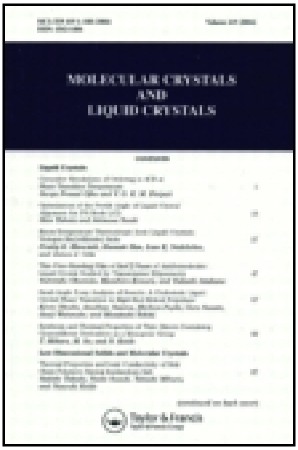

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Motions by ^{1}H NMR in Crystalline Phases of β-Naphthol and β-Naphthylamine

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Motions by ^{1}H NMR in Crystalline Phases of β-Naphthol and β-Naphthylamine

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For **β-naphthol**, where the measurements have been made above the ambient temperature, we observed the fast hydroxyl proton jump. Its mean correlation time is ~5 10^{-7} *s* at ambient temperature. Around 350 K, a low temperature transition seems correlated with a frequency independent relaxation contribution and leaves the above motion unaffected. Above this transition, a very slow motion appears (20 s^{-1} at 365°K) which is modified by the high temperature transition (385 K).

For **β-naphthylamine**, only one motion is present between 200 K and the melting point: the 180° jumps of the amino group around its axis. A large distribution of correlation times can explain the relaxation features.

INTRODUCTION

The present work was taken up to study the kinetics of the whole molecule and of the hydroxyl or amino group reorientation in the crystal structures of **β-naphthol** and **β-naphthylamine**.

For the first compound, a phase transition was previously observed by calorimetric and X-ray diffraction studies.[1,2] A disordered high temperature phase appears just below the melting point (phase I): the

OH group is distributed over the four beta positions of the **naphthalene** molecule with the same probability. When the temperature is lowered, an ordered stable phase (phase II) occurs at a temperature dependent on the cooling rate lying around 380 K.[2] The nature of this transition is of the first order:[2] existence of a latent heat, hysteresis, discontinuities in X-ray diffraction images. The crystalline structures in the two phases are known:[2,3,4] at low temperature, hydrogen bonds link molecules along a crystallographic axis. The transition could be due to the break of these hydrogen bonds, giving rise to an abrupt variation of the electrical conductivity.[5] Infrared spectroscopic studies[1,6] showed that in phase I, the OH vibration is similar to that one in the molten compound.

For the **β naphthylamine**, a broad line PMR study was carried out.[7] A fall in proton second moment with rise in temperature around 320 K has been attributed to the reorientation of the NH_2 group and an activation energy of 8.4 kJ $mole^{-1}$ has been deduced from the line width measurements.

MATERIALS AND METHODS

The compounds were purified by crystallization from CCl_4, vacuum sublimation and zone refining; approximately 100 zone passes were made. The crystals of phase II were grown from the vapor by the method described previously.[8]

Proton nuclear magnetic resonance spectra and relaxation times were recorded with a Bruker SXP spectrometer, principally at 90 MHz. The free induction decay (F.I.D.) was obtained by the solid echo sequence,[9] in order to be free from the dead time of the receiver (5 μs at 90 MHz).† The NMR line width and second moment were derived, after accumulation, by Fourier Transform of the FID. The second moment has been also directly deduced from the free induction decay. The spin lattice, spin lattice in the rotating frame, and dipolar relaxation times have been measured with the classical pulses sequences, respectively $180° - \tau - 90°$ for T_1, spin locking for $T_{1\rho}$ and $90° - t_1 - 45° - \tau - 45°$ for T_{1D}.[10] Measurements were made over the temperature range from ambient temperature to the melting point; however in the case of β-naphthylamine, we have decreased the temperature up to 200 K. Temperature was controlled to better than

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† The use of a single 90° pulse leads to broaden highly the resonance line and to a very important overestimate, up by a factor 2, of the second moment.

one degree (Bruker regulator BVT 1000) and the inhomogeneity of the temperature in the sample did not exceed one degree.

EXPERIMENTAL RESULTS AND DISCUSSION

1. β-naphthol

Line width and second moment The lineshape and width depend highly on the settings of the FID accumulator. It is necessary that the digital accumulation starts exactly at the top of the solid echo, otherwise one narrows or broadens the resonance line. So the precision is not very good (10%).

The temperature dependence of the observed line width is shown in Figure 1a. The line-width is constant over the whole temperature range, and is equal to 8.2 ± 0.6 G. The experimental second moment of the absorption line has been derived directly from the FID[11] (Figure 1b) and amounts to 8.5 ± 0.5 G^2. This method to measure the second moment is more accurate than that from the resonance line. With this last one, we obtain the second moment as 7.5 to 10.2 G^2, according to the spectra.

