945 (1936).
[8] Klug, Zeits. f. Krist. **90**, 495 (1935).
[9] Wilson, Ind. and Eng. Chem. **27**, 867 (1935).

EXPERIMENTAL METHOD AND RESULTS

Cooling and heating curves were run on the ethylene chloride, bromide, and cyanide by well-known methods. The calibration of Southard and Andrews[10] was used for converting the observed potential E_o of the copper-constantan thermo-couples to temperature, after correcting with the equation

$$E = 1.0056 E_o + 0.005 \text{ millivolts.}$$

The condensers used for dielectric measurement are illustrated in Fig. 1 and Fig. 2. They are designed for use in glass containers so that phase changes in the dielectric may be visually observed. The design of Fig. 1 is for grounded capacity measurements, and was used for all liquids and those solids which melt below room temperature. The outside plates are grounded, and are separated from the central electrode by clear fused quartz washers and bushings. The error due to edge effect was minimized by calibration of the condenser with benzene. In solids a more important source of error is the formation of voids upon solidifying or cooling. With ethylene cyanide and thiocyanate it was possible to reduce this error by using the condenser of Fig. 2
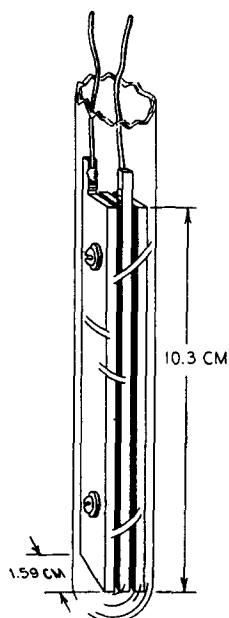

FIG. 2. Condenser for measurement of solid sheets.

for measurement of pressed sheets of the material. The capacity of the leads was eliminated by making direct capacity measurements and using a shielded lead to the high potential electrode. The correction for the edge effect was calculated. Homogeneous sheets of ethylene cyanide about 1.0 mm thick were obtained by pressing the waxy material under 2500 pounds ram pressure in a 5.08×1.75 cm mold. Gold plated brass electrodes 0.8 mm thick were pressed on each side of the sheet to facilitate its separation from the plungers of the press and to insure good electrical contact upon measurement. These added electrodes are not shown in Fig. 2, which illustrates the manner in which a steel spring holds the condenser together. Some air was entrapped in the sheets of ethylene thiocyanate, which was much harder than the cyanide and not so readily formed even at 20,000 pounds ram pressure. The low temperature form of the cyanide could also be seen to be inhomogeneous, due probably to the development of cracks associated with a sharp density change at the transition. In such cases the error in the measurement of dielectric constant is difficult to estimate, but the observed values may be safely said to be too low. Even in the most favorable circumstances the observed results are probably low, and no accuracy greater than 5 percent can be claimed for the measurement of solids. The values of conductivity, recorded in

FIG. 1. Condenser for measurement of liquids.

10 Southard and Andrews, J. Frank. Inst. 207, 323 (1929).

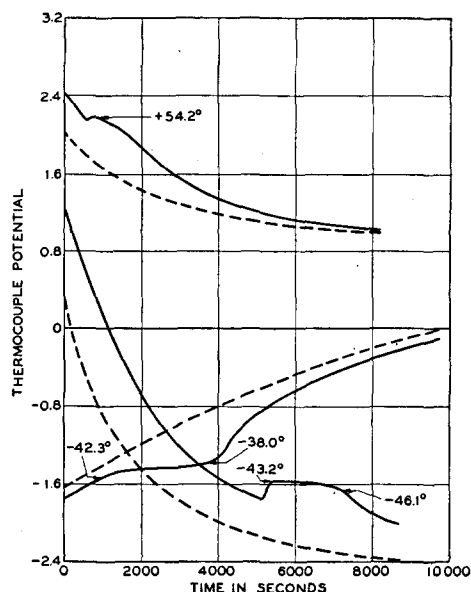FIG. 3. Cooling and heating curves for ethylene cyanide; broken lines represent bath temperatures.

ohm^{-1} cm^{-1}, are of assistance in interpreting the behavior of dielectric constant, but are not to be taken as physical constants of the compounds in question.

The equipment used for measurement of the capacity, conductance and temperature and for control of the temperature was essentially that previously described.[11]

Figures 3 and 4 show the cooling and heating curves for ethylene cyanide and bromide; bath temperatures are represented by broken lines. Both heating and cooling curves display well-defined arrests in the solid state below the m. p., indicative of thermal transitions which have not previously been reported. The data do not supply quantitative heats of fusion and transition, but they clearly indicate that in the ethylene cyanide the heat of transition is very much larger than the heat of fusion, while the converse is true in ethylene bromide. The same sample of ethylene cyanide was used for the two cooling curves; the experiment was divided into two parts because of the wide temperature range involved.

