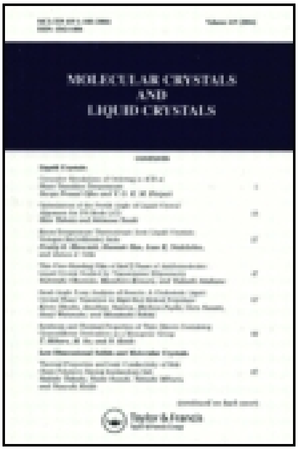

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Molecular Motion in Solid Pentachlorobenzenethiol by N. M. R.

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Molecular Motion in Solid Pentachlorobenzenethiol by N. M. R.

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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 pentachlorobenzenethiol (PClBT) crystal, from 120 K to the melting point. The results have been interpreted in terms of the various molecular motions occurring in this compound. We observed successively as the temperature increases: the fast jump of the proton around the C—S bond, even at low temperature. The associated activation enthalpy is 7.95 ± 0.2 KJ mole^{-1} and correlation time at 125 K is about $\simeq 2.8\ 10^{-8}$s. Then appears the in plane molecular reorientation around the pseudo hexad axis, with activation enthalpy equal to 48.5 ± 2 KJ mole^{-1} and correlation time of $1.6\ 10^{-7}$s at ambient temperature. These last results are in good agreement with those obtained by Brot by dielectric methods. Before the transition (435 K) a slow motion, molecular self diffusion or tumbling occurs. The hindering energy for this process is found to be 160 ± 30 KJ mole^{-1}. The T_{1D} results allow the calculation of the correlation frequency for this motion: at the melting point, it approaches 150 s^{-1}, which is still too slow to average the dipolar interactions and thus reduce the second moment. We do not observe the rigid and diffusive phases that were seen in a similar compound, pentachlorophenol. The pentachlorobenzenethiol behavior is closer to that of pentachlorophenol-hexachlorobenzene mixed crystals. At low temperature, the T_{1D} relaxation time is mainly due to dipolar "second kind" relaxation with chlorines, rapidly relaxed by quadrupolar interaction.

INTRODUCTION

The present work was undertaken in order to provide a quantitative account of the motions occurring in solid pentachlorobenzenethiol and to try to explain the nature of the phase transition, at 435 K, previously observed by calorimetric and electrical conductivity measurements.[21] Proton spin-lattice and dipolar relaxation times T_1 and T_{1D}, and proton second moments M_2 have been measured. From these data, it is possible to infer all the motions whose rate is greater than ~ 1 s^{-1} and to obtain associated correlation times and activation enthalpies. Our results are compared with those of Brot[1] who first investigated this compound by n.m.r. broadline and dielectric methods.

MATERIALS AND METHODS

PClBT was provided by ICN Pharmaceuticals, Inc., purified by recrystallization from CCl_4 and twice sublimed under vacuum of 10^{-5} Torr.

Proton nuclear magnetic resonance spectra were recorded at two Larmor frequencies of 90 and 20 MHz, using a Bruker SXP 4-100 spectrometer. The resonance line was obtained by Fourier transform of the F.I.D. following a single 90° pulse, with the assistance of a Nicolet computer and fast Bruker sampler (BC104). The spin-spin relaxation time T_2 and the second moment M_2 of the resonance line were directly derived from the half height line width $\Delta\nu$ by the following expressions, valid for gaussian lines:†

$$\gamma\sqrt{M_2} = 1/T_2 = 2\pi\Delta\nu/\sqrt{8\text{Ln}2^2} \qquad (1)$$

where γ is the gyromagnetic ratio for the proton ($\gamma = 2.675\ 10^4\ \text{rds}^{-1}\ \text{G}^{-1}$). T_2 and thus M_2 values were corrected for inhomogeneity of the Zeeman field,[3] which contributes to a significant extent to the line width, specially above 280 K ($T_2 \simeq 1$ ms, at 90 MHz, for a diamagnetic liquid sample of the same volume).

The spin lattice relaxation time T_1 was measured using the 180°-τ-90° pulse sequence and the dipolar relaxation time T_{1D} by the 90°-t_1-45°-τ-45° pulse sequence.[4]

Measurements were made over the temperature range from 120 K to the melting point (515 K). The sample temperature was controlled to better than 0.5 K (Bruker cryostat and regulator BVT 1000).