We have calculated the second moment, using Van Vleck's formula[12] taking into account the proton-proton intra- and inter-molecular interactions. The crystal structure is given by Watson.[3] The calculation has been carried out over all the interproton distances lower than 6 Å, in the following cases:

—rigid case 1: the molecule stays fixed and the proton of the hydroxyl group is located at 1 Å from the oxygen, on the line joining the oxygen atoms of the two nearest molecules bonded by hydrogen bond.

—rigid case 2: the location of the hydroxyl proton is different here. Its position is at the center of the hydrogen bond.

—rotating proton: the molecule is still fixed but the hydroxyl proton rotates around the C—O axis, so rapidly that its apparent position is along C—O bond, 0.5 Å beyond the oxygen atom.

The results are given in Table I.

We can ascertain that:

—the calculated second moment is only slightly modified by the hydroxyl proton motion: from 0.152 to 0.279 G^2, according to the position of the proton in the rigid case. This change is principally of intramolecular origin.

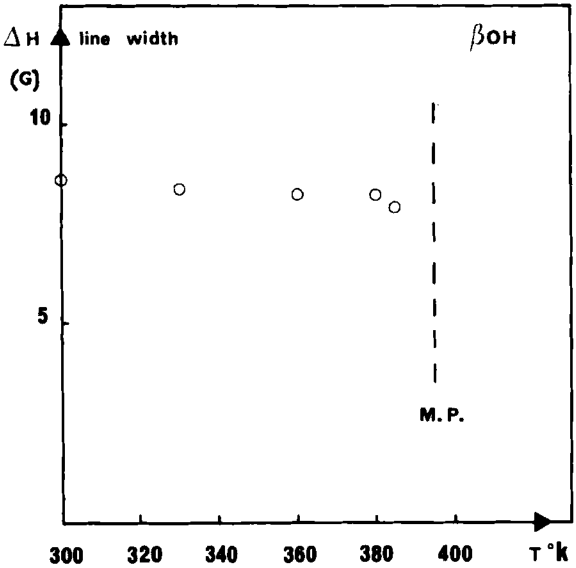

FIGURE 1a The proton resonance line width, in gauss, for β-naphthol as a function of temperature (M.P.: melting point).

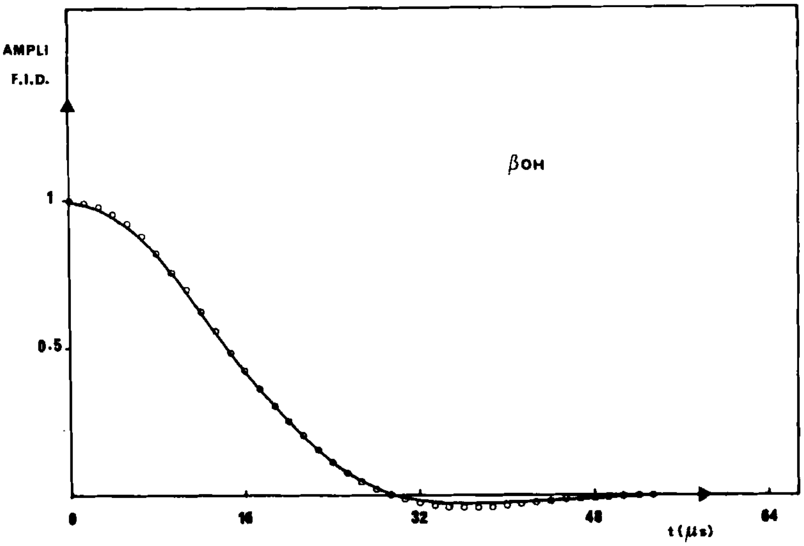

FIGURE 1b (O): the free induction decay, observed in β-naphthol at 375°K, as a function of time (in μs). —— fit calculated with the function $G(t) = e^{-1/2a^2t^2} \sin bt/bt$ and the following parameters: $a^2 = 3.0\ G^2$; $b^2 = 16.02\ G^2$. The second moment value is then given by $M_2 = a^2 + b^2/3 = 8.34\ G^2$.

TABLE I

Calculated second moment in β-naphthol

State of motion		Rigid 1	Rigid 2	Rotating
	Intramolecular	3.003	2.963	2.776
$M_2(G^2)$	Intermolecular	3.353	3.519	3.428
	Total	6.356	6.483	6.204

—The experimental value is greater than all the calculated ones. This disagreement can be due to an underestimate of the intermolecular contribution and from the difficulty to place the OH proton.