The upper curve of Fig. 3 shows a very short arrest at 54.2° for the freezing of the cyanide, with a freezing range extending at least to 52.0°. According to the van't Hoff law, however, a

relatively small amount of impurity is capable of producing this effect where the heat of fusion is so low. The cooling curve shows supercooling of about 6° before the transition at −43.2° sets in. Even after starting, the transition is not very sharp in this sample; its range extends to about −46.1°. Upon heating, the same transition begins at −42.3° and appears to progress most rapidly at about −40°. On the whole, the evidence favors the existence of a temperature hysteresis at the transition, although the absence of stirring makes this conclusion uncertain.

Figure 4 shows that freezing in ethylene bromide continues for about two degrees below the initial freezing point. The transition is found at about −24°. Here again there is some evidence of temperature hysteresis of the transition, which is observed at −24.6° with cooling and −23.0° with heating.

The heating curve for ethylene chloride, which is not shown, reveals no transition between −95° and its m. p.

The dielectric properties of ethylene cyanide are recorded in Fig. 5 and Table II. Above room temperature the specific conductivity Γ is high because of ionization.[12] Electrode polarization capacity therefore increases the apparent value of dielectric constant at low frequencies. This effect was eliminated by extrapolating the dielectric constant ϵ to high frequencies.[13] The resulting values of the true dielectric constant are given in Table II in the column headed ϵ_t and in Fig. 5 by filled circles. The only other value of the
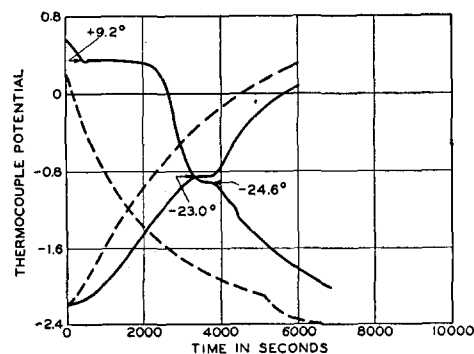
FIG. 4. Cooling and heating curves for ethylene bromide; broken lines represent bath temperatures.

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

[12] Walden, Zeits. f. physik. Chemie 54, 128 (1906).
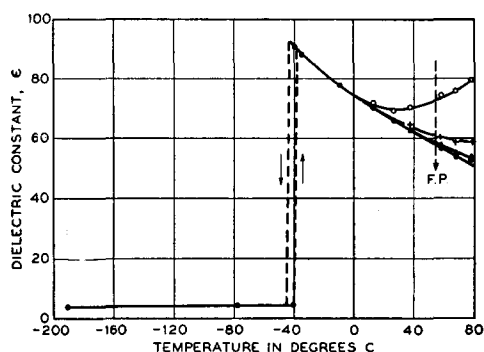[13] Vd., e.g., Yager and Morgan, J. Phys. Chem. 35, 2039 (1931).

FIG. 5. Dielectric constant of ethylene cyanide; circles, 10 kc; crosses, 30 kc; triangles, 100 kc; dots, corrected for electrode polarization capacity.

dielectric constant of the solid recorded in the literature, 66.6 at 23°,[14] falls almost exactly on the curve of Fig. 5. The two values reported for the liquid, 61.2 at 60° [14] and 57.3 at 58° [15] are both higher than our value of 56.5 at 57.4°.

Figure 5 shows no significant discontinuity of dielectric constant at the freezing point. In the crystal ϵ rises rapidly with declining temperature, in a manner characteristic of polar liquids, down to the transition temperature, where its value drops abruptly to about 4.4. This figure is likely to be too low, as indicated by the less homogeneous appearance of the dielectric below the transition, which is taken to be evidence of the appearance of voids.

The temperature of the dielectric transition was determined by using a condenser of the type of Fig. 1, in which good thermal contact is obtained. The actual values of dielectric constant thus observed are not recorded, being too low,

[14] Schlundt, J. Phys. Chem. **5**, 503 (1901).
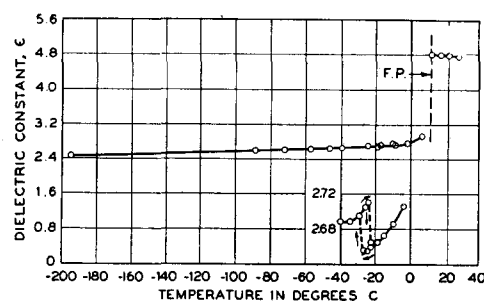[15] Walden, Zeits. f. physik. Chemie **46**, 103 (1903).