EXPERIMENTAL RESULTS AND DISCUSSION

Second moment (Figure 1)

The temperature dependence of the observed second moment of the absorption line, M_2, is shown in Figure 1 and differs significantly from measurements

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† We have verified that the value of the second moment obtained by this relation differs by less than ± 10% from the value deduced from the lineshape. This percentage represents approximately the error limit of these n.m.r. measurements.

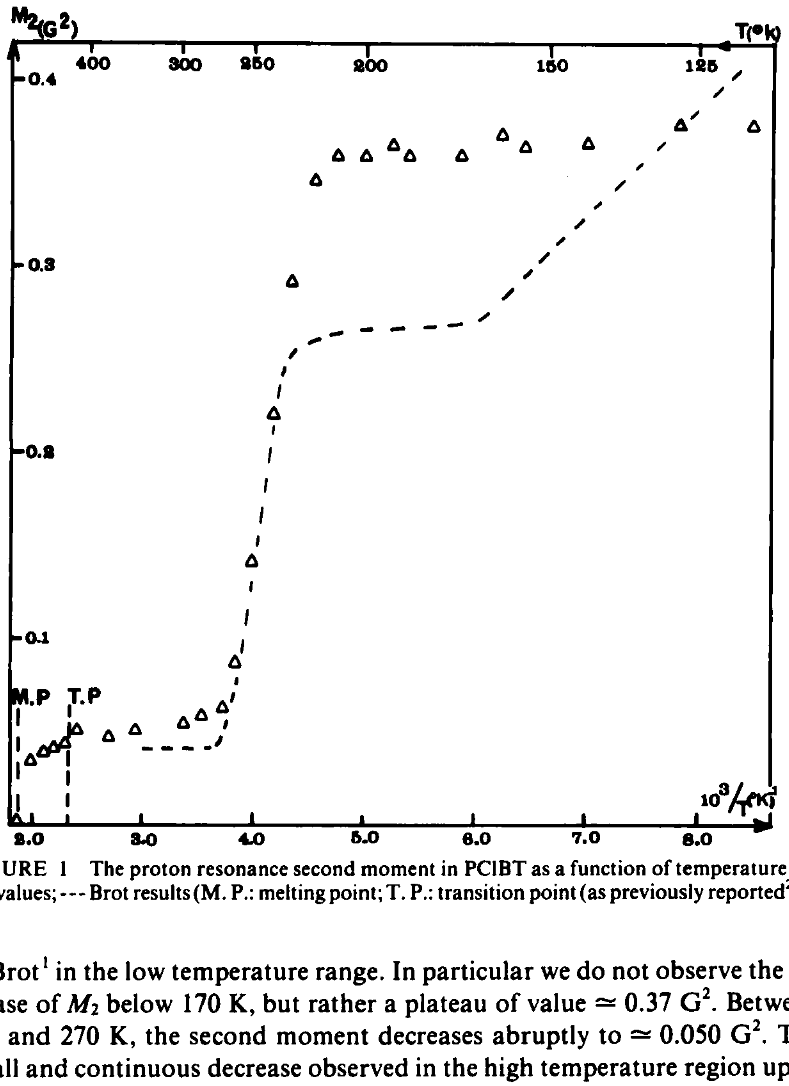

FIGURE 1 The proton resonance second moment in PClBT as a function of temperature. Δ, our values; --- Brot results (M. P.: melting point; T. P.: transition point (as previously reported[21])).

of Brot[1] in the low temperature range. In particular we do not observe the increase of M_2 below 170 K, but rather a plateau of value $\simeq 0.37$ G^2. Between 220 and 270 K, the second moment decreases abruptly to $\simeq 0.050$ G^2. The small and continuous decrease observed in the high temperature region up to the melting point (515 K), 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 (435 K).

