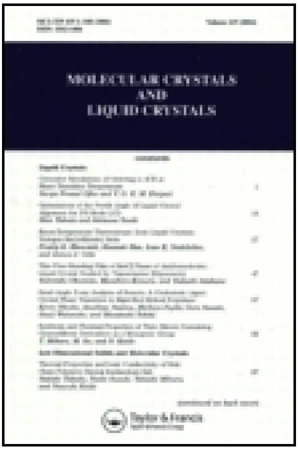

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N. M. R. Investigations of Phase Transitions in Pure and Mixed Crystals of Pentachlorophenol

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N. M. R. Investigations of Phase Transitions in Pure and Mixed Crystals of Pentachlorophenol

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The nuclear magnetic resonance line width, second moment and the relaxation times T_1 and T_{1D} have been measured for protons in a pentachlorophenol (PClPh)-hexachlorobenzene (HClB) mixed crystal (70% in concentration of PClPh), from 120 K to the melting point. The results have been interpreted in terms of the various molecular motions occurring in this crystal. We first observed, as the temperature increased, the fast jump of the proton around the C—O bond, even at low temperature. The activation enthalpy for this motion is 7.5 ± 0.2 KJ mole^{-1} and its correlation time of $\simeq 2.3.10^{-8}$ s at ambient temperature. Before the transition (410 K), a slow motion occurs, molecular self diffusion or tumbling, which exhibits a discontinuity in its correlation time at the transition. The hindering enthalpy for this process is found to be 100 ± 20 KJ mole^{-1} above the transition. The associated correlation frequency is estimated from T_{1D} to be 50 s^{-1} near the melting point.

These results can be extended to other mixed PClPh-HClB crystals, for which we have made T_1 and line-width measurements.

Pure pentachlorophenol presents a different picture with two transitions. Below the first (355 K), the structure is rigid, the molecules being linked by hydrogen bonds, in agreement with the X-ray results of Sakurai. Above it, its behavior is similar to that observed for the mixed crystals, up to the high transition (435 K). Above this temperature up to the melting point, a diffusive phase is evident; the diffusion coefficient being 2 10^{-5} cm^2/s at 460 K.

At low temperatures, the dipolar relaxation time is mainly due to dipolar "second kind" relaxation with chlorine nuclei which are strongly relaxed by quadrupolar interactions.

INTRODUCTION

Two phase transitions in pentachlorophenol (PClPh) have been observed: at 335 and 435 K. The following notation will be used here:

Phase I	The phase below 335 K
Phase II	The phase between 335 and 435 K
Phase III	The phase between 435 K and melting point (464 K).

The phase transition at 335 K has been investigated by numerous methods: dielectric,[1,2] near infrared,[3] electrical conductivity,[4] calorimetric,[4,5] nuclear quadrupole resonance and Raman spectra.[6] The crystal structure of phase I is reported to be monoclinic with characteristic hydrogen bond chains.[7] Structural disorder in phase II was suggested by X-ray measurements.[8] In phase II the crystals possess the symmetry of $P\,2_1/c$ space group, isomorphous with the structure of hexachlorobenzene (HClB). The phase transition in the pentachlorophenol at 435 K was first observed by calorimetric measurements.[4]

In spite of the numerous investigations, the nature and mechanism of the phase transitions in pentachlorophenol have not been explained convincingly.

We suppose, by analogy with other hexasubstituted benzenes, that in the phase II of PClPh the hindered jumps of the molecules around their pseudohaxed axis take place. Further our observations suggest that phase III could be a phase with considerable translational motion (diffusion phase). We decided to check these hypotheses by NMR spectroscopic methods. Both pure PClPh and solid solutions of PClPh with HClB have been investigated because it has been found previously[9] that mixed crystals can exist in the whole range of concentration. It has also been shown previously that these mixed samples can exist below the transition temperature (below 335 K) in the undercooled state[8] of phase II. This fact makes possible the measurements on single crystals.

MATERIALS AND METHODS

The pentachlorophenol and hexachlorobenzene were purified by crystallization from CCl_4, vacuum sublimation and zone-refining; approximately 100 zone passes were made. The mixed single crystals of phase II were grown from the vapor by the method described previously.[10] This method enables us to obtain an homogeneous composition of the mixed crystals.

Proton nuclear magnetic resonance spectra and relaxation times were recorded at 90 MHz using a Bruker SXP-4/100 spectrometer. The spin-lattice relaxation time T_1 was measured by the π, τ, $\pi/2$ pulse method and the relaxation time T_{1D} by the $\pi/2$, t_1, $\pi/4$, τ, $\pi/4$ pulse method.[11] The second moment of the NMR line was obtained by Fourier transform of the F.I.D. following a single $\pi/2$ pulse. (Nicolet BNC 12 computer and fast Bruker sampler BC104). Measurements were made over the temperature range from 120 K to the melting point, unless T_1 was too long (larger than $\simeq$ 200 s). Temperature was maintained constant to better than 0.5 K (Bruker cryostat and regulator).

EXPERIMENTAL RESULTS AND DISCUSSION

Pentachlorophenol-Hexachlorobenzene mixed crystals

As mentioned above, the addition of HClB to PClPh extends the region of existence of the samples in the undercooled phase II. Owing to this fact, the measurements of n.m.r. parameters for phase II can be made down to temperatures far below the phase transition. Figures 1 and 2 show the M_2, T_1, T_2, T_{1D} experimental curves for the sample containing 70% of PClPh. T_2 and M_2