FIG. 6. Dielectric constant of ethylene bromide at 100 kc; large scale inset shows behavior at transition temperature.

but the break in the curve was found to occur between −42.6° and −44.9°, as determined through a declining sequence of constant temperatures. Reversing the temperature sequence, the rise of dielectric constant had just started at −40.4° and was complete at −38.0°. These temperature ranges agree well with those observed thermally, and tend to confirm the reality of the temperature hysteresis of the transition, since a different sample was used and much better thermal equilibrium was possible than in the thermal measurements.

The dielectric constant of ethylene bromide breaks sharply at the freezing point, as may be seen in Fig. 6 and Table III. Some premelting probably affects the values observed at about 5°. When the first two runs were made on this material, no evidence of a transition was noticed. After the thermal transition was observed, more careful measurements (run No. 3) in the indicated temperature range revealed an extremely small but quite definite break in the curve, as shown in the large-scale inset of Fig. 6. The only

TABLE II. *Dielectric properties of ethylene cyanide.*

| $t°C$	1 KC ϵ	1 KC Γ	3 KC ϵ	3 KC Γ	10 KC ϵ	10 KC Γ	30 KC ϵ	30 KC Γ	100 KC ϵ	100 KC Γ	ϵ_t
78.2 Liquid	600	1.7×10^{-5}	170	1.7×10^{-5}	79.2	1.7×10^{-5}	58.4	1.7×10^{-5}	53.5	1.7×10^{-5}	52.3
67.7	521	1.4	157	1.4	75.5	1.4	58.2	1.4	54.5	1.4	53.6
57.4	440	1.2	143	1.2	74.5	1.2	59.9	1.2	57.4	1.2	56.5
36.7 Solid	113.5	1.3×10^{-6}	73.1	1.3×10^{-6}	69.1	1.3×10^{-6}	64.4	1.3×10^{-6}	63.2	1.4×10^{-6}	62.6
25.7	101.3	1.0	74.3	1.0	69.0	1.0	66.9	1.0	65.9	1.1	65.5
12.8	88.3	6.9×10^{-7}	74.9	6.9×10^{-7}	71.8	6.9×10^{-7}	70.4	7.0×10^{-7}	69.8	7.0×10^{-7}	69.6
−10.0							77.4	2.1	77.3	2.2	77.3
−34.7							87.7	2.2×10^{-8}	87.7	3.2×10^{-8}	87.7
−40.7	4.41	$<3.4\times10^{-11}$							4.41	$<3.4\times10^{-11}$	4.41
−76.8	4.24	<3.4							4.24	<3.4	4.24
−190	3.90	<3.4							3.90	1.6×10^{-10}	3.90
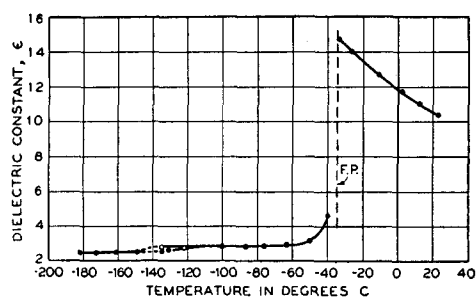
FIG. 7. Dielectric constant of ethylene chloride; circles, 10 kc; dots, 100 kc.

accuracy claimed for the fourth significant figure in these results is that relative to temperature variation in this particular sample. Virtual dielectric constant rises below this transition. With heating, the break occurs between $-24.0°$ and $-22.0°$, in agreement with the thermal results; with cooling, it falls between $-26.6°$ and $-29.0°$, fully two degrees below the thermal arrest. The dielectric data confirm the existence but not the magnitude of the temperature hysteresis. A plot of the data of runs No. 1 and No. 2 on a very large scale gives results consistent with the existence of the transition between $-20°$ and $-30°$, but in both cases shows a drop of about 0.04 units in dielectric constant in place of the rise of similar magnitude observed in run No. 3. The results are those to be expected at a transition involving a small change of density and homogeneity of the sample but no change of molar polarization.