The crystalline structure of PClBT being unknown,† we have not calcu-

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† It has been recently published by G. Fulinska-Wojcik, G. P. Charbonneau.[5] As expected (particularly, from the existence of solid solutions of pentachlorobenzenethiol-pentachlorophenol) this structure is isomorphous and very near to those of hexachlorobenzene[6] and pentachlorophenol in high temperature phase.[7]

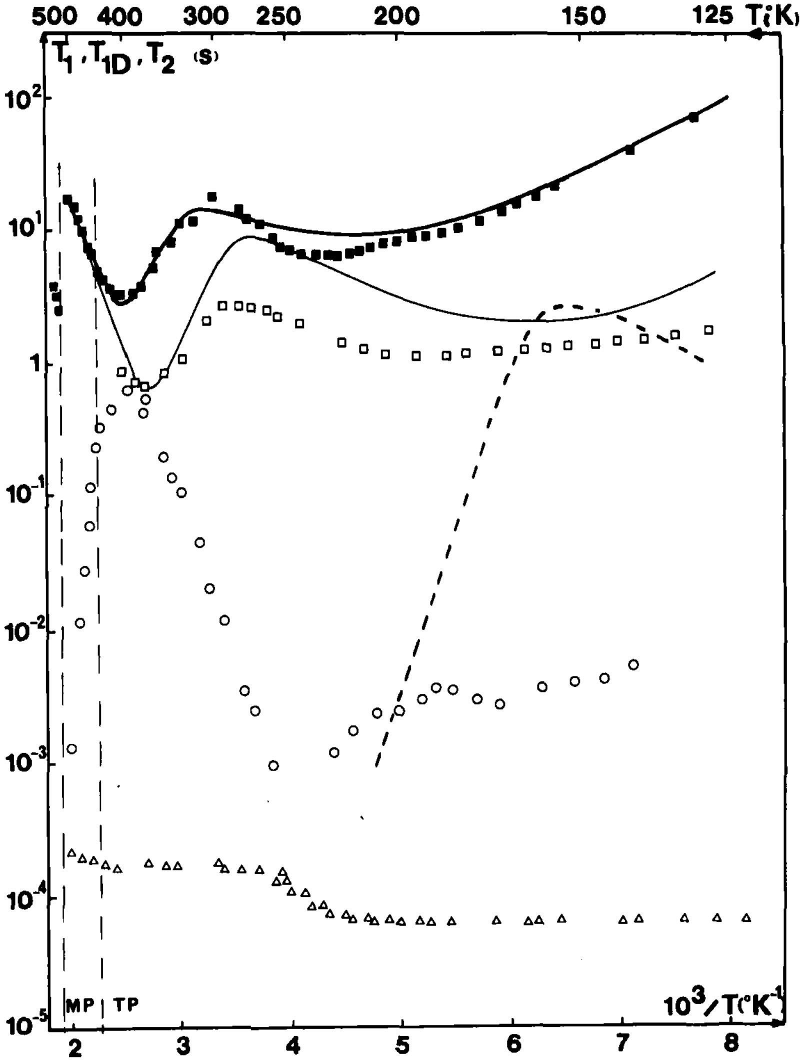

FIGURE 2 T_2, T_1 and T_{1D} temperature dependence for protons in PClBT. Measured values: Δ, T_2 at 90 or 20 MHz; ■, T_1 at 90 MHz; □, T_1 at 20 MHz; ○, T_{1D} at 90 MHz. The lines are drawn, using the B.P.P. theory, fitted to the high temperature T_1 minimum and the low temperature T_1 behavior ——— T_1 at 90 MHz; ——— T_1 at 20 MHZ; --- T_{1D}. (M.P.: melting point; T. P.: transition point[21]).

lated the theoretical second moments for various assumed types of motion. However, we find that the experimental values of M_2 on each side of the second moment transition around 250 K are very similar to those calculated for pure pentachlorophenol (to be published): 0.39 G^2 and 0.054 G^2, respectively for motions as follows:

—jumping proton: the molecules stay fixed but the proton jumps from one to the second equivalent site, around the C—O axis.

—molecular rotation: the molecules reorient around the pseudohexad axis and proton jumps.

Calculations for the rigid structure give a value of 0.507 G^2.

Thus, as suggested by Brot, the rapid decrease of M_2 near 250 K is certainly due to the speeding up of in plane molecular reorientation. This motion superposes on the jumping motion of the proton which still exists at the lowest temperatures attained. The T_1 results corroborate these conclusions and show that the jumping correlation rate is still very fast (~ 10^8 s^{-1} at 120 K), much greater than the line width for a rigid structure (~ 7 $10^3 s^{-1}$), and therefore averages the dipolar interaction responsible of the second moment.