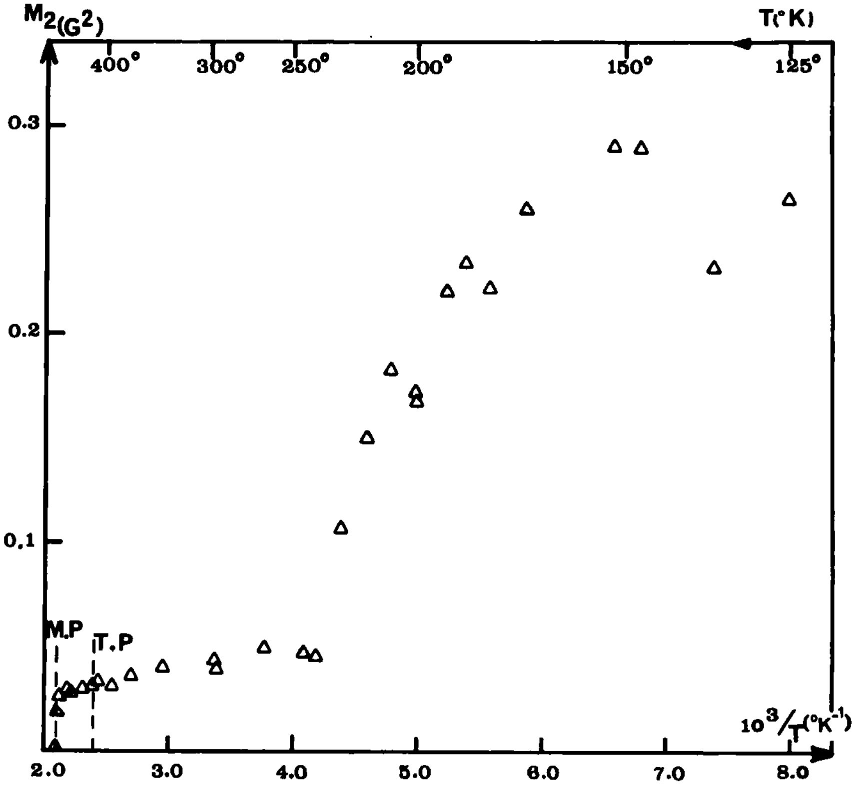

FIGURE 1 The proton resonance second moment for a mixed powder crystal PClPh 70% — HClB 30% as a function of temperature. (M.P.: melting point; T.P.: transition point, as observed in T_{1D} results).

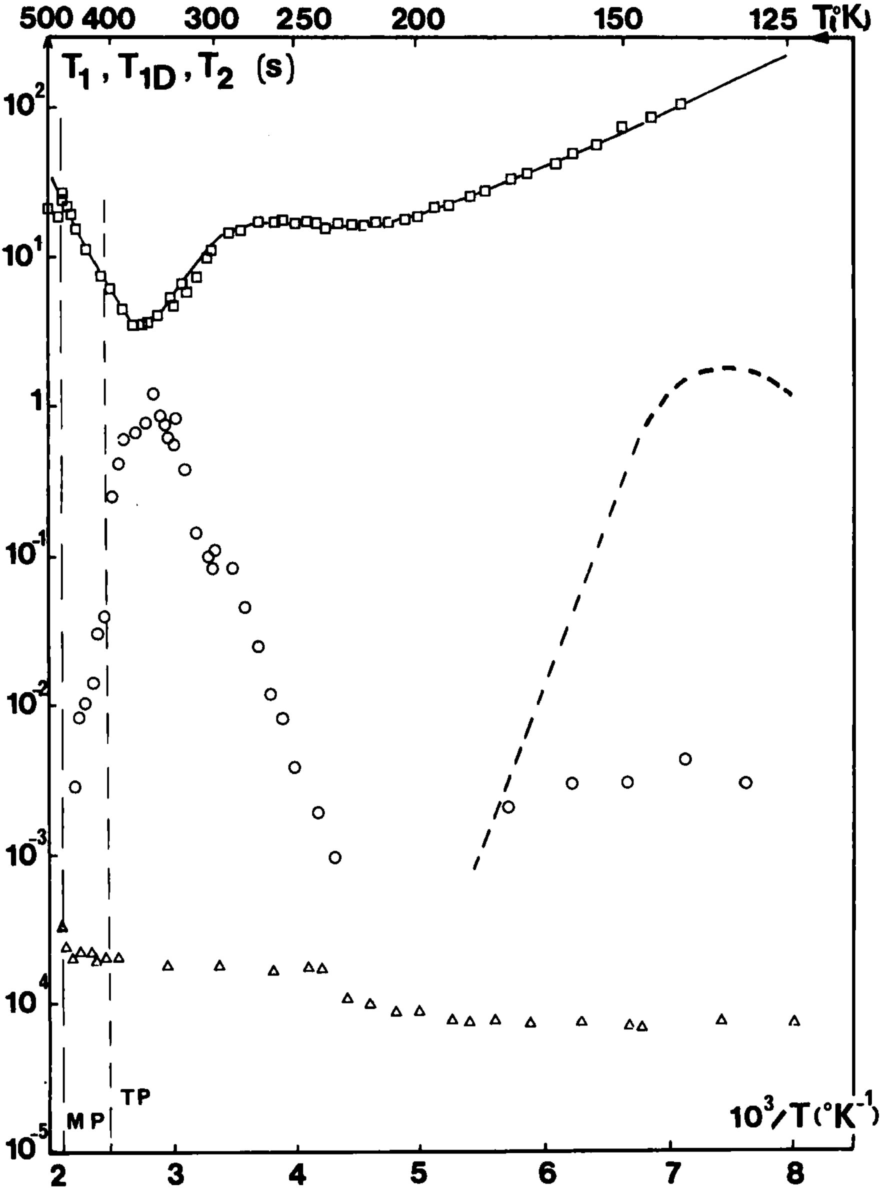

FIGURE 2 T_2, T_1 and T_{1D} temperature dependence for protons in a mixed powder crystal PClPh 70% — HClB 30%. Measured values at 90 MHz: Δ, T_2; □, T_1; O, T_{1D}. The solid line is drawn, using the BPP theory, fitted to the high temperature T_1 minimum and the low temperature T_1 behavior. The broken line is derived for T_{1D} with the same theoretical model.

values were deduced from the half height line width of the resonance line, $\Delta\upsilon$, by the following expressions, valid for gaussian lines:†

$$\gamma\sqrt{M_2} = 1/T_2 = 2\pi\Delta\upsilon/\sqrt{8\ \ln\ 2}^{12} \tag{1}$$

(γ: gyromagnetic ratio of the proton: 2.675 10^4 rd s^{-1} G^{-1})

They were corrected for inhomogeneity of the zeeman field[13] which contributes significantly to the line width, particularly above 250 K. ($T_2^* \simeq 1$ ms for a diamagnetic liquid sample of the same volume.)

At the lowest temperatures attained (120 K), M_2 shows a plateau of value $\simeq$ 0.25 G (Figure 1). Between 160 K and 250 K, the second moment decreases to $\simeq$ 0.04 G^2, and above 250 K, remains almost unchanged up to the melting point (472 K); the small and continuous decrease in this last temperature range is probably due to lattice expansion, the intermolecular contribution to the second moment being the greater part. No special feature is apparent at the transition point. (410 K in this mixed crystal, as we shall see below, rather than 435 K for pure PClPh.)