As consequence, it is not possible to conclude from this resonance line experiment on the state of motion of the hydroxyl proton. However, there is no doubt that the molecule stays fixed, on the NMR time scale, in the crystalline structure, up to the melting point; rather that its possible motion is too slow to have an effect upon the NMR spectrum.

Relaxation times T_1 *and* T_{1D} (*Figure 2*) The measurements have been made at the two resonance frequencies 90 and 25 MHz.

We distinguish three parts in the curves: at low temperature, between about 298 and 350 K: T_1 and T_{1D} variations are linear, in opposite senses and have the same slope in absolute value, approximately 19.5 ± 1 kJ mole^{-1}. This behavior can be explained by the modulation of dipolar interactions between protons. What is the motion responsible of these time dependent interactions?

In Figure 3, we have plotted the frequency dependence of the spin lattice relaxation rate at ambient temperature. We have a linear plot on ω_0^{-2} (ω_0: resonance pulsation), for the frequency range considered here, so we can write:

$$T_1^{-1} = A + B\,\omega_0^{-2}$$

A: frequency independent term, obtained by extrapolation of the curve to the T_1^{-1} axis. Its value, 0.0025 s^{-1}, is very weak. It corresponds likely either to a very rapid motion like a molecular libration or OH vibration or to paramagnetic impurities contribution.

B: the slope of the dispersion curve, amounts 4.2 ± 0.2 10^{14} s^{-3}.

If the B.P.P.[13] theory is appropriate, the factor B is given by:

$$B = 2C_j/\tau_{cj} \qquad (1)$$

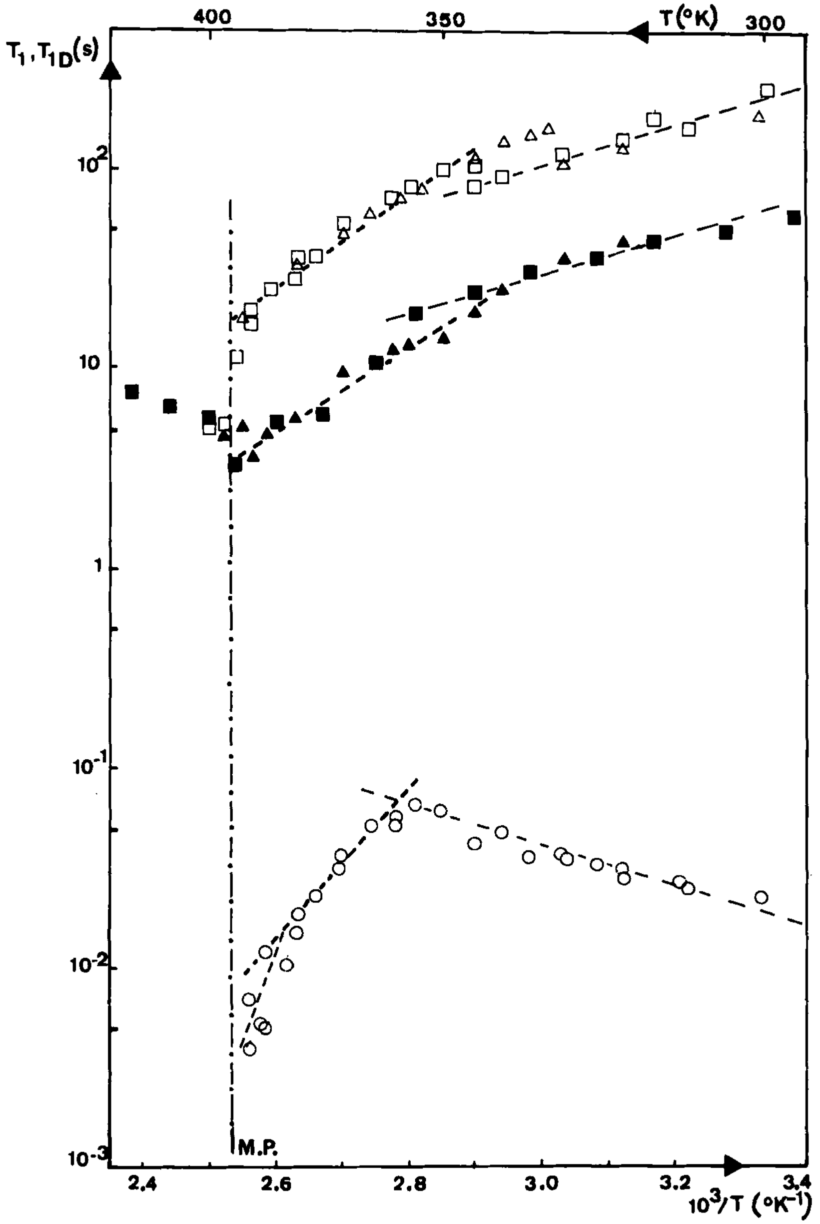

FIGURE 2 T_1 and T_{1D} temperature dependence in β-naphthol 90 MHz: □ T_1, rising; △ T_1, decreasing temperature experiment; ○ T_{1D} 25 MHz: ■ T_1, rising; ▲ T_1, decreasing temperature experiment (MP: melting point).