From the line narrowing attributed to molecular reorientation we can derive a reorientational correlation time τ_{CR} given by[8,9]

$$\tau_{CR} = 8 \text{ Ln } 2/\gamma\Delta H| \tan \pi/2\,(\Delta H^2 - B^2/C^2 - B^2)| \qquad (2)$$

where ΔH is the line width in the transition region, C the line width before and B after the narrowing. These values of τ_{CR} are plotted on Figure 3.

Spin lattice relaxation time (Figure 2)

T_1 temperature dependence curves exhibit two minima for each Larmor frequency but at 20 MHz the low temperature minimum is very flat.

The T_1 minimum at high temperature (400 K at 90 MHz) has a value ~ 3.0 s (at 90 MHz). The B. P. P. theory,[8] modified by Kubo and Tomita[9] yields a relation between T_1 and the second moment:

$$T_1^{-1} = \tfrac{2}{3}\,\gamma^2\, M_{2\text{mod}}\,(\tau_C/1 + \omega_0^2\tau_C^2 + 4\tau_C/1 + 4\omega_0^2\tau_C^2) \qquad (3)$$

where $\omega_0 = \gamma H_0$, resonance angular velocity. $M_{2\text{ mod}}$, is that part of the second moment modulated by the motion of correlation time τ_C and includes both inter and intramolecular contributions.[10]

This function has a minimum for $\omega_0\tau_C = 0.62$, so that the T_1 minimum is given by:

$$T_{1\text{min}} = 1.05\ \omega_0/\gamma^2 M_{2\text{mod}} \qquad (4)$$

From the $T_{1\text{ min}}$ experimental value of 3.0 s, we deduced the modulated second moment: $M_{2\text{ mod}} = 0.28$ G^2; this value is close to the observed change in second moment ($\simeq$ 0.32 G^2) around 250° K. So, the T_1 minimum in the high temperature range is associated with the molecular reorientational motion, in agreement with the general results obtained for hexasubstituted benzenes.[11-14]