The second moment for this mixed crystal (70% PClPh) has been calculated, using Van Vleck's formula,[14] taking into account the proton-proton intermolecular interactions and the proton-chlorine (^{35}Cl and ^{37}Cl, with their relative isotopic abundance) intra- and intermolecular interactions. The crystal structure is isomorphous with that of HClB and lattice parameters are taken from references.[8,15] The calculations have been carried out over 17 unit cells for the following cases of motion:

rigid case: the molecule is not reorientating and the proton is located at 1 Å from the oxygen, in the plane of the molecule, with the C—O—H angle equal to 120°.‡

jumping *H*: the molecule stays fixed but the proton jumps from one to the second equivalent site, around the C—O axis, so rapidly that the apparent position of *H* is along C—O axis, 0.5 Å from the oxygen (Figure 8a).

rotating case: the molecule reorients around its pseudo-hexad axis, perpendicular to its plane, and the proton jumps faster.

In the first and second cases, we calculated the statistical mean value of the second moment over the six possible sites of the proton in each molecule. We

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† We have verified that the value of the second moment obtained by this relation does not differ from the value deduced from the lineshape by more than ±5%, which represents approximately the error limit in these n.m.r. measurements.

‡ This case does not correspond to the rigid phase I but rather to a hypothetical phase similar in its structure to phase II, where molecules and protons would be fixed.

TABLE I

Calculated and experimental second moments

State of molecular motion		Rigid	Jumping H	Rotating molecule
M_2 calculated in G^2	$x = 0.7$	0.386	0.292	0.042
	$x = 1$	0.507	0.390	0.054
M_2 experimental	$x = 0.7$		$\simeq 0.25$	$\simeq 0.04$
Temperature range			$120 < T < 160$K	$250 < T < 472$K

took account of the relative abundance of PClPh, x, using the expression below:[12]

$$M_2 = M_2|_{\text{intra}} + x\, M_2|_{\text{inter } H\text{-}H} + |(6 - x)/5)|\, M_2|_{\text{inter } H\text{-Cl}} \tag{2}$$

(where intra stands for intramolecular and inter H—H for intermolecular contribution due to interactions between two protons; inter H—Cl for intermolecular contributions due to interactions between protons and chlorine spins).

The calculated values of the proton absorption line second moments for $x = 1$ (pure PClPh) and $x = 0.7$ are compared with experimental results in Table I. We note good agreement between calculated and experimental values. Thus, the decrease of the second moment around 200 K corresponds to the onset of the in plane molecular reorientation around the pseudo-hexad axis and, therefore, phase II is a rotator phase. This conclusion is in general agreement with the behavior found in hexasubstituted benzenes.[16–20]

The T_1 curve exhibits two minima (Figure 2). At low temperature, ($T \simeq 230$ K), the minimum value is $\simeq 16.0$ s; at high temperature ($T \simeq 365$ K), T_1 minimum is $\simeq 3.5$ s. Two kinds of motion are indicated. The high temperature minimum is approximately the same value as observed in pure PClPh (2.8 s) and occurs at almost the same temperature (360 K). More generally, the T_1 behavior in the high temperature range is very similar for pure pentachlorophenol and the mixed crystals. This is not surprising, the crystalline phase II should be a similar rotator phase in both cases.

The B.P.P. theory[21] modified by Kubo and Tomita[22] yields:

$$T_1^{-1} = \frac{2}{3}\gamma^2 M_{2\,\text{mod}}\,(\tau_c/1 + \omega_0^2\tau_c^2 + 4\tau_c/1 + 4\omega_0^2\tau_c^2) \tag{3}$$

where $\omega_0 = \gamma H_0$, the resonance angular velocity. In Eq. 3, $M_{2\,\text{mod}}$ is the part of the second moment modulated by the motion considered and includes both inter- and intramolecular contribution.[23]

Using $\omega_0\tau_c = 0.62$ at the minimum, we obtain the following values of $M_{2\,\text{mod}}$ for the two motions:

$M_{2\ \mathrm{mod}} \simeq 0.24\ \mathrm{G}^2$, for the motion responsible for T_1 behavior above 300 K.
$M_{2\ \mathrm{mod}} \simeq 0.053\ \mathrm{G}^2$, for the motion effective at low temperature.

These values can be compared with theoretical values deduced from Table I ($0.250\ \mathrm{G}^2$; $0.094\ \mathrm{G}^2$ respectively). The agreement is fairly good, since the application of Eq. 3 to this system is an approximation and also the exact location of the H atom in the molecule is uncertain.

The minimum in the high temperature range is then associated with the reorientational motion of the whole molecule around the hexad axis, according to the second moment experimental results. The minimum at 230 K corresponds to the jumping H motion. The asymmetry of the T_1 curve around the high temperature minimum is due of course to the fact that the two motions are contributing to the spin lattice relaxation. We have tried to fit the T_1 experimental curve by a simple model using two correlation times: τ_{CR} and τ_{Cj}; τ_{CR}, the mean time between two successive reorientational jumps of the molecule; τ_{Cj}, the mean time between two jumps of the proton around the C—O axis. We have

$$T_1^{-1} = T_{1R}^{-1} + T_{1j}^{-1} \tag{4}$$

$$T^{-1}_{1_{R,j}} = C_{R,j}\,(\tau_{CR,j}/1 + \omega_0^2\tau^2_{C_{R,j}} + 4\tau_{CR,j}/1 + 4\omega_0^2\tau^2_{C_{R,j}}) \tag{5}$$

$$\tau_{C_{R,j}} = A_{R,j}\exp\,(E_{R,j}/RT) \tag{6}$$

The fit obtained for T_1 (solid line in Figure 2) with the values of the six parameters given below is excellent over the whole temperature range studied, confirming the above description of the motions.

$$C_j = \frac{2}{3}\gamma^2 M_{2j\ \mathrm{mod}} = 2.34\ 10^7;\ (M_{2j\ \mathrm{mod}} = 0.05\ \mathrm{G}^2)$$

$$C_R = \frac{2}{3}\gamma^2 M_{2R\ \mathrm{mod}} = 1.0\ 10^8;\ (M_{2R\ \mathrm{mod}} = 0.21\ \mathrm{G}^2,$$

experimental value, deduced from M_2 measurements).