TABLE III. *Dielectric properties of ethylene bromide.*

t°C		1 KC		10 KC		100 KC	
		ϵ	Γ	ϵ	Γ	ϵ	Γ
Run No. 1:							
25.9	Liquid	4.79	1.7×10^{-9}			4.74	2.0×10^{-9}
20.5		4.80	1.5	4.77	1.6×10^{-9}	4.77	1.7
15.3		4.82	7.9×10^{-10}	4.80	1.4	4.79	1.5
10.5		4.84	11	4.82	1.2	4.81	1.3
5.9	Solid	3.03	1.9	2.95	2.5×10^{-10}	2.94	5.4×10^{-10}
-0.2		2.85	1.1	2.80	1.6	2.78	
-9.3		2.79	6.7×10^{-11}	2.75	1.2	2.74	4.3
-19.3		2.76	5.1	2.73	1.0	2.72	3.8
-31.6		2.69	3.1	2.68	7.0×10^{-11}	2.67	4.3
-195.8		2.46	1.9			2.45	$<3. \times 10^{-11}$
Run No. 2:							
5.0		3.07	1.4×10^{-10}	3.02	2.0×10^{-10}	3.01	6.5×10^{-10}
-2.6		2.86	7.2×10^{-11}	2.82	1.4	2.80	6.0
-10.7		2.81	5.3	2.78	1.1	2.76	5.1
-25.0		2.76	3.4	2.73	8.7×10^{-11}	2.73	4.3
-32.4		2.71	2.5	2.69	6.5	2.68	4.3
-39.5		2.70	1.9	2.68	6.5	2.67	4.6
-46.6		2.69	1.5	2.67	5.4	2.67	4.6
-57.6		2.66	1.1	2.64	5.4	2.64	3.2
-72.6		2.63	7.3×10^{-12}	2.62	4.6	2.62	2.7
-94.4		2.62	5.4	2.60	3.8	2.59	2.7
Run No. 3:							
Falling temperature:							
-4.0		2.850	1.02×10^{-10}	2.745	2.9×10^{-10}	2.710	6.4
-10.0		2.808	8.7×10^{-11}	2.712	2.4	2.688	6.6
-15.0		2.778	7.6	2.694	2.0	2.674	4.4
-22.7		2.727	5.7	2.670	1.3	2.661	2.0
-24.1		2.718	5.2	2.667	1.1	2.656	2.6
-26.6		2.712	4.7	2.664	1.0	2.656	2.3
-29.0		2.736	4.0	2.703	7.7×10^{-11}	2.697	2.1
-34.3		2.718	2.8	2.694	4.8	2.691	1.3
-39.8		2.706	2.0	2.697	3.5	2.691	1.2
Rising temperature:							
-26.0		2.736	3.7	2.712	6.7	2.706	1.1
-24.0		2.742	4.2	2.715	6.9	2.712	1.9
-22.0		2.709	3.9	2.685	8.0	2.670	1.1
-18.4		2.703	5.4	2.682	10.	2.670	2.1

TABLE IV. *Dielectric properties of ethylene chloride.*

$t°C$		1 KC ϵ	1 KC Γ	10 KC ϵ	10 KC Γ	100 KC ϵ	100 KC Γ
22.2	Liquid	10.45	1.5×10^{-9}	10.43	1.5×10^{-9}	10.39	1.6×10^{-9}
11.4		11.07	2.0			11.02	2.0
+1.3		11.73	2.0			11.69	2.0
−12.0		12.71	1.7			12.67	1.7
−27.2		14.01	1.4			13.98	1.4
−34.7		14.72	1.3			14.68	1.3
−40.0	Solid	4.82	1.0	4.66	1.1	4.65	1.1
−50.1		3.48	1.1	3.14	1.3	3.13	1.3
−63.1		3.29	1.1	2.94	1.3	2.93	1.4
−76.1		3.12	7.5×10^{-10}	2.87	9.2×10^{-10}	2.86	9.2×10^{-10}
−86.6		3.01	5.5	2.84	6.4	2.84	6.6
−100		2.80	1.2	2.77	1.5	2.75	5.2
−109		2.77	4.0×10^{-11}	2.76	6.9×10^{-11}	2.75	4.6
−119						2.74	7.5
−122		2.75	6.3×10^{-12}	2.75	3.5×10^{-10}	2.70	8.9
−131						2.66	4.9×10^{-9}
−135		2.75	7.8	2.75	3.2	2.54	3.4
−149		2.50	1.1	2.48	5.8×10^{-11}	2.46	4.0×10^{-10}
−161		2.48	3.5	2.47	2.6	2.47	2.3
−172		2.47	2	2.47	1.7	2.46	2.3
−182		2.45	4			2.45	3.5

