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Dielectric Absorption in Crystalline Pentachloronitrobenzene

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Dielectric measurements have been performed with pentachloronitrobenzene in polycrystalline state using a trans-former bridge, between 30 Hz and 1 MHz and in the temperature range 20—99°C. The substance shows distinct dielectric absorption in the frequency and temperature ranges, presumably due to molecular rotation in the solid state similar to that of pentachlorotoluene and 1,2,4-trimethyl-3,5,6-trichlorobenzene as has been found by Turney. The frequency factor and the energy of the barrier for the rotation are $\log A = 15.2$ (A in sec^{-1}) and $\Delta H = 16.1$ kcal/mol. A possible mechanism for the rotational transition of the molecule in the crystalline lattice has been discussed. The dipole moment of this substance in benzene solution has been measured, the result being $\mu = 2.33$ Debye.

Despite the fact that both pentachlorotoluene and 1,2,4-trimethyl-3,5,6-trichlorobenzene in crystalline state show anomalous dielectric dispersion at radio frequencies, without undergoing any phase transitions,[1] hexasubstituted benzenes with the nitro group as one of the substituents have been thought to show no molecular rotation in the solid state.[2] Of six hexasubstituted benzenes with one or two nitro groups among the substituents, only 1,2,3,4-tetramethyl-5,6-dinitrobenzene has been referred to by White, Biggs and Morgan[3] as a substance showing molecular rotation in the solid state.

Pentachloronitrobenzene, whose molecular shape and symmetry might be regarded as similar to that of pentachlorotoluene, is a substance left so far uninvestigated in relation to this problem. Thus, with a view that this substance may also exhibit molecular rotation in the crystalline state, a dielectric investigation on pentachloronitrobenzene has been performed. The result seems to confirm our view that the dielectric absorption should be due to rotational movement of the molecule.

In connection with this, the dipole moment of this molecule, too, has been measured in benzene solutions.

Experimental

Material. Commercial product was first recrystallized from ethanol several times and then purified by means of zone-refining. The sample was subjected to dielectric measurements as a disc of 4 cm in diameter

1) A. Turney, *Proc. Instn. Elect. Engrs.*, IIA, **100**, 46 (1953).

2) C. P. Smyth, "Physics and Chemistry of the Organic Solid State," ed. by D. Fox, M. M. Labes and A. Weissberger, Interscience, New York, 1963, p. 723.

3) A. H. White, B. S. Biggs and S. O. Morgan, *J. Amer. Chem. Soc.*, **62**, 16 (1940).

and 1.08 mm in thickness, which was shaped under the pressure of 3 ton/cm^2.

Apparatus. Measurements of dielectric permittivity and loss in the solid phase were performed with a transformer bridge*1 over the frequency range of 30 Hz to 1 MHz and at temperatures 20—99°C. The measuring cell consists of two circular plate electrodes and a guard ring, the diameters of the main electrode being 37 mm. The separation of the two electrodes can be adjusted so as to make close contact with the surface of samples.

The dipole moment of the substance in benzene solution was measured with a heterodyne double-beat permittivity measuring equipment (1 MHz).[4]

Results and Discussion

In view of the possible effect of cold working on dielectric loss factors, the sample was kept at a temperature some degrees below the melting point 151.0°C for several hours prior to the measurement. After repeating runs three times, observed values of ε' and ε'' were found to remain almost invariant.

The plot of ε' and ε'' as a function of frequency at several temperatures are shown in Fig. 1. We see that pentachloronitrobenzene exhibits distinct anomalous dispersions in the frequency and temperature ranges investigated, region of the dispersion making a gradual shift toward the higher frequency range with the rise of temperature.

The absorption curves are somewhat broader than the normal Debye absorption due presumably to the distribution of relaxation times, while the heights of the absorption curves, that is the intensity of maximum absorption, ε''_{max}, show a slight tendency to decrease with the rise of temperatures.