with $C_j = \frac{2}{3} \gamma^2 M_{2\mathrm{mod}}$

τ_{cj}: correlation time of the motion

$M_{2\mathrm{mod}}$: modulated part of the second moment

γ: gyromagnetic ratio of the proton spin ($\gamma = 2.675\ 10^4\ s^{-1}\ \mathrm{G}^{-1}$)

At this temperature, the correlation time value is such that $\omega_0\tau_{cj} \gg 1$, and also, from T_{1D} experimental curve, satisfies the condition: $\omega_D\tau_{cj} \ll 1$ ($\omega_D = \gamma\sqrt{M_{2R}}$; M_{2R}: second moment in the rigid case; $\omega_D \sim 7.7\ 10^4\ s^{-1}$). Thus, T_{1D} is related to τ_{cj} by the simplified expression:[14]

$$T_{1D}^{-1} = C_j\tau_{cj} \tag{2}$$

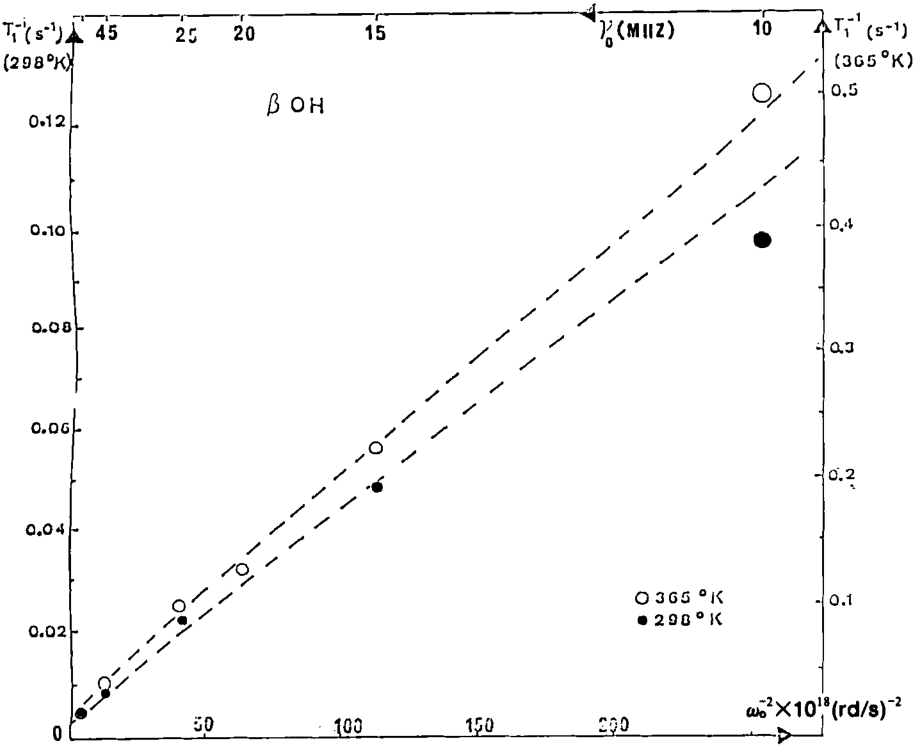

FIGURE 3 The frequency dependence of the spin lattice relaxation rate in β-naphthol at 298°K and 365°K.

From Eqs. (1) and (2) we obtain:

$$C_j^2 = 0.5\ B\ T_{1D}^{-1}\ \#\ 1.10\ 10^6\ s^{-4}$$

$$\tau_{cj}^2 = 2\ (B\ T_{1D})^{-1}\ \#\ 25\ 10^{14}\ s^2$$

We deduce the value of τ_{cj} at ambient temperature: $\tau_{cj} = 5\ 10^{-7}\ s$ and for $M_{2\text{mod}}$: 0.219 G^2.

This modulated second moment value just lies between the calculated ones in the case of a rotating hydroxyl proton, according to the rigid crystalline structure considered.