In addition, we find that these T_1 minima are in the ratio of their Larmor

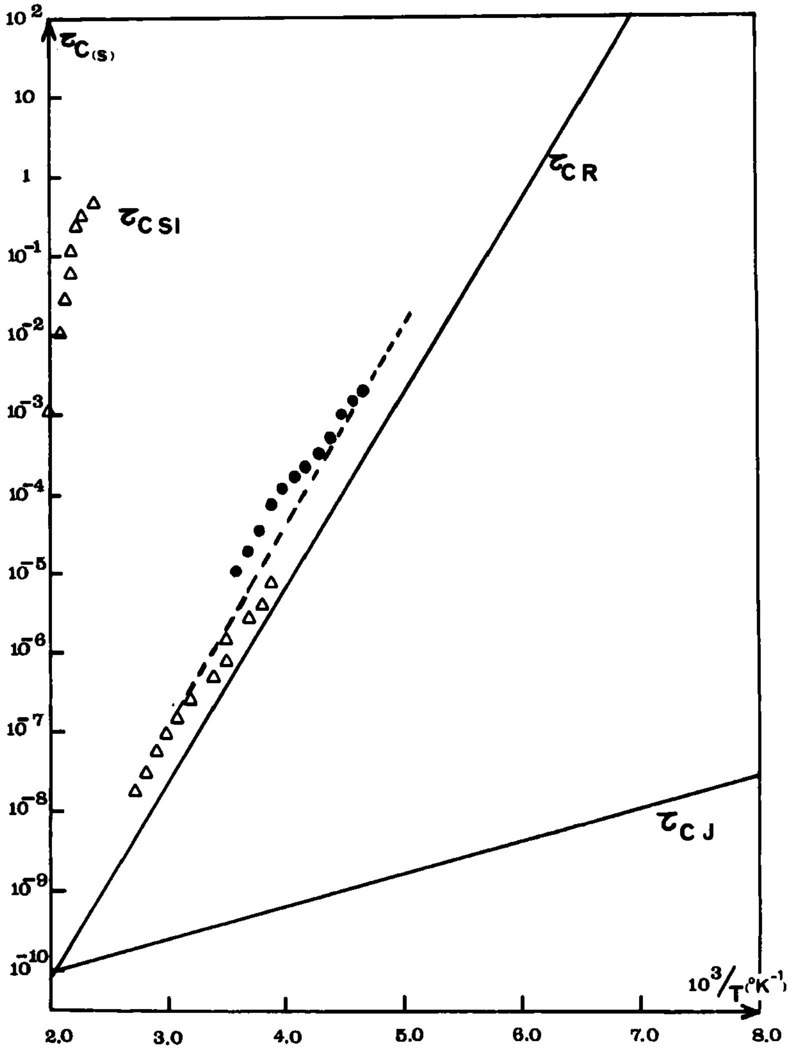

FIGURE 3 The temperature dependence of the various correlation times for the motions occurring in PClBT: τ_{Cj}, for the proton jumping; τ_{CR}, for in plane molecular reorientation; τ_{Csl} for the slow motion (tumbling or diffusing). Measured values: Δ, from T_{1D} results; ●, from line width values. The solid lines are derived from T_1 results using the B.P.P. model. The broken line is from experimental dielectric results of Brot.

frequencies (T_1 (90)/T_1 (20) = 3/0.65 = 4.6), which indicates that, in this temperature range, T_1 is controlled by first kind dipolar interactions modulated by the reorientational motion.

The T_1 minimum at low temperature ($\simeq$ 230 K at 90 MHz) probably corresponds to jumping of the proton. Its value, 6.5 s, allows an estimate of the modulated second moment $\simeq 0.13\ G^2$, which agrees with the calculated value ($0.117\ G^2$) obtained in the case of pure PClPh. However, several points lead us to think that the situation in the low temperature range is not so simple. First the ratio of T_1 minima at 90 and 20 MHz is appreciably different from the frequency ratio: 5.4 in place of 4.5. Secondly, the T_1 curves both possess a high asymmetry. Thirdly, as we shall see below, T_{1D} in the low temperature region cannot be explained using the first kind dipolar interactions alone; the most important contribution to T_{1D} in this temperature range is provided by cross-relaxation with the chlorines, nuclei which are themselves undergoing rapid relaxation due to their electric quadrupolar interaction.

We have tried to fit the T_1 experimental curves by a simple model using two correlation times τ_{CR} and τ_{Cj}; τ_{CR}, for the mean time between two successive reorientational jumps of the molecule; τ_{Cj}, for the mean time between two jumps of the proton around the C—S axis.

We obtain the following expressions:

$$T_1^{-1} = T_{1R}^{-1} + T_{1j}^{-1} \tag{5}$$

$$T_{1_{R,j}}^{-1} = C_{R,j}\,(\tau_{CR,j}/1 + \omega_0^2\tau_{CR,j}^2 + 4\tau_{CR,j}/1 + 4\omega_0^2\tau_{CR,j}^2) \tag{6}$$

$$\tau_{C_{R,j}} = A_{R,j}\exp(E_{R,j}/RT) \tag{7}$$

We were unable to obtain a satisfactory fit for T_1 over the entire temperature range with one set of parameters. The best fit at 90 MHz is obtained for the six values given below:

$C_J = \frac{2}{3}\gamma^2 M_{2j\ \mathrm{mod}} = 4.4\ 10^7$; ($M_{2j\ \mathrm{mod}} = 0.092\ G^2$)

$C_R = \frac{2}{3}\gamma^2 M_{2R\ \mathrm{mod}} = 1.32\ 10^8$; ($M_{2R\ \mathrm{mod}} = 0.28\ G^2$; deduced from experimental T_1 minimum at 400° K)

$E_j = 7.95$ KJ mole^{-1}, activation energy for the jumping motion; estimated from the linear part of the T_1 curve in the low temperature region.

$E_R = 48.5$ KJ mole^{-1}, activation energy for the reorientational motion of the molecule, measured from the slope of the T_{1D} curve, for the increasing high temperature part of this curve (for this temperature range, the contribution of jumping motion to T_{1D} relaxation is negligible, τ_{Cj} being lower than ω_0^{-1}, so that T_{1D} is only sensitive to rotation).

$A_j = 1.38\ 10^{-11}$ s; this choice is made to fit the T_1 value at $T^{-1} = 7.5\ 10^{-3}\ K^{-1}$

$A_R = 5.5\ 10^{-16}$ s, value obtained to fit the T_1 minimum at 400° K.