The Cole-Cole plots of ε' versus ε'' (Fig. 2) form arcs, the values of distribution parameters decreasing from $\beta=0.21$ at 20.0°C to 0.05 at 99.1°C. It is obvious that the absorption will become a real Debye type at higher temperatures. The values of static and optical permittivities, ε_0' and ε_∞', have been determined from these diagrams as listed in Table 1.

Table 1. Experimental values of static permittivities (ε_0'), optical permittivities (ε_∞'), maximum loss factors (ε''_{max}), and distribution parameters (β)

Temp. °K	ε_0'	ε_∞'	$(\varepsilon_0'-\varepsilon_\infty')$	$2\varepsilon''_{max}$	β
293.2	4.09	2.58	1.51	1.16	0.21
313.6	4.00	2.55	1.45	1.12	0.15
333.2	3.87	2.52	1.35	1.10	0.14
353.9	3.74	2.49	1.25	1.08	0.08
373.2	3.65	2.46	1.19	1.06	0.05

The dielectric dispersion $(\varepsilon_0'-\varepsilon_\infty')$ which should be equal to $2\,\varepsilon''_{max}$ if the absorption follows the Debye mechanism, increases almost linearly with $1/T$, T being the temperature expressed in °K. A comparison of $(\varepsilon_0'-\varepsilon_\infty')$ with $2\,\varepsilon''_{max}$ (experimental) is also shown in the table. Considering the rather broad feature of these absorptions, $(\varepsilon_0'-\varepsilon_\infty')/2$ should be

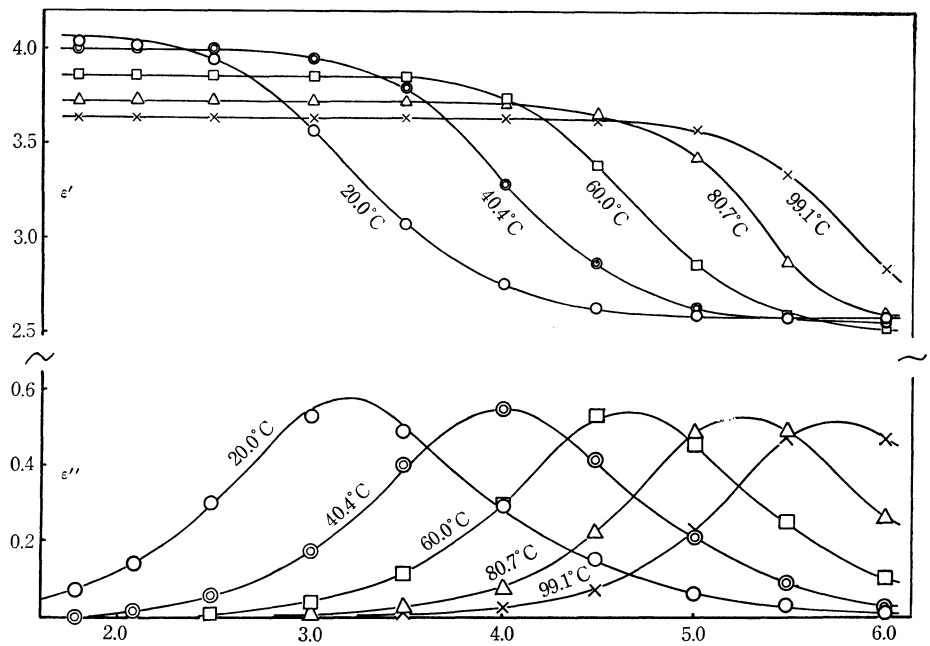

Fig. 1. Dielectric dispersion and absorption of pentachloronitrobenzene crystal.

4) C. Kitazawa and A. Aihara, *Nippon Kagaku Zasshi*, **90**, 365 (1969).

*1 Ando Electric Co. TRS-1B.