Therefore, even at ambient temperature, the structure is not completely rigid and in this temperature range the proton spin relaxation is due to rapid rotation of the hydroxyl group around the CO axis.

The correlation time τ_{cj} can be derived from the experimental points, assuming an Arrhenius equation:

$$\tau_{cj} = \tau_{cj\infty} \exp(Ea_j/\text{RT}) \tag{3}$$

$$\tau_{cj} = 1.93\ 10^{-10} \exp(19.5\ 10^3/\text{RT}) \tag{4}$$

τ_{cj} values are plotted on Figure 4.

At 340 K, the spin lattice relaxation rate follows a similar dispersion curve, linear on ω_0^{-2}, with a slope equal to $1.08 \pm 0.1\ 10^{15}\ s^{-3}$. The ratio of the slopes at the two temperatures 298 and 340 K must be in inverse ratio of the τ_{cj} values [from Eq. (1)]. This result is well verified. We obtain respectively 2.57 and 2.64.

At ~350 K, we notice an abrupt variation of T_1, specially at 90 MHz, with a large hysteresis. So we have a transition but this term does not involve that there is a change in the crystalline structure.

From ~350 K to 380 K, the relaxation times behave differently from what we have observed at low temperature.

T_{1D} decreases in a linear fashion, showing the onset of a very slow motion, still too slow to reduce the line width and T_1. The experimental points must be corrected in order to account for the contribution of the fast hydroxyl rotation. We can infer the hindering energy for this slow motion ~116 kJ mole^{-1}. An overestimate of the associated correlation time τ_{csl} plotted on Figure 4, is given by $\tau_{csl} = T_{1Dsl}$,[14] where T_{1Dsl} is the corrected value of the dipolar relaxation time in this temperature range.

We cannot define this slow motion from our NMR results: molecular reorientation around an axis, or tumbling or diffusion. Neither can we specify it if we refer to the hindering energy values in this type of compounds: 120 kJ mole^{-1} for diffusion in chloro 2 and fluoro 2 naphtha-

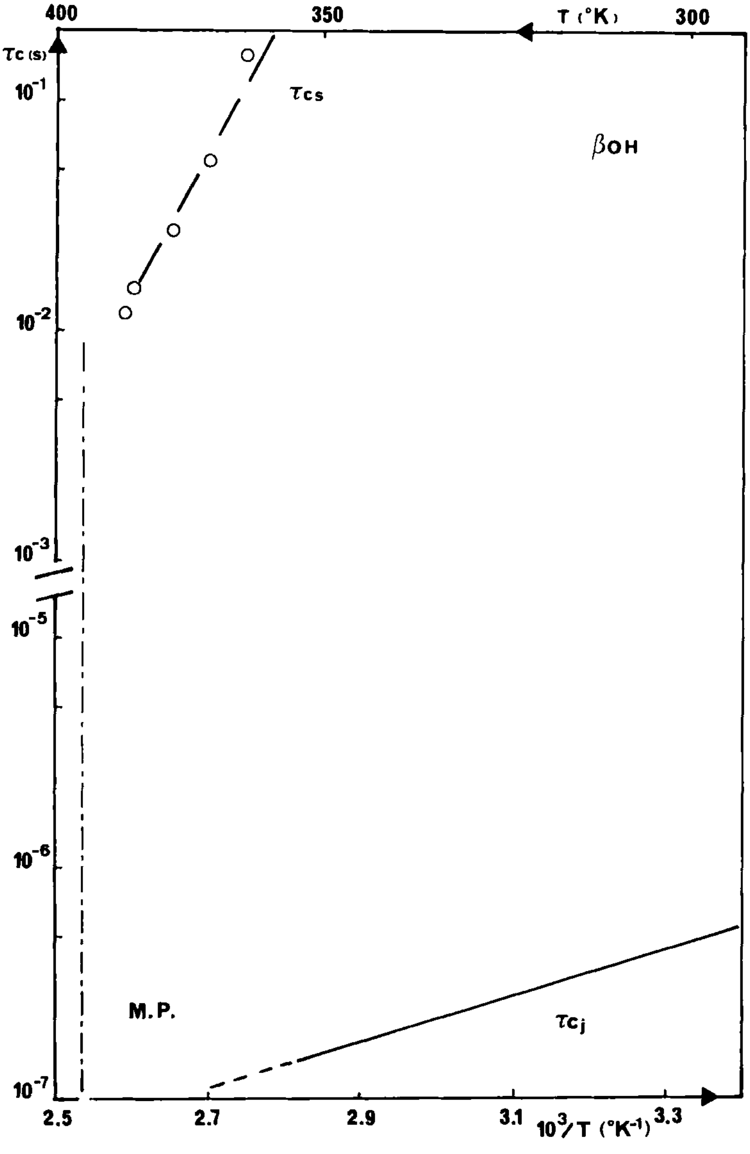

FIGURE 4 The temperature dependence of the correlation times occurring in β-naphthol. τ_{c_j}: hydroxyl proton jumping τ_{c_s}: slow motion; M.P.: melting point.