We observe, in the medium temperature range a large difference between T_1 experimental and calculated values. This disagreement is more pronounced at 20 MHz, except in the high temperature range. These results indicate that another contribution to T_1 exists which is more efficient at twenty than at ninety megahertz, and contributes at temperatures mainly below ambient temperature. From the best fit, we have deduced the temperature dependence of τ_{Cj} and τ_{CR} (Figure 3):

$$\underset{(\bullet)}{\tau_{Cj}} = 1.38\ 10^{-11} \exp (7.95\ 10^{3}/RT) \tag{8}$$

$$\underset{(\blacksquare)}{\tau_{CR}} = 5.5\ 10^{16} \exp (48.5\ 10^{3}/RT) \tag{9}$$

Dipolar relaxation time (Figure 2)

T_{1D} exhibits two regions of very different behavior, depending on temperature.

In the high temperature range, above 250 K, T_{1D} is only governed by dipolar interactions with protons and chlorines, modulated by motions of these nuclei. T_{1D} first increases by three orders of magnitude, becoming almost equal to T_1 near its minimum at 20 MHz. The slope of this linear part has allowed an estimate of the hindering energy for the rotating motion of the molecule, responsible for this increasing relaxation rate: 48.5 KJ mole^{-1}. This value is well within the range observed in similar compounds like hexasubstituted chloromethylbenzenes[13] for in plane reorientation.

Then, T_{1D} begins to decrease before the transition temperature and, above the transition, decreases sharply, in a linear fashion, inferring an activation energy, which amounts to 160 ± 30 KJ mole^{-1}, for a new molecular motion which is still too slow at the melting point to reduce the second moment and T_1. This motion is probably similar to that occurring in other hexa-substituted benzenes,[12,13,15] where it has been suggested that an out-of-plane molecular tumbling or molecular self diffusion takes place in the high temperature crystalline phase. However the observed hindering energy is four to six times higher than in these last compounds and is more typical of values found for self-diffusion in molecular crystals. Unfortunately the T_2 values are too low (0.2 ms) to allow an n.m.r. experimental test for self-diffusion using spin echoes in a magnetic field gradient. The diffusion constant is, in any case, low, being smaller than $\simeq 10^{-10}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, near the melting point. An investigation of the dielectric properties in this high temperature range and/or an n.m.r. study on a monocristal would help to determine the type of motion occurring.

From T_{1D} results, we have calculated the correlation times τ_{CR} (reorientational jumping) and τ_{Csl} (slow motion), plotted on Figure 3. We used the following simplified relations[16]

$$\tau_{CR} = \frac{1}{C_R} T_{1D}^{-1} = 0.76\ 10^{-8}\ T_{1D}^{-1} \text{ for } 2.6\ 10^{-3} < T^{-1} < 3.9\ 10^{-3\circ}\mathrm{K}^{-1} \tag{10}$$

$$\tau_{C_{sl}} = [(M_{2\,\mathrm{mod}})sl/M_{2R}] \cdot T_{1D} \text{ for } T^{-1} < 2.3\ 10^{-3\circ}\mathrm{K}^{-1} \tag{11}$$

with $(M_{2\,\mathrm{mod}})sl$: part of the second moment modulated by the slow motion; M_{2R}: value of the second moment before the onset of this motion ($M_{2R} \sim 0.05$

G^2). The ratio $(M_{2\,\mathrm{mod}})sl/(M_{2R})$ has a maximum value equal to unity, so that the τ_{Csl} values derived using

$$\tau_{Csl} = T_{1D} \tag{12}$$

is an overestimate for τ_{Csl}.

We observe on Figure 3 some discrepancies between the τ_{CR} results obtained from T_1, T_{1D} or ΔH measurements. Differences between 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 anyway. Without a very detailed model for the motions, it is probably the best agreement to be expected.

We have also plotted on Figure 3 the τ_{CR} values obtained by Brot[1] from dielectric measurements between 200 K and 320 K. We note a very good agreement with our results, for both absolute values and for activation energy (49.3 KJ mole^{-1} in Brot's paper).

In the low temperature range (below 240 K) T_{1D} does not follow the behavior predicted by the theoretical model above (broken line in Figure 2): T_{1D} values can be estimated from the simplified relation[16]

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

with

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

We took for T_2 the value at low temperature: 7.25 10^{-5} s. The above equations are approximate but the disagreement between experiment and predicted curve is not a consequence of the approximation.