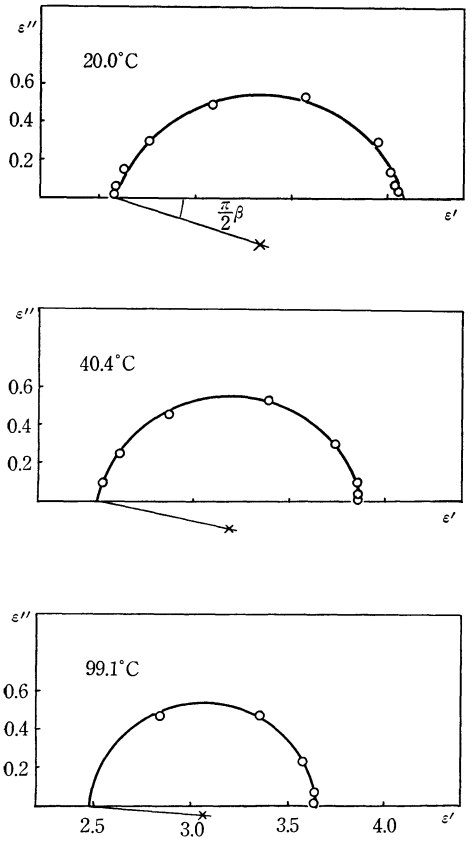

Fig. 2. Cole-Cole arc plots of ε'' versus ε'.

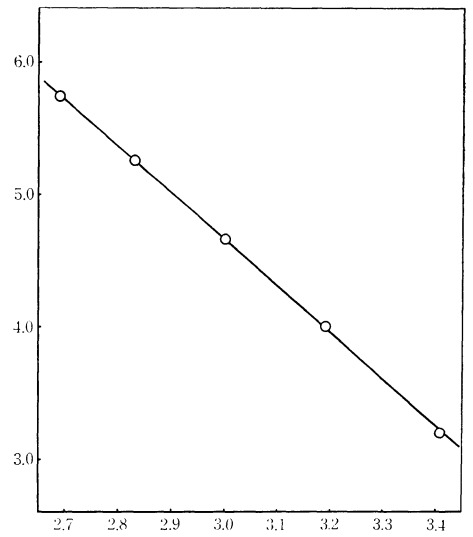

Fig. 3. Relation between $\log f_{max}$ and $1/T$.

TABLE 2. COMPARISON OF FREQUENCY FACTORS, ENERGY BARRIERS, AND OTHER ENERGY DATA

Substances	$\log A$ (A in sec^{-1})	ΔH kcal/mol	ΔS e.u.	$\Delta F^{20°}$ kcal/mol	ΔE_0 kcal/mol
$C_6Cl_5NO_2$	15.2	16.1	12.8	12.4	0
$C_6Cl_5CH_3$[1]	14.1	11.6	9.3	8.9	0
$C_6(CH_3)_3Cl_3$[1]	14.7	10.3	12.3	6.7	0

taken to stand for the intensity of maximum dielectric absorption.

The enthalpy of activation for the molecular rotation in the solid state ΔH as well as the frequency factor A have been calculated with the use of the equation[5,6]

$$f_{max} = A \exp(-\Delta H/\boldsymbol{R}T), \quad (1)$$

where f_{max} means the frequency at which the absorption becomes of maximum value, $\boldsymbol{R}$ is the gas constant and T is the absolute temperature;

$$\Delta H = 16.1 \text{ kcal/mol},$$
$$\log A = 15.2 \ (A \text{ in } sec^{-1}).$$

These values can be compared with those of pentachlorotoluene and 1,2,4-trimethyl-3,5,6-trichlorobenzene obtained by Turney[1] as shown in Table 2.