TABLE V. *Dielectric properties of ethylene diamine.*

$t°C$	1 KC ϵ	1 KC Γ	3 KC ϵ	3 KC Γ	10 KC ϵ	10 KC Γ	30 KC ϵ	30 KC Γ	100 KC ϵ	100 KC Γ
26.5 Liquid	146	1.12×10^{-5}			18.8	1.12×10^{-5}	13.6	1.12×10^{-5}	13.5	1.12×10^{-5}
17.4	117	1.00			16.3	1.00	14.5	1.00	14.5	1.00
9.7	81.9	7.4×10^{-6}			16.3	7.4×10^{-6}	15.4	7.4×10^{-6}	15.2	7.4×10^{-6}
6.7 Solid	16.9	5.5×10^{-7}	9.57	5.6×10^{-7}	7.93	5.6×10^{-7}	7.05	5.8×10^{-7}	5.88	6.4×10^{-7}
1.7	9.83	1.5	7.90	1.5	6.77	1.6	5.93	2.1	5.13	3.3
−8.1	8.03	5×10^{-8}	6.75	5.5×10^{-8}	5.64	6.0×10^{-8}	4.76	6.9×10^{-8}	3.98	9.8×10^{-8}
−26.4	5.46	2.9×10^{-9}	4.61	4.1×10^{-9}	3.92	6.9×10^{-9}	3.45	1.2	3.11	2.4×10^{-8}
−46.0	3.53	4.4×10^{-10}	3.17	8.1×10^{-10}	2.93	1.6	2.81	2.7×10^{-9}	2.73	4.9×10^{-9}
−78.5	2.63	2.1×10^{-11}	2.60	3.7×10^{-11}	2.60	7.2×10^{-11}	2.60	1.4×10^{-10}	2.60	3.2×10^{-10}

TABLE VI. *Dielectric properties of ethylene thiocyanate.*

$t°C$	1 KC ϵ	1 KC Γ	10 KC ϵ	10 KC Γ	100 KC ϵ	100 KC Γ
84.6	21.8	6.6×10^{-8}	8.61	8.8×10^{-8}	5.05	1.4×10^{-7}
68.9	3.73	3.5×10^{-10}	3.41	8.7	3.32	2.3
47.9	3.36	2.7×10^{-11}	3.31	1.3	3.29	1.1
24.8	3.41	9.3	3.38	1.4	3.33	1.7
0	3.36	9.0×10^{-12}	3.34	1.3	3.30	1.2×10^{-9}
−78.5	3.23	1.7×10^{-11}	3.18	1.2×10^{-10}	3.17	5.6×10^{-10}
−195.8	3.10	7×10^{-13}	3.09	$<3\times10^{-12}$	3.10	7×10^{-11}

The observed dielectric constant of the liquid at 18° is 1.6 percent lower than that recorded in the I. C. T. Near −30° our values are about 10 percent below those obtained at low frequency by Fleming and Dewar,[16] who have not recorded the m. p. or b. p. of their material.

[16] Fleming and Dewar, Proc. Roy. Soc. (London) **61**, 316 (1897).

The behavior of ethylene chloride at the freezing point is similar to that of the bromide, as shown in Fig. 7 and Table IV. Below −86.6° the data were obtained by embedding the tube containing the condenser in aluminum granules in a Dewar flask, cooling with liquid nitrogen, and afterwards making measurements as the system drifted to higher temperatures. There is

a region of anomalous dispersion between $-150°$ and $-120°$ in the 1–100 kc band, as shown by the maxima of conductivity in this temperature range and the successive increases of dielectric constant for the various frequencies from about 2.47 to about 2.75. There is no dielectric evidence of a transition of any magnitude in the solid state.

In the liquid state the observed values of dielectric constant differ from those of Smyth, Dornte and Wilson[3] by an average of less than 1 percent. No data for the solid have been found in the literature.

The real dielectric constant of ethylene diamine drops sharply at the freezing point. In Table V the variation of ϵ and Γ with temperature and frequency above $-60°$ is characteristic of electrolytic polarization capacity, as might be expected from the electrolytic action of the compound in solution.[17] This behavior may mask any small discontinuity of true dielectric constant, but the results are essentially normal for an organic crystal of high ionic conductivity. Measurement below $-80°$ was abandoned when the sample exploded upon being cooled to liquid nitrogen temperature.[18]

The observed dielectric constant of the liquid is about 10 percent lower than that reported by Mathews, whose sample boiled in the range 118–121°.[19] In this case, where great care is required to prevent contamination of the sample with water, it is likely that the lower value is the better.

In Table VI the dielectric constant of ethylene thiocyanate is shown to be almost independent of temperature between $-195.8°$ and $+68.9°$, indicating that there are no dielectrically observable transitions in this region. At 84.6° visually evident decomposition and the tremendous increase of conductivity indicate that even at 100 kc the observed value of dielectric constant includes the spurious effects of electrolytic polarization capacity.

DISCUSSION OF RESULTS

The continuity of dielectric constant through the freezing point of ethylene cyanide is evidence

that: (1) its polar molecules rotate in the solid state to much the same extent as in the liquid; (2) the dipole moment of the molecule is unchanged upon solidification; and (3) the dielectric constant of the single crystal is isotropic. Conclusion (3) may indeed be inferred from (1), since it is very likely that rotation of the individual molecule in the liquid and hence in the solid occurs about the three Cartesian axes. Directly, however, anisotropy of dielectric constant in the single crystal would be almost certain to produce a discontinuity of measured dielectric constant of the mass of randomly oriented crystals at the melting point.