$E_j = 7.50$ KJ/mole is the activation energy for the jumping motion, estimated from the linear part of the T_1 curve in the low temperature region. $E_R = 41.8$ KJ/mole is the activation energy for the rotational motion, measured from the slope of the T_{1D} curve in the region where T_{1D} increases with temperature (for this temperature range, the contribution of the proton jumping motion to T_{1D} relaxation is negligible ($\tau_{Cj} < \omega_0^{-1}$), so that T_{1D} is only sensitive to rotation). $A_j = 2.5\ 10^{-11}$ s; this choice is made to fit the T_1 value at $T^{-1} = 7\ 10^{-3}\ \mathrm{K}^{-1}$. $A_R = 1.15\ 10^{-15}$ s; the value obtained to fit the T_1 minimum at high temperature ($T^{-1} = 2.75\ 10^{-3}\ \mathrm{K}^{-1}$).

No discontinuity is observed in T_1 at the transition point (410 K); no discontinuous change in correlation time or activation energy is apparent for the reorientational motion here.

We have deduced, from this fit, the values of τ_{Cj} and τ_{CR} and their variation with temperature (Figure 3):

$$\tau_{Cj_{(\blacksquare)}} = 2.5\ 10^{-11} \exp (7.5\ 10^3/RT) \tag{7}$$

$$\tau_{CR_{(\blacksquare)}} = 1.15\ 10^{-15} \exp (41.8\ 10^3/RT) \tag{8}$$

Figure 3 shows that τ_{CR} and τ_{Cj} become approximately equal at the transition point.

T_{1D} exhibits two very different types of behavior, depending on the temperature (Figure 2). In the high temperature range, above about 230 K, T_{1D} is governed by dipolar interactions between protons and chlorine modulated by the relative motions of these nuclei, as the T_1. As the temperature is raised, T_{1D} first increases by three orders of magnitude, becoming almost equal to T_1 near its minimum. The temperature dependence in this region permits an estimate of the activation enthalpy for the motion responsible, in-plane rotational motion of the whole molecule. The value obtained, 41.8 ± 2 KJ mole^{-1}, lies in the range observed for hexasubstituted chloromethylbenzenes[18] for in-plane reorientation. At higher temperatures T_{1D} decreases, undergoes a marked discontinuity at 410 K, which seems to be the transition point (previously observed near 425 K[9]) and above this temperature decreases sharply. This decrease near the transition we attribute to a new molecular motion, which is still not fast enough at the melting point to reduce the second moment and T_1. Above the transition temperature, the barrier hindering this motion, estimated from the T_{1D} results, has a value of 100 ± 20 KJ/mole. This motion is probably similar to that occurring in other hexasubstituted benzenes,[17,18,24] where it has been suggested that an out-of-plane molecular tumbling or molecular self-diffusion takes place in a high temperature crystalline phase. However, the observed activation enthalpy is three to four times higher than in these last compounds, and lies in a range more typical of molecular self-diffusion. A test for self-diffusion using the technique of nmr spin echo measurement in the presence of a large magnetic field gradient is useless, at the T_2 value is too small (0.22 ms) and the diffusion constant should be low, less than 10^{-10} cm^2 s^{-1} even at the melting point. An investigation of the dielectric properties in this high temperature range and an nmr study on a monocrystal would help to determine the character of this motion.

From the above T_{1D} behavior we have deduced the correlation times of the two motions which contribute to T_{1D}, τ_{CR}, the rotational motion and τ_{Csl} the slow motion. Their temperature dependence is plotted on Figure 3.

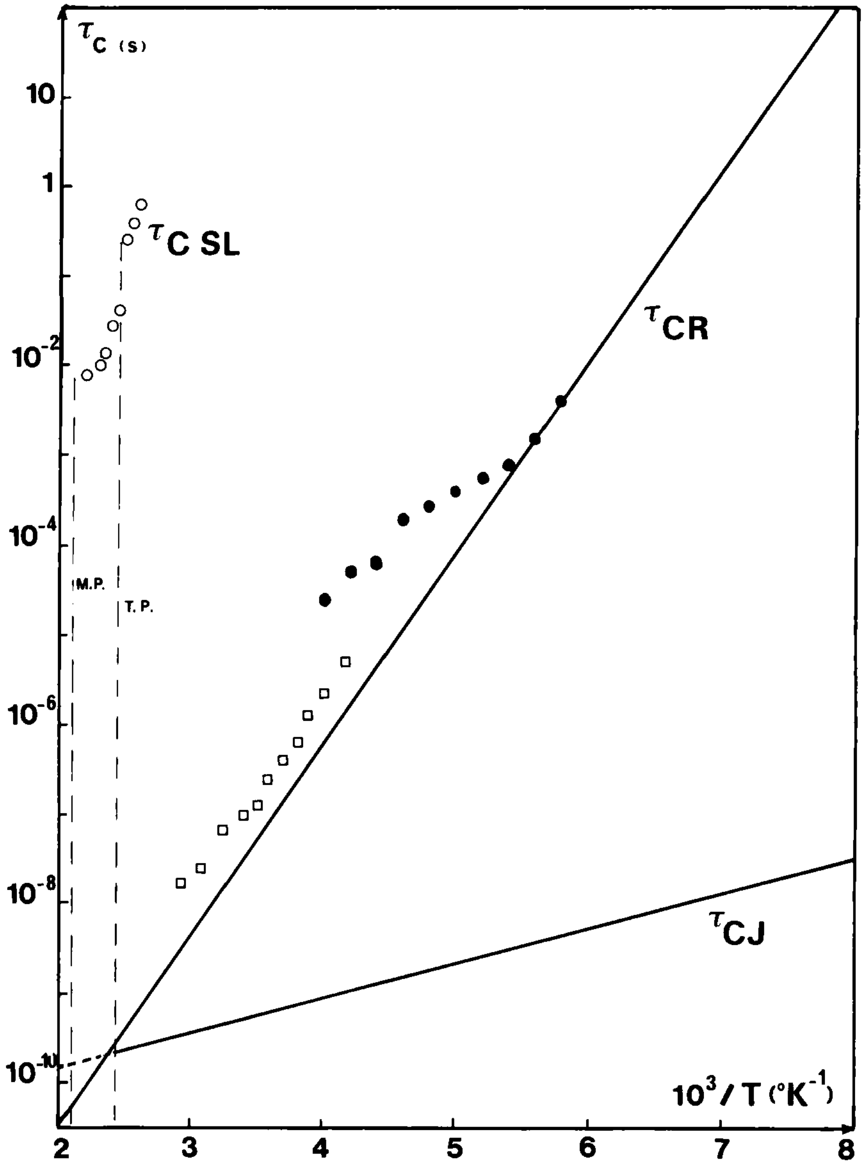

FIGURE 3 The temperature dependence of the various correlation times for the motions occurring in the mixed powder crystal PClPh 70% — HClB 30%; τ_{CJ}, for the proton jumping; τ_{CR}, for in plane molecular reorientation; τ_{Csl} for the slow motion (tumbling or diffusing). Measured values: □ (τ_{CR}), ○ (τ_{Csl}), from T_{1D} results; ●, from line width values. The solid lines are derived from T_1 results using the BPP model.