ΔE_0, the difference of energy in equilibrium positions between which the rotational transitions of the dipole might occur in the crystalline lattice, can be calculated according to the equation[6]

$$\varepsilon_0' - \varepsilon_\infty' = C/T\{1 + \cosh(\Delta E_0/\boldsymbol{R}T)\}, \quad (2)$$

where C is a constant. This expression approximates to

$$\varepsilon_0' - \varepsilon_\infty' = B \exp(-\Delta E_0/\boldsymbol{R}T)/T \quad (3)$$

when $\Delta E_0 \gg \boldsymbol{R}T$, B being a constant. If $\Delta E_0 \fallingdotseq 0$, we get a simple relation

$$\varepsilon_0' - \varepsilon_\infty' = C/2T, \quad (4)$$

that is, the magnitude of dielectric dispersion is inversely proportional to temperature. Conversely, we may safely conclude that the energy difference ΔE_0 must be almost zero when $(\varepsilon_0' - \varepsilon_\infty')$ increases with 1/T, as is the case with pentachloronitrobenzene.

An inspection of Table 2 leads to an interesting conclusion that despite a bulky substituent, $-NO_2$, instead of $-CH_3$, the molecule of pentachloronitrobenzene can perform a rotational transition in the solid state probably about an axis perpendicular to the molecular plane, as has been found with pentachlorotoluene by Turney,[1] but with a larger potential barrier as well as a larger entropy change for rotation. The difference of entropy between the stationary and transitional positions, ΔS, was calculated assuming $f_0/\pi = 10^{12} \ sec^{-1}$ [6] in the following relation between A and ΔS.

5) H. Fröhlich, "Theory of Dielectrics," Oxford Univ. Press, Oxford (1949), Section 11.

6) J. S. Dryden and R. J. Meakins, *Rev. Pure Appl. Chem.*, **7**, 15 (1957); R. J. Meakins, *Progress in Dielectrics*, **3**, 150 (1961).

$$A = f_0/\pi \cdot \exp(\Delta S/R), \quad (5)$$

where f_0 is the frequency of oscillation of the dipole about the equilibrium position. Due to this rather unfavorable assumption, no serious conclusion should be drawn from the larger value of ΔS, 12.8 cal/deg. mol, for pentachloronitrobenz enecompared with that of pentachlorotoluene, 9.3 cal/deg. mol,[1] although the difference suggests the more regular arrangement of molecules in the crystalline lattice in the case of pentachloronitrobenzene.

In relation to the mode of aggregation of molecules in crystalline state, Fröhlich's $B(T)$ function has also been examined.

$$B(T) = 4\pi N_0 \overline{\mathbf{mm}^*}/3k = (\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)T/3\varepsilon_\infty \quad (6)$$

where $\overline{\mathbf{mm}^*}$ is the average value of the product $\mathbf{mm}^*$, $\mathbf{m}$ and $\mathbf{m}^*$ being a dipole moment and a moment polarized by the former, respectively, k is Boltzmann's constant and N_0 is the number of dipoles per unit volume. According to Fröhlich,[7] $B(T)$ should be constant independent of temperature, "if Onsager's equation holds, *i. e.*, if the dipole moment of a molecule can be considered as a constant, and if there are no short-range forces leading to mutual orientation of dipole." Actually the calculated values of $B(T)$ with pentachloronitrobenzene remain almost constant independent of the rise of temperature as shown in Table 3, suggesting that there is no particular preferential interaction between neighboring molecules, such as a pair formation. In Table 3 are also shown the values of dipole moment in the solid state calculated tentatively with the use of Onsager's equation which has been derived for the pure dipolar liquid:[8]

$$\varepsilon_0 - \varepsilon_\infty = 4\pi N_0 \mu^2 \varepsilon_0 (\varepsilon_\infty + 2)^2 / 9kT(2\varepsilon_0 + \varepsilon_\infty) \quad (7)$$

where ε_0, ε_∞, N_0, k and T have the same meanings as in (6), and μ is the dipole moment.

Table 3. Fröhlich's $B(T)$ function and the dipole moment in solid state

Temp. °C	$B(T)\times 10^{-2}$ deg.	μ Debye (solid phase)
20.0	3.88	1.18
40.4	4.01	1.19
60.0	3.98	1.20
80.7	3.94	1.21
99.1	3.95	—[a]

a) The μ value at 99.1°C was not calculated because of the lack of the density value: μ values at other temperatures were calculated using the density values, 1.959 (20.3°C), 1.954 (40.4°C), 1.949 (60.0°C), 1.944 (80.7°C), g/cc, measured with a pycnometer.