T_{1D} stays low and has a weak temperature dependence. Therefore another efficient relaxation mechanism must exist in the low temperature range, which may be dipolar "second kind" relaxation, first involved by Norris *et al.*[17] to explain T_1 and $T_{1\rho}$ measurements in low temperature crystalline phases of HBr and HCl crystals.

To ascertain this possible contribution to proton relaxation times, we have made a study of T_1 (^1H) versus the proton resonance frequency ν_0, between 90 and 6.4 MHz, for different temperatures. We obtained a high enhancement of the relaxation rate when the proton Larmor frequency matches the chlorine guadrupolar frequency, near 35 MHz.[18] The Figure 4 presents the results at room temperature and compares them with the calculated T_1 values deduced from the above model. Outside the range 20–60 MHz, the agreement is rather good considering the simplicity of the model. We observe in both experimental and theoretical curves a strict dependence on ν_0^{-2}, which comes from the contribution of the molecular reorientational motion. The slope of the linear part of the dispersion curve, 0.27 10^{14} s^2 differs, by a factor of 33% from its calculated value (0.41 10^{14} s^2). The frequency independent term, due to the jumping H motion, has a value equal to 0.070 s^{-1} ($T_{ij}^{-1} = 5\, C_j\, \tau_{Cj} = 0.070\ s^{-1}$

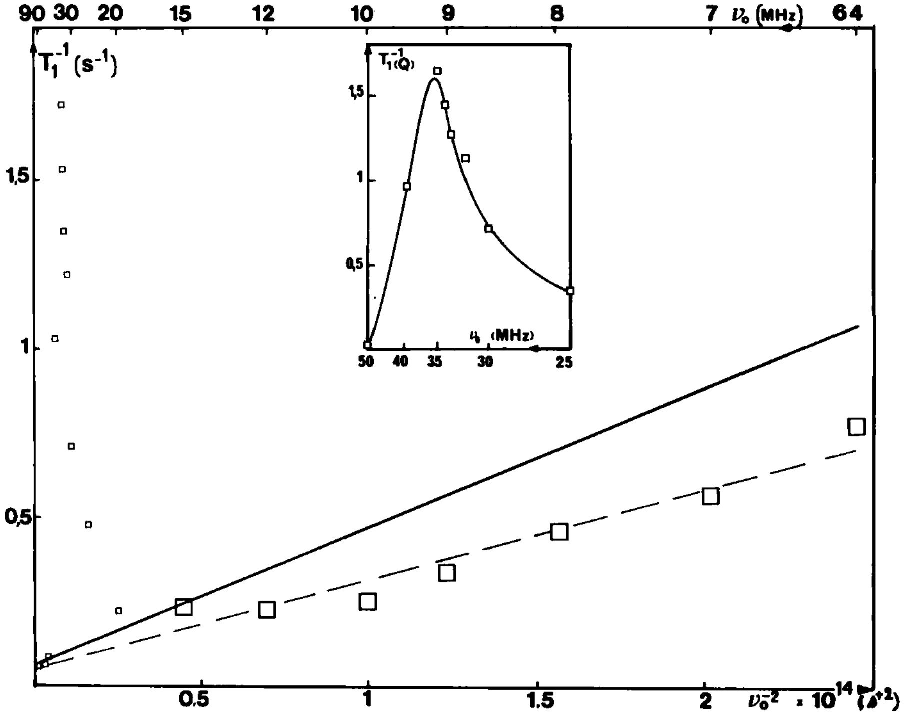

FIGURE 4 The frequency dependence of the proton spin-lattice relaxation rate in PClBT. □, experimental value in high frequency range (good precision); □, experimental value in low frequency range (weak precision). The broken line, drawn between experimental points, shows the linear dependence of T_1^{-1} versus ν_0^{-2} (ν_0: Larmor proton resonance frequency). The solid line is the calculated dependence, also linear, 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.

for $\omega_0^2 \tau_{Cj}^2 \ll 1$) and an experimental one (extrapolation of the curve up to the T_1^{-1} axis) of 0.060 s^{-1}.