lene,[15] 105 kJ mole^{-1} for rotation in naphthalene,[16] 46 kJ mole^{-1} for the reorientation around the axis perpendicular to the molecular plane in fluoro-2 naphthalene.[17,18]

The frequency dependence of the spin-lattice relaxation rate at 365 K (Figure 3) follows the relation:

$$T_1^{-1} = 0.016 + 1.80 \pm 0.1\ 10^{15}\ \omega_0^{-2}$$

We cannot apply the previous calculation in order to obtain the values of the modulated second moment and of the correlation time at this temperature, because T_1 and T_{1D} are relaxed by different motions. We can only compare the experimental value of the slope of this linear dispersion curve with the value that we would obtain in absence of the transition, that is if the expression (4) was still valid at this temperature. The slope is inversely proportional to τ_{cj}, thus

$$(B)_{365\mathrm{K}} = (B)_{298\mathrm{K}} \frac{(\tau_{cj})_{298\mathrm{K}}}{(\tau_{cj})_{365\mathrm{K}}} = 4.20\ 10^{14} \times 4.24 = 1.78\ 10^{15}\ s^{-3}$$

This calculated value is almost equal to the experimental one. This result does signify the following:

Either that the modulated second moment and the associated correlation time vary strictly in the same ratio through the transition, which is rather improbable and should be expressed in the same manner at the two resonance frequencies or they maintain approximately their values at the transition, that is the transition does not affect the motion of the hydroxyl group. This second hypothesis is more advisable because it allows to interpret the different behaviors of the measured spin-lattice relaxation times at the transition, where the discontinuity is only observed at 90 MHz. We know that at ninety megahertz, the most contribution to the relaxation is due to the frequency independent term, while at twenty five megahertz, it is quite the contrary: this contribution is negligible with regard to the term connected with the OH rotating motion. Therefore, it appears that the above transition does correspond to the variation of the only frequency independent term. Is it connected with a change in crystalline structure? From the previous studies[1,4] it is not the case. Is it a change in nature or importance of crystalline defects? We don't know; we observe only that above this transition, a slow motion appears and the apparent activation energy for the fast rotating hydroxyl motion has increased. In the temperature range 350–380 K, this hindering energy amounts 45 kJ mole^{-1}.

Above ~380°K, the compound undergoes a transition, with a large hysteresis, from the T_{1D} experimental points. On the other hand,

T_1 does not vary at all. This second transition is well known, already observed by numerous technical methods[1,6] and corresponds to the appearance of a disordered crystalline phase. Our measurements show that the fast motion is unaffected by the transition whereas the slow motion is modified (net decrease of its correlation time; assumption shown on Figure 4) or a new motion superimposes.

Meresse[2] thinks that the disorder in phase I of these compounds could be described by diffusion jumps of the molecule and simultaneously by reorientation of the molecule in its plane with a frequency around $10^3\ s^{-1}$. Our results go in this direction, specially the frequency seems well of this magnitude (Figure 4). Owing to the narrowness in temperature of this phase, we cannot infer the hindering energy of the slow motion from T_{1D} experimental points.

We have also found out the important hysteresis connected with the crystallization:[2] melting ocurs at 395 K in rising and at 388 K in decreasing temperature measurements.

2. β-naphthylamine

Line width and second moment The observed line width is constant (9.0 ± 0.6G) over the temperature range, from 250 K up to the melting point. Below 250 K, it increases slightly and at 200 K, the lowest temperature studied, it becomes equal approximately to 10 ± 1 G (Figure 5a).

The experimental second moment, directly derived from the free induction decay, is estimated to be 10.5 ± 0.5 G^2 (Figure 5b). From the resonance line, we obtain a very near value of 10.6 G^2 but with a bad precision (±2.5 G^2).

The theoretical second moment has been evaluated in the three following cases. The molecule is supposed to be motionless except the motion of the NH_2 group:

—the group is rigid.

—the group rotates around its axis, by jumps of 180°.

—the group rotates freely around its axis (more than two equilibrium positions, in this case).

The results are given in the Table II.