We have used the following simplified relations:[25]

$$\tau_{CR} = \frac{1}{C_R} T_{1D}^{-1} = 10^{-8}\, T_{1D}^{-1} \text{ for } 3\ 10^{-3} < T^{-1} < 4.4\ 10^{-3}\ \mathrm{K}^{-1} \tag{9}$$

$$\tau_{Csl} = [(M_{2\ \mathrm{mod}})_{sl}/(M_{2R})] \cdot T_{1D} \text{ for } T^{-1} < 2.5\ 10^{-3}\ \mathrm{K}^{-1} \tag{10}$$

where $(M_{2\ \mathrm{mod}})_{sl}$ is that part of the second moment modulated by the slow motion; (M_{2R}) is the value of the second moment before the onset of this motion ($M_{2R} = 0.04$. The ratio $(M_{2\ \mathrm{mod}})_{sl}/(M_{2R})$ has a maximum value equal to unity and then τ_{Csl} is given by the relation:

$$\tau_{Csl} = T_{1D} \tag{11}$$

This possibility overestimates τ_{Csl} but is the relation used for Figure 3.

We have also put on Figure 3 the τ_{CR} values obtained from line narrowing[21,22] using the relation

$$\tau_{CR} = 8 \ln 2/\gamma\Delta H \left| \tan\left(\frac{\pi}{2} (\Delta H^2 - B^2)/(C^2 - B^2) \right) \right| \tag{12}$$

where ΔH is the line width in the transition region, expressed in Gauss, C the line width before and B after the narrowing.

We observe some discrepancies between τ_{CR} values obtained from T_1, T_{1D} and ΔH measurements. Differences from T_1 and T_{1D} data are probably due to the assumed exponential correlation function and the powder average. ΔH data often give rather poor agreement with T_1; the theory is only approximate. Without a very detailed model for the motion, it is probably the best agreement to be expected.

At low temperatures (below 180 K), T_{1D} departs from the behavior predicted by the above model (broken line in Figure 2). T_{1D} values should be given by the simplified relation[25]

$$T_{1D}^{-1} = C_j\, \tau_{Cj} + 3/2 \cdot C_R/\gamma^2 M_{2R} \cdot 1/\tau_{CR} \tag{13}$$

with

$$\gamma\sqrt{M_{2R}} = 1/T_2 \tag{14}$$

where we have taken the low temperature value for T_2 of $8\ 10^{-5}$ s.

Measured values of T_{1D} are low and exhibit a weak temperature dependence. Therefore, in this temperature region, a more efficient relaxation mechanism exists. This we attribute to dipolar cross-relaxation with chlorine nuclei, themselves rapidly relaxed by quadrupolar interaction. This dipolar "second kind" relaxation was first invoked by Norris *et al.*[26] to explain T_1 and $T_{1\rho}$ measurements in the low temperature phases of HBr and HCl crystals.

To confirm the existence of this contribution to proton relaxation, we have made a study of T_1 (^1H) versus the proton resonance frequency ν_0 between 6.4 and 90 MHz, for different temperatures. We obtained, as expected, considerable enhancement of the relaxation rate when the proton resonance frequency matched the chlorine quadrupolar frequency, which lies near 35 MHz.[27] Figure 4 presents the results at room temperature and compares them with the calculated T_1 values deduced using the above model and ignoring "second kind" relaxation. Outside the range 20–60 MHz, the agreement is quite good: the dependence on ν_0^{-2} is the same (linear below 15 MHz; experimental values are lower at low frequency, when the condition $\omega_0 \tau_{CR} \gg 1$ is no longer fulfilled); the difference between the calculated and experimental values amounts to approximately 30% which is reasonable considering the simplicity of the model. The frequency independent term (extrapolation of the curve to the T_1^{-1} axis) has an experimental value of 0.060 s^{-1} and is exactly equal to the calculated value given by 5 $C_j\ \tau_{Cj}$ (Eqs. 4 and 5).

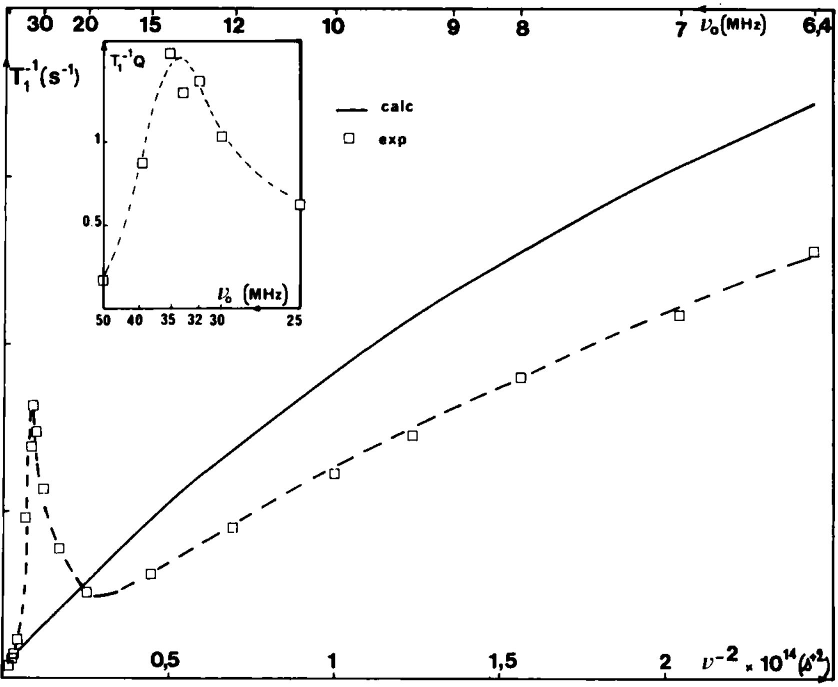

FIGURE 4 The frequency dependence of the proton spin-lattice relaxation rate in the mixed powder crystal PClPh 70% — HClB 30%. □, experimental value. The line shows the calculated dependence derived from the theoretical model. The insert gives the spin-lattice relaxation rate increase, from quadrupolar chlorine origin, T_1^{-1} (Q), around 35 MHz.