The dipole moment values in Table 3 are definitely lower than those in benzene solutions, 2.33 and 2.32 Debyes (28.8°C), obtained by following the usual Halverstadt-Kumler procedure and that of Guggenheim-Smith, respectively.

Experimental details of the measurement of dipole moment in benzene solutions are to be published elsewhere,[9] but some of the data are shown in Table 4.

The fact that the moment values, estimated for a molecule in the solid state, applying Onsager's equation, are far smaller than the actual value of the dipole moment in benzene solutions, offers clear evidence that the equilibrium positions for the dipole to perform rotational transitions in the crystalline lattice should be less than 180° apart instead of being located in completely opposite directions, *i. e.*, 180° separation.

Thus, the molecule of pentachloronitrobenzene in the crystalline state is supposed to perform rotational transitions between several equilibrium posi-

Table 4. Experimental data on the dipole moment measurement in benzene solution (28.8°C)

$W_2\times 10^2$	ε_{12}	d_{12}	n_{12}	H-K	G-S
0.000	2.2650	0.8685	1.4956	P_2=164.1 (cc)	
0.867	2.2832	0.8725	1.4961		
1.213	2.2887	0.8741	1.4963	MR=54.7 (cc)	
2.220	2.3088	0.8789	1.4970		
3.244	2.3300	0.8837	1.4975	P_0=110.4 (cc)	P_0=108.3 (cc)
6.753	2.4068	0.9002	1.4995		
	α=2.10	β=0.47	γ=0.17	μ =2.33D	μ =2.32D

W_2=weight fraction of the solute; ε_{12}=dielectric permittivity of the solution; d_{12}=density of the solution; n_{12}=refractive index of the solution (D line); α, β, γ are the rates of increase of ε_{12}, d_{12} and n_{12} with concentration, respectively; H-K and G-S stand for Halverstadt-Kumler' and Guggenheim-Smith' procedures, respectively; P_2=total polarization of the solute; P_0=orientation polarization of the solute; MR=molar refraction of the solute; μ=dipole moment of the solute. Atomic polarization is assumed to be negligible.

7) H. Fröhlich, *loc. cit.*, pp. 136—138.
8) L. Onsager, *J. Amer. Chem. Soc.*, **58**, 1486 (1936).
9) C. Kitazawa and A. Aihara, *J. Denki-Tsushin Univ.*, **28**, 105 (1970).

tions, equal in energy but separated from each other by potential barriers of different magnitude, which are most likely to become identical at temperatures higher than 100°C leading to a single relaxation time.

No mention has been made so far of the molecular structure of pentachloronitrobenzene. Problems to be solved in this connection are whether the molecule is distorted or not with respect to the C–Cl bonding, on the one hand, and how far twisted the nitro group is about the C–N bond, on the other.

This twisting of the nitro group may be inevitable for reducing the steric repulsion between oxygen and chlorine atoms on both ortho positions to the nitro group,[10] which in turn produces a possibility of the molecule existing as two isomeric conformations, with a nitro group twisted clockwise and with a group twisted anti-clockwise, and consequently, interconversion between the two isomers may happen through a potential barrier separating the two equilibrium orientations of the nitro group. It is probable, therefore, that the nitro group will acquire, on the average, almost axial symmetry around the C–N bond and hindrance against rotation of the molecule as a whole, in the crystalline lattice, will be fairly reduced.

In order to discuss the mechanism of dielectric absorption more precisely, details of molecular as well as crystal structure of this substance are necessary. A three-dimensional X-ray crystal structure analysis with pentachloronitrobenzene is now in progress.

10) J. R. Holden and C. Dickinson, *J. Phys. Chem.*, **73**, 1199 (1969).