Some symplifying assumptions have been made:

1. In the cases of motion, the two NH_2 group protons have been located in the middle of the H—H bond, for the calculation of interactions between these protons and the others (intra and intermolecular).

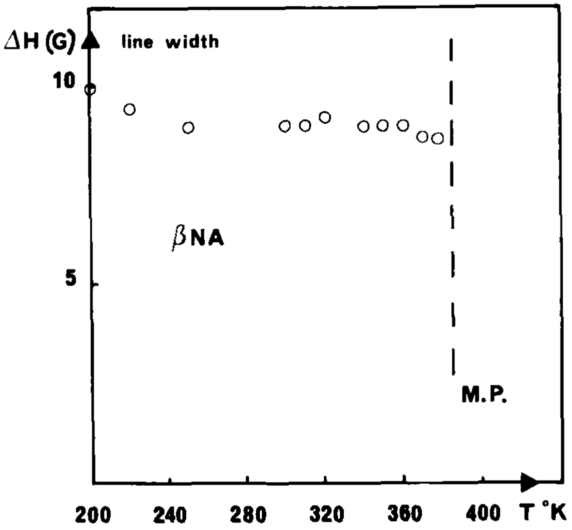

FIGURE 5a The resonance line width, in gauss, for β-naphthylamine as a function of temperature (M.P.: melting point).

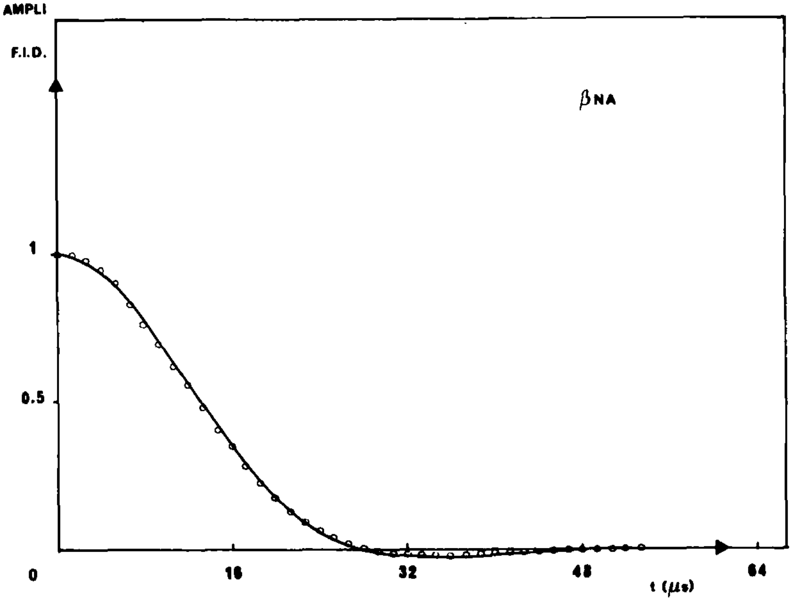

FIGURE 5b (O): the free induction decay, observed in β-naphthylamine at 375°K as a function of time (in μs). —— fit calculated with the function $G(t) = e^{-1/2a^2t^2} \sin bt/bt$ and the following parameters: $a^2 = 4.5\ G^2$; $b^2 = 17.94\ G^2$. The second moment value is then given by $M_2 = a^2 + b^2/3 = 10.48\ G^2$.

TABLE II

Calculated second moment in β-naphthylamine

Motion of NH_2 group		Rigid	Jump	Rotation
	Intramolecular	7.422	7.045	3.751
$M_2(G^2)$	Intermolecular	3.772	3.856	3.856
	Total	11.194	10.901	7.607

2. The intermolecular contribution has been estimated from its value in β-naphthol, multiplying it by 9/8, the ratio of the numbers of protons in the two molecules. In the rigid case, the reference is the first of the Table I.

It is probable that this estimation is slightly too weak, because the mean volume available for a molecule is lower in β-naphthylamine (173.5 $Å^3$, see Ref. 19) than in β-naphthol (189.8 $Å^3$, see Ref. 2). We observe that the experimental value lies between the calculated ones if NH_2 group rotates; 180° jumps seem more likely.

We must note however that the value of the second moment, in the third hypothesis depends highly on the interproton distance in the amino-group, and therefore on the angle between the NH bonds. In the case considered above, the angle equals 107°. With an angle of 120°, M_2 becomes 9.224 G^2.