The results at low temperatures (230 and 160 K) are very similar. The agreement between the theoretical and experimental frequency dependence is satisfied by Eqs. 4 to 6 except in the medium frequency range, near 35 MHz, where we observe an enhanced relaxation rate. This effect is greater at 230 K than at 160 K. On the other hand, at high temperature (360 K), the experimental T_1 frequency behavior follows the theoretical one in the whole frequency range, no peak of relaxation rate being present. All these features clearly show that chlorine nuclei contribute strongly to proton spin-lattice relaxation at room temperature and below, when the proton Larmor frequency is close to the chlorine quadrupolar resonance frequency. However, outside the range 20–60 MHz, this chlorine contribution becomes negligible, the factor $(\omega_0 - \omega_Q^{\mathrm{Cl}})^2 (T_{2Q}^{\mathrm{Cl}})^2$ being too large. At high temperature, the molecular motion is fast enough to average the quadrupolar interaction as observed by quadrupolar resonance on pure PClPh.[6] These results confirm that T_1, at ninety megahertz, is controlled by dipolar interaction modulated by the molecular motions described above.

Above 230 K, T_{1D} depends only on dipolar relaxation of the first kind. Below 180 K, the contribution from chlorine relaxation is dominant. In this temperature region, if (^1H) T_{1D} is proportional to (Cl) T_1, the weak temperature dependence of T_{1D} suggests that chlorine relaxation is due to lattice vibrations.[28]

The study of other mixed crystals (90%, 80%, 60%, 40% concentration of PClPh) shows similar features. The values and behavior of T_1 and T_2 (we have not measured T_{1D}) show that three different motions occur in these crystals: jumping of the protons, reorientation of the whole molecules and tumbling or

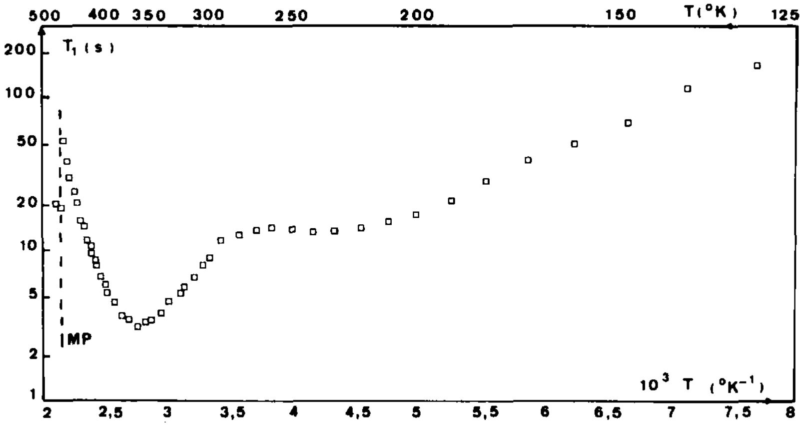

FIGURE 5 The T_1 temperature dependence for a mixed powder crystal PClPh 90% — HClB 20%.

diffusing of the molecules. Each appears successively as the temperature increases. For example, Figure 5 gives the T_1 temperature dependence in a 90% PClPh mixed crystalline powder sample.

Figure 6 shows the dependence of the line width $\Delta\nu_{1/2}$ on the amount of PClPh at 160 K. Experimental data and values calculated from the second moment (using Eqs. 1 and 2) are in close agreement, indicating that the samples were homogeneous.

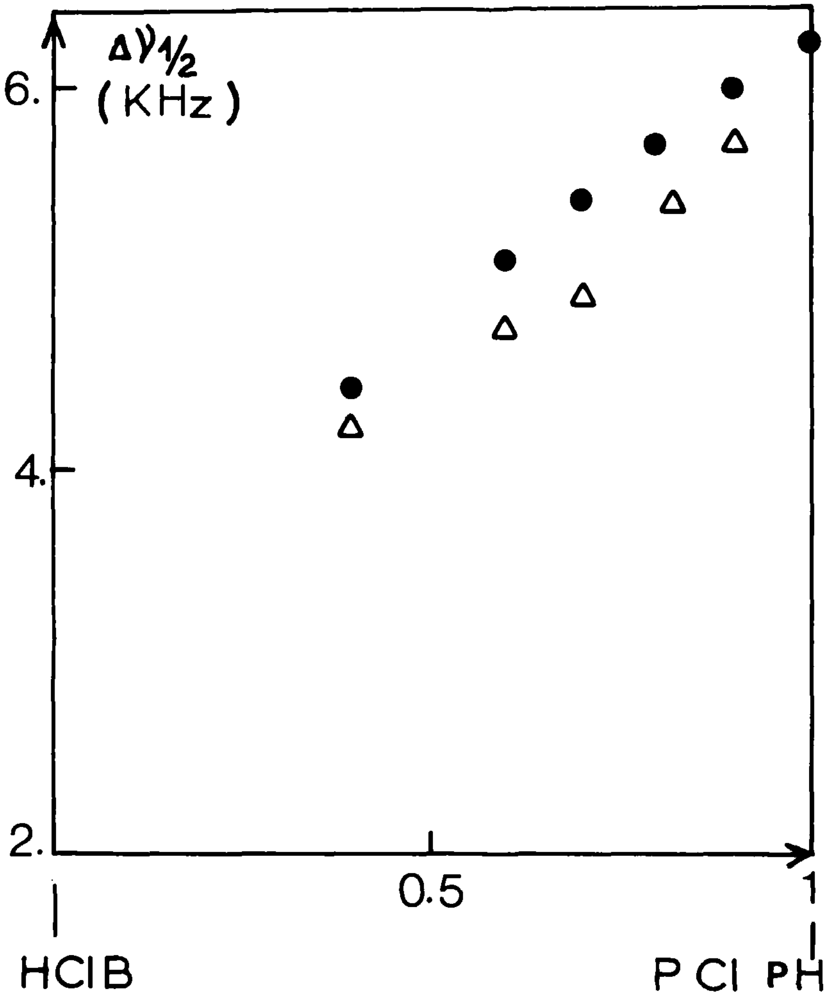

FIGURE 6 The half line width of resonance spectrum versus the amount of pentachlorophenol (PClPh), in mixed powder crystals with hexachlorobenzene (HClB) at 160 K; Δ, exp. value; ●, calc. value.