The thermal data show the heat of fusion of ethylene cyanide to be less than its heat of transition. The value of the former found in the *International Critical Tables*, 940 calories per mole, is also much less than that of similar compounds in whose crystals there is no evidence of molecular rotation, as for example ethylene diamine, whose heat of fusion at 0°C is 4600 cal./mole.[9] Such thermal behavior is to be expected of crystals whose molecules are rotating, according to Clusius,[20] who suggested that when this rotation sets in at a transition, the entropy of melting is less than would otherwise be expected by approximately the amount of the entropy of transition. Similarly low heats of fusion[21] have been observed in those cyclohexane and camphor derivatives which have been found by dielectric measurement[2, 22] to rotate below the melting point. Thus the thermal evidence is consistent with the view that ethylene cyanide molecules rotate in the crystal above the transition temperature.

Smyth, Dornte and Wilson[3] have found that when the polarization of ethylene chloride in heptane solution is measured through the concentration range, it fails to decline with increasing concentration as would be expected in view of the usual effects of molecular association and of the limitations of the Clausius-Mosotti equation.[23] They regard this as evidence of increased

[17] Bredig, Zeits. f. physik. Chemie 13, 289 (1894).
[18] It has been suggested that this was due to the liquefaction of oxygen from the air in the tube on cooling to $-195°$.
[19] Mathews, J. Phys. Chem. 9, 641 (1905).

[20] Clusius, Zeits. f. Elektrochem. 39, 598 (1933).
[21] Kelley, J. Am. Chem. Soc. 51, 1400 (1929); Parks and Huffman, ibid. 52, 4381 (1930); Pirsch, Ber. 68, 67 (1935).
[22] Yager and Morgan, J. Am. Chem. Soc. 57, 2071 (1935).
[23] Wyman, J. Am. Chem. Soc. 56, 536 (1934); v. Arkel and Snoek, Trans. Faraday Soc. 160, 707 (1934); Kumler, J. Am. Chem. Soc. 57, 100 (1935).

molecular dipole moment due to reduced interaction of the two internal dipoles of the molecule in the more concentrated solutions. Any factor which directly reduces the electrostatic interaction between the charges within such a molecule should similarly reduce the energy of quantummechanical exchange interaction, since the former is the perturbation in the wave equation out of which the latter arises. Hence it may be inferred that the freedom of internal rotational motion of the molecule of ethylene cyanide should similarly increase in concentrated solution, regardless of the relative importance of repulsive and attractive forces in determining its configuration. In the absence of evidence to the contrary, these cyanide molecules may therefore be expected to have more internal freedom of motion in the pure liquid than in benzene solution.

Any significant change in the freedom of internal motion about the central $C-C$ bond in the ethylene cyanide molecule at the freezing point would be reflected by a change in its effective dipole moment. The evidence practically excludes this possibility. Hence it is fully as probable in the crystal as in the liquid that the rotating ethylene cyanide molecules are characterized by a very considerable internal rotational motion.

The dielectric constant of 4.4 or more which is found immediatey below the transition in ethylene cyanide is in itself an unusually high value for an organic solid. Assuming that at $-40.7°$ the density is no more than 1.15, about 12 percent greater than that at $+45°$,[24] the molar polarization at the former temperature is found to be at least 37 cc. The molar refraction or electronic polarization found by extrapolating the refraction values of Landolt-Bornstein to low frequencies is only 20.0 cc, equivalent to a dielectric constant of 2.22. It is almost impossible to account for the remaining polarization of 17 cc on the basis of a residual molecular rotation below the transition temperature, for this quantity is still quite large at liquid air temperature, where the dielectric constant is at least 3.9. The conductivity at this temperature and 100 kc is so low as to indicate that the natural frequency

---

[24] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Co., 1936), p. 750.

of any remaining rotational polarization is greater than 10^7 c.p.s.; otherwise the dielectric loss always observed when the measuring frequency is within two decades of the natural frequency of rotation would appear. At $-190°$ it is very unlikely that any untransformed fraction of the ethylene cyanide crystal would contain molecules rotating 10^7 c.p.s., when it is remembered that in organic crystals such as cyclohexanol, for example, the natural frequency of rotational motion may be inferred from the anomalous dispersion to be about 10^5 c.p.s. at $-50°C$.[2] Since accepted methods of accounting for this polarization in terms of molecular or electronic motion fail, it is reasonable to conclude that it is associated with the motions of the atomic nuclei within the molecule. It may then be said that the atomic polarization of ethylene cyanide at $-40.7°$ is at least 17 cc, an unusually high value.