The results at low temperatures (230 K, 160 K) are similar: the agreement between theoretical and experimental frequency dependence is correctly satisfied except in the medium frequency range, near 35 MHz where we observe a peak in the relaxation rate. On the other hand, at high temperature (400 K), the experimental T_1 behavior follows the theoretical curve over the whole frequency range: no peak of relaxation rate is present. All these features clearly show that chlorine nuclear relaxation contributes strongly to proton spin-lattice relaxation at room temperature and below, when the proton Larmor frequency matches the chlorine quadrupolar resonance frequency. However, out of the range 20–60 MHz, this chlorine contribution becomes negligible, the factor $(\omega_0 - \omega_Q^{Cl})^2 (T_{2Q}^{Cl})^2$ becoming large. At high temperature, the molecular in plane reorientation is fast enough to average the quadrupolar interaction, as has been observed in the similar compound, pentachlorophenol,[19] by a loss of the nuclear quadrupole resonance signal.

Thus, above 250 K, the dipolar relaxation time T_{1D} depends only on dipolar relaxation of the first kind and relaxation is due to in plane molecular reorientation. This process is also evident in the T_1 data. At the highest temperatures T_1 indicates another motion, a reorientation or diffusion process with high activation enthalpy. Below 230 K, the contribution of chlorine relaxation to the proton T_{1D} 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.[20] The low temperature T_1 results have been satisfactorily explained by a jumping process of the proton around the C—S bond.

CONCLUSION

We have ascertained that three types of molecular motion in pentachlorobenzenethiol influence the proton n.m.r. relaxation. At the highest temperatures a motion with a high activation enthalpy, 160 ± 30 KJ mole^{-1}, rather characteristic of self-diffusion, exists. An in-plane reorientation with an activation enthalpy of 48.5 ± 2 KJ mole^{-1} is observable from 250 K to the melting point. At lower temperatures a fast proton jumping around the C—S bond with an activation enthalpy of 7.95 ± 0.2 KJ mole^{-1} is observed. Some apparent anomalies in some of the proton relaxation data have been satisfactorily explained by a dipolar "second kind" relaxation mechanism involving the chlorine nuclei. The phase transition at 435 K, previously reported,[21] presents no apparent discontinuity in n.m.r. parameters. It is associated with the slow diffusive motion appearance.

References

1. C. Brot and I. Darmon, *J. Chim. Phys.*, **1**, 100 (1966).
2. A. Abragam, *Les Principes du Magnètisme Nucléaire PUF* (1961). p. 115.
3. T. C. Farrar and E. D. Becker, *Pulse and Fourier Transform NMR*, Academic Press, New York (1971). p. 4.
4. J. Jeener and P. Brockaert, *Phys. Rev.*, **157**, 2, 232 (1966).
5. G. Fulinska-Wojcik and G. P. Charbonneau, *Acta Cryst.*, **A36**, 51-53 (1980).
6. T. Sakurai, *Acta Cryst.*, **15**, 1164 (1962).
7. J. W. Rohleder and G. Fulinska-Wojcik, *Rocz. Chem.*, **46**, 493 (1972).
8. N. Bloembergen, H. M. Purcell and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).
9. R. Kubo and K. Tomita, *J. Phys. Soc. Jpn.*, **9**, 888 (1954).
10. H. A. Resing, *Mol. Cryst. Liquid Cryst.*, **9**, 101 (1969).
11. P. S. Allen and A. Cowking, *J. Chem. Phys.*, **47**, 4286 (1967).
12. H. W. Bernard, J. E. Tanner and J. G. Aston, *J. Chem. Phys.*, **50**, 5016 (1969).
13. J. M. Chezeau, J. H. Strange and C. Brot, *J. Chem. Phys.*, **56**, 1380 (1972).

14. M. Eveno and J. Meinnel, *J. Chim. Phys.*, **1**, 108 (1966).
15. R. Van Steenwinckel, *Z. Naturforsh.*, **27a**, 1526 (1969).
16. J. Virlet, Thèse Orsay (1971).
17. M. O. Norris *et al.*, *J. Phys. C.* (*Proc. Phys. Soc.*) *2*, **1**, 422 (1968).
18. T. P. Das and E. L. Hahn, *Nuclear quadrupole resonance spectroscopy*. Academic Press (1958) New York.
19. H. F. Shurvell, J. Korppi-Tommola and R. J. C. Brown, *Can. J. Chem.*, **56**, 3, 359 (1978).
20. D. Wolf, Oxford University Press, (1979).
21. R. Radomski, B. Gola and M. Radomska, Int. Coll. Ag. Ph. Sol. Diel. Wr (1975) Pl. Wr. Nr 12 pp. 175.