Measurements have also been made on a single crystal (90% PClPh) at room temperature (Figure 7). The variation of the experimental second moment with the orientation of the crystal in the Zeeman field follows the curve calculated assuming rapidly rotating molecules, thus confirming the existence of this motion at ambient temperature.

Pure pentachlorophenol

At room temperature, phase I, the resonance spectrum of a polycrystalline sample of pure pentachlorophenol was measured. This was obtained by accumulation of repeated free induction decay signals for twenty hours, owing to a very long T_1. The half height width $\Delta\nu$ was found to be 18 kilohertz. Using Eq. 1 we obtained a second moment, M_2, of 3.2 G^2.

The second moment of the resonance spectrum was calculated for an infinite line of protons arranged as shown in Figure 8b. Using Van Vleck's[14] expression:

$$M_2 = \frac{6}{5}\gamma^2 \hbar^2 I(I+1) N^{-1} \sum_{j>k} r_{jk}^{-6} \qquad (15)$$

where N is the number of protons in the line (N tends to infinity), r_{jk} is the distance between protons *h* and *k*, defined by Sakurai's crystal structure data,[7]

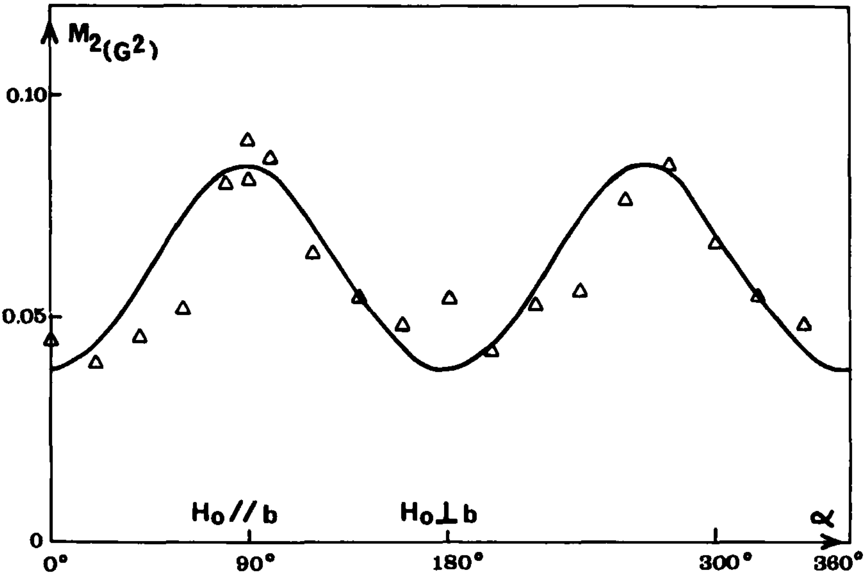

FIGURE 7 The proton resonance second moment for a mixed monocrystal PClPh 90% — HClB 10% as a function of the Zeeman field orientation, at room temperature. Δ, experimental value. The line is calculated second moment.

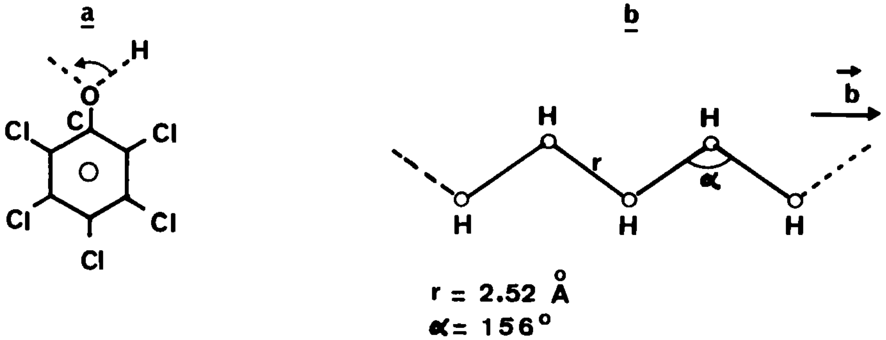

FIGURE 8 a: jump of the proton around C—O axis of the pentachlorophenol molecule; b: array of protons arranged along a broken line from Sakurai crystalline data[7] of pentachlorophenol rigid phase. The angle between the crystal axis **b** and the interprotons vectors equals 12°.

(the distance between O and H in the PClPh molecule being equal to 1 Å); $\hbar = h/2\pi$; h is Planck's constant and I is the spin quantum number; $I = \frac{1}{2}$ for the proton.

The calculated second moment value is 2.80 G^2, which is close to the experimental one. This result together with the very high T_1 value (greater than 1000 at 90 M) indicates a rigid structure of PClPh molecules in phase I, due to the existence of hydrogen bonds between the molecules laying in the same stack.

Above the lower transition temperature T.P.I at 335 K, the T_1, T_{1D} and T_2 temperature dependence has been measured and is plotted on Figure 9. Spin-lattice relaxation time data show a minimum value of 2.8 s, around 360 K. Between T.P.I and the higher transition temperature, T.P.II (which occurs at 435 K, rather than 430 K, as previously reported[9]) the T_1 and T_{1D} temperature dependence is very similar to that observed with mixed crystals and may be similarly explained by the simultaneous existence of the three motions: jumping of the proton around the C—O axis, in-plane molecular reorientation and the onset of a slow motion, diffusion or tumbling of the molecules. Above 435 K, pure pentachlorophenol crystals exhibit a more unusual behavior. The resonance line becomes very narrow, its width being just controlled by the Zeeman field inhomogeneity. The dipolar interactions are thus completely averaged and the apparent second moment approaches zero. This indicates rapid translational self-diffusion of the resonant nuclei. T_1 decreases sharply with temperature, following a barely perceptible discontinuity at the transition. It then seems to approach a minimum value ($\simeq$ 14.0 s) at the melting point 464 K, suggesting that the diffusion correlation time τ_d reduces to 10^{-9} s in this phase.