Accepting Mizushima's conclusion[7] that ethylene bromide is in a nearly pure *trans* state below the freezing point, the sharp drop of dielectric constant at that point does not exclude the possibility of rotation of the nonpolar form of the molecule in the crystal. It seems likely that the thermal transition at $-24°$ marks the rise of molecular rotation of a nonpolar kind, since the absence of dielectric effects excludes the alternate possibility that rotation of the polar $-CH_2Br$ groups within the molecule sets in at this temperature. The Raman data also show that regardless of the rotational motion of the unit molecule within the crystal, the internal motion of one end with respect to the other is greatly restricted upon solidification. This must be explained in terms of crystal forces. Such a specific effect of these forces in fixing the shape of the molecule would not be expected if it were rotating about three axes, particularly when the *trans* configuration thus fixed is the longest and hence the least favorable, geometrically, for end-over-end rotation. Experimental evidence against the onset of three-dimensional molecular rotation at $-24°$ is furnished by the small value of the heat of transition, which may be roughly estimated from Fig. 4 to be only about one-fourth as large as the heat of fusion. The entropies of transition and fusion must be in substantially the same ratio. Table VII compares the corre-

sponding ratio for a number of organic compounds for which the dielectric or structural evidence supplies definite information as to the number of degrees of rotational freedom above the transition temperature. The magnitude of the ethylene bromide transition favors its classification with those of the paraffin derivatives, which rotate about only one axis. It is therefore believed that if the transition in ethylene bromide at $-24°$ is due to molecular rotation, that rotation must be about only one axis. Obviously, the most likely axis for such a rotation of the *trans* form of this molecule is that of the zigzag $Br-C-C-Br$ chain. Rotation about this long axis is consistent with the sudden restriction of intramolecular motion in favor of the *trans* form at the freezing point, since this form requires a much smaller volume for such a rotation than does the *cis*.

The dielectric constant of solid ethylene bromide is 2.80 at $-2.6°$, a value sufficiently low to indicate that the atomic polarization is not unusually large. Assuming a reasonable minimum of 2.3 for the density at this temperature, the corresponding maximum for the total polarization is 30.6 cc. Extrapolation of the molar refraction as recorded in Landolt-Börnstein yields an electronic polarization of 26.3 cc. Hence the atomic polarization is probably less than 4 cc.

In ethylene chloride the absence of any thermal transition above $-95°$ indicates that there is no significant molecular rotation about any axis in the crystal, except for the rather remote possibility that a transition occurs below $-95°$. The sharp drop of dielectric constant at the freezing point to a relatively low value tends to confirm Mizushima's conclusion that there is little rotational vibration within the molecule in the crystal. However, a small polarization remains even at $-100°$, and disappears with anomalous dispersion below this temperature. The source of this effect is not known. Below $-150°$ the dielectric constant of 2.46 shows at most only a small atomic polarization.

There is then strong evidence that in the ethylene cyanide crystal above $-40°$ a remarkably free molecular rotation is associated with relatively free rotational motion of atomic groups within the molecule, while in the crystalline ethylene chloride the absence of molecular rotation is associated with a corresponding lack of

group rotation. If there is any molecular rotation in the ethylene bromide crystal above $-24°$, it is probably restricted to that about the long axis of the *trans* form of the molecule; here again, the absence of extensive group rotation within the molecule below the freezing point is quite definite. Now such factors as strength of dipole moment and length of the carbon chain would ordinarily be expected to make the ethylene chloride and bromide molecules more likely than ethylene cyanide to rotate end for end in the crystal. It is therefore believed that the greater freedom of internal motion in the latter molecule is the factor which makes possible a molecular rotation which would not otherwise occur below the freezing point. The presumed effect of the internal motion may be described by saying that it increases the time-average symmetry of the molecule, thus reducing the variability of its interaction with its neighbors as a function of the angle of molecular orientation. This reduces the magnitude of the potential energy hump which according to Pauling's theory[25] restrains the rotation of a molecule in the crystal.

In view of the irregular behavior of the atomic polarization of cyanides,[26] the large value of P_A observed below the transition in ethylene cyanide seems most easily accounted for on the assumption that the unusually free rotational vibration

TABLE VII.