The spin-spin relaxation time T_2 is constant in phase II, at about 160 μs. This value is derived from the line width corrected for field inhomogeneity

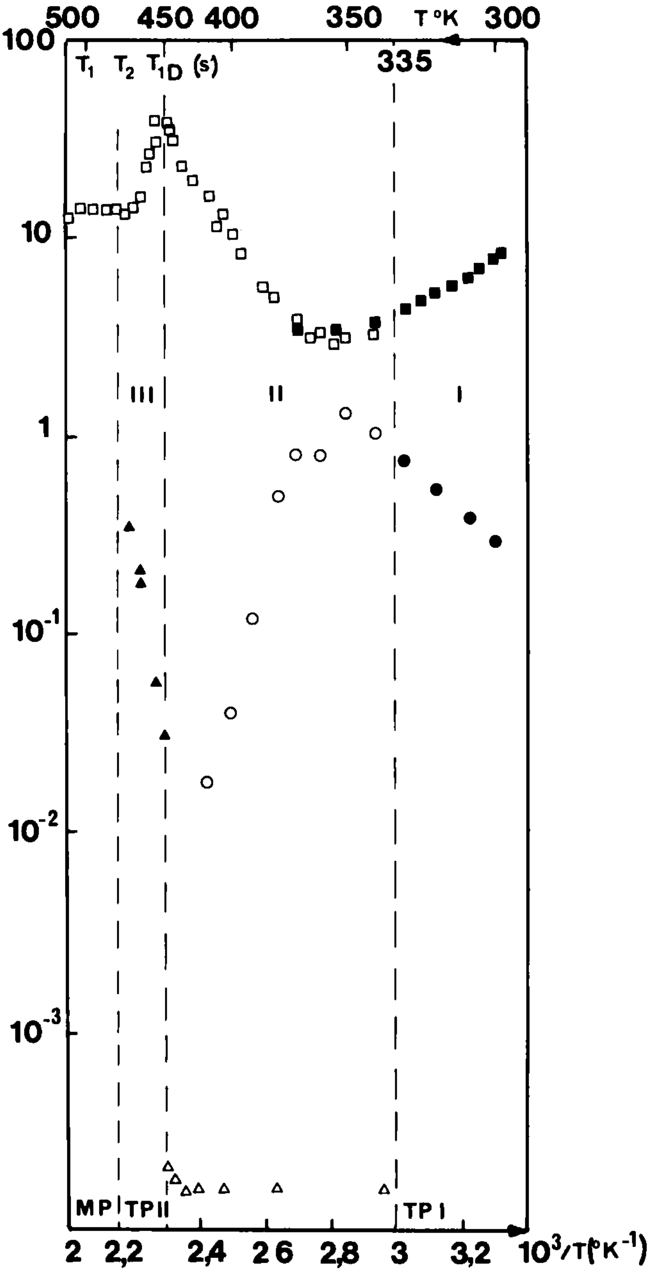

FIGURE 9 T_2, T_1 and T_{1D} temperature dependence for pure PClPh above room temperature. Measured values at 90 MHz: □, T_1; ○, T_{1D}; △, T_2 (from line width); ▲, T_2 (from Hahn echo[13]); ■, decreasing temperature experimental T_1 points; ●, decreasing temperature T_{1D} points. On Figures 2, 3, 5 and 9, TP means transition point; MP means melting point.

using Eq. 1. The second moment value in this phase, obtained from the same relation is $M_2 \simeq 0.055\ G^2$, almost equal to the theoretical one calculated in pure pentachlorophenol for the rotating molecule (Table I).† Just before the transition temperature at 435 K, T_2 begins to increase, the dipolar interactions being slightly reduced by the slow motion. Above 435 K T_2 is very much greater, indicating an abrupt increase of the diffusion correlation frequency. In this temperature region T_2 is obtained by the spin echo sequence ($90° - \tau - 180°$). The plot of the echo amplitude $M(2\tau)$, on a logarithmic scale, versus the echo spacing 2τ allows us to measure the actual value of T_2 and also the diffusion coefficient constant D, from the relation:[13]

$$M(2\tau) = \mathrm{M}_0 \exp \left| -\frac{2\tau}{T_2} - \frac{2}{3}\gamma^2 G^2 D \tau^3 \right| \tag{16}$$

where M_0 is the equilibrium magnetization and G the field gradient over the sample. We can only obtain an estimate of the D value because the field gradient is not linear nor is precisely known; the diffusion constant is approximately $2 \pm 1\ 10^{-5}$ cm^2/s at 460 K, in the diffusive phase and increases to $\simeq 4 \pm 2\ 10^{-5}$ cm^2/s at 470 K, in the liquid state.

From the T_{1D} results below the 435 K transition, we can deduce the activation energy hindering the slow motion: 124 ± 12 KJ mole^{-1}, in phase II. The corresponding correlation time τ_d was obtained by putting $\tau_d = T_{1D}$, as in Eq. 11, giving $\tau_d \simeq 10^{-3}$ s at the high transition temperature. In phase III, the T_1 and T_2 measurements are not precise enough to give a reliable value for the barrier for diffusion; however, it remains at a high value (~ 100 KJ mole^{-1}), while τ_d ranges from 10^{-7} to 10^{-9} s.

Below the temperature of T.P.I, measurements of the supercooled phase II were possible (filled points in Figure 9). However, the sample converted to the thermodynamically stable phase I after holding at room temperature for several hours and the T_1 relaxation time then became very long. From the T_{1D} results, we can infer an hindering energy of 28.7 ± 2 KJ mole^{-1} for the molecular reorientational motion, which is lower than that observed in the mixed crystals.

The following conclusions covering the nature of the molecular motion in pure pentachlorophenol can be drawn from this study. In phase I (rigid) the molecules are linked by hydrogen bonds. At $T = 335$ K a breaking of hydrogen bond chains occurs and a transition to phase II (rotational) appears. In phase II hindered reorientation of the molecules around their pseudohexad axis is evident with jumps of the proton around the C—O bond. The onset of

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† Note that if we take this value of the second moment modulated by the diffusive motion for the determination of the T_1 minimum, we obtain, using Eq. 3, a minimum T_1 value of 15 s, very close to the experimental one obtained at the melting point.

another slower reorientational motion or possibly the start of the diffusion motion apparent in phase III is detected. This remains slow ($\tau_d < 10^{-3}$ at 435 K). At $T = 435$ K there is a sudden increase of the diffusive correlation frequency. In phase III (diffusive phase) the diffusive correlation time approaches 10^{-9} s and the diffusion constant becomes 2 10^{-5} cm^2/s near melting point. The nature of this motion is a subject of further investigation.

For pentachlorophenol-hexachlorobenzene mixed crystals, the picture is appreciably different. The rigid and the diffusive phases do not appear. The slow motion observed, possibly diffusive, remains too slow for a thorough investigation even at the melting point.

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