	ENTROPY OF TRAN- SITION	ENTROPY OF FUSION	S_T/S_F
Rotation about three axes:			
Methane[a]	0.95	2.47	0.39
Carbon tetrachloride[b]	4.80	2.30	2.09
Cyclohexanol[c]	7.44	1.37	5.43
d-Camphor	7.65^2	3.61^d	2.12
Rotation about one axis:			
n-$C_8H_{17}COOH$[e]	5.0	17.0	0.29
n-$C_{10}H_{21}COOH$[e]	6.4	19.8	0.32
n-$C_{22}H_{46}$[f]	22.0	37.0	0.59
n-$C_{26}H_{54}$[f]	25.9	42.7	0.61
n-$C_{30}H_{62}$[f]	26.2	48.7	0.54
n-$C_{34}H_{70}$[f]	33.7	55.4	0.61

[a] Clusius, Zeits. f. physik. Chemie **B3**, 41 (1929).
[b] Johnston and Long, J. Am. Chem. Soc. **56**, 31 (1934).
[c] Kelley, J. Am. Chem. Soc. **51**, 1400 (1929).
[d] Framdsen, Nat. Bur. Stand. J. Research **7**, 477 (1931). This figure was obtained for dl-camphor, but probably represents d-camphor with sufficient accuracy for the purpose.
[e] Garner and Randall, J. Chem. Soc. **125**, 881 (1924).
[f] Garner, Van Bibber and King, J. Chem. Soc. 1533 (1931).

[25] Pauling, Phys. Rev. **36**, 430 (1930).
[26] Sugden, Trans. Faraday Soc. **30**, 734 (1934).

of the polar $-CH_2CN$ groups within the molecule persists to a certain degree below the transition temperature. The natural frequency of such a polarization should be high and relatively unaffected by temperature. It is not certain that the decline of dielectric constant from 4.4 at $-40.7°$ to 3.9 at $-190°$ is real, because of the possibility of increased void formation. If it is real, the objection might be raised that an atomic polarization should not vary with temperature. However, there is in the classical theory no reason for expecting a polarization due to vibration to be independent of temperature unless the oscillation in question is simple harmonic. Hooke's law is usually assumed to apply only to small displacements in molecular systems. By hypothesis the vibration in question involves unusually large displacements. It is pertinent that there is no indication of a large atomic polarization in the ethylene chloride and bromide, in which molecules there is independent evidence that the torsional vibration is more restricted in both the solid and liquid states.

The proposed explanation of the dielectric properties of these disubstituted ethanes could be checked by a number of experiments. Raman spectra should reveal any internal rotational motion within the ethylene cyanide molecule in the liquid and the two solid phases. Measurement of the variation of dipole moment with temperature should show whether the *cis* or the *trans* configuration is the more stable. The symmetry of the ethylene cyanide crystal should be greater above the transition, with cubic or hexagonal structures most probable.[27] If the ethylene bromide molecule is rotating about one axis above the transition, X-ray measurements should show anisotropic thermal expansion similar to that found in the paraffins.[28]

There is little independent evidence regarding the internal motion of the ethylene diamine and thiocyanate molecules. It is certain from the dielectric data that neither case resembles ethylene cyanide. There is no great amount of atomic polarization at or below $-46°$ in the ethylene diamine, nor does the polar form of the molecule rotate end-over-end below the melting point. Ethylene thiocyanate also shows no evidence of molecular rotation in the crystal. The observed dielectric constant, 3.33 at room temperature, is somewhat high for an organic solid and may indicate that the atomic polarization is large for the same reason as in the ethylene cyanide. The inability of so long a molecule to rotate end-over-end in the crystal is not surprising, even granting a considerable increase in symmetry due to inner rotation about the central $C-C$ bond.

If the proposed explanation of molecular rotation in ethylene cyanide is correct, it would be expected that this rotation should be found in other ethane derivatives. A transition has been found at $71.1°$ in hexachloroethane which we believe marks the rise of molecular rotation in that crystal, although dielectric measurement should yield no information, because the molecule is nonpolar. Parijs[29] found the entropy of this transition, 7.26 E.U., to be greater than the entropy of fusion at the same temperature, 5.84 E.U. Wiebenga[30] found the crystal to change from the triclinic to the cubic form at this temperature. In both cases the behavior is typical of a rotational transition.[31]

---

[27] Vd., e.g., Smyth, Proc. Am. Phil. Soc. **76**, 485 (1936).
[28] A. Müller, Proc. Roy. Soc. **127A**, 417 (1930).

[29] Parijs, Zeits. f. anorg. allgem. Chemie **226**, 425 (1936).
[30] Wiebenga, Zeits. f. anorg. allgem. Chemie **225**, 38 (1935).
[31] While this paper was in press, it was found that the dielectric constant of solid *sym*-tetramethyl ethylene dichloride (m.p. 159–160°) rises from 2.5 at $-80°C$ to 4.5 at $+5°C$, then falls gradually to 4.3 at $+60°C$. This behavior suggests molecular rotation at the higher temperatures.