We neither agree with the second moment values obtained by Gupta *et al.*,[7] nor with the decrease of the second moment around 320 K that they observed. We are also at variance with them about the calculated intra- and inter-molecular second moments. (We have taken however approximately the same values for the bond lengths and angles: C—C: 1.40 Å; C—H: 1.08 Å; C—N: 1.42 Å; N—H: 1.01 Å; H—N—H: 107°). On the other hand, we agree with their conclusion that "above 350 K, the reduced second moment value confirms the rotation of the NH_2 group". But this motion is present well below 350 K. It is only at about 220 K that this motion seems too slow to narrow the resonance line. Our relaxation times measurements corroborate this result.

Relaxation times T_1, $T_{1\rho}$, T_{1D} ***(Figures 6 and 7)*** The temperature dependence of the three relaxation times involves the presence of one motion whose mean correlation time varies from $\sim \omega_1^{-1}$ ($\sim 10^{-6}$ *s*) at ambient temperature up to ω_0^{-1} ($\sim 10^{-8}$ *s*) just below the melting point. The hindering energy value, associated with this motion, differs according

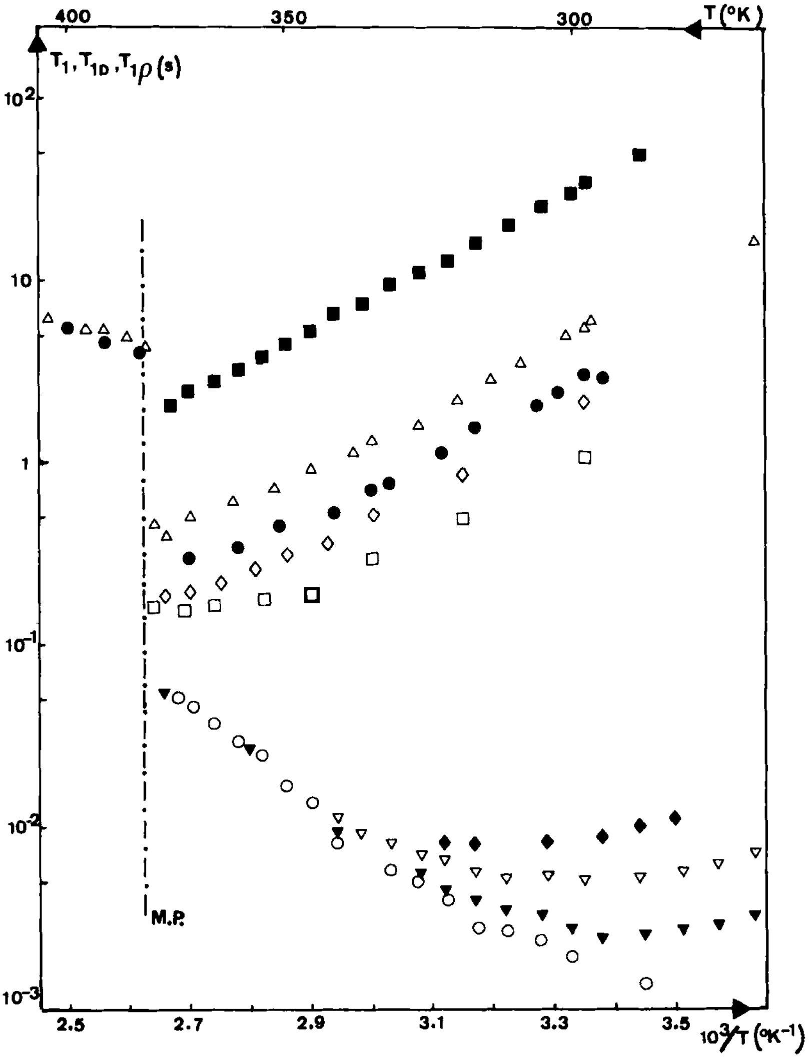

FIGURE 6 T_1, $T_{1\rho}$ and T_{1D} temperature dependence in β-naphthylamine T_1: ■, 90 MHz; Δ, 32 MHz; ●, 20 MHz; ◇, 15 MHz; □, 10 MHz. $T_{1\rho}$: , 60 MHz; ◆, 15.4 G; ▽, 9.4 G; ▼, 3.5 G. T_{1D}: ○, 90 MHz. (M.P. melting point).

to the NMR parameter chosen. From T_1 relaxation time, we obtain a value of 33.0 ± 2 kJ mole^{-1}, for this energy, whereas from T_{1D} experimental points above 340 K, the value is 47.0 ± 2 kJ mole^{-1}, and below 320 K it is approximately 30.0 ± 2 kJ mole^{-1}. Such differences are distinctly larger than the inaccuracy of the measurements.

Moreover, the $T_{1\rho}$ minima experimental values are higher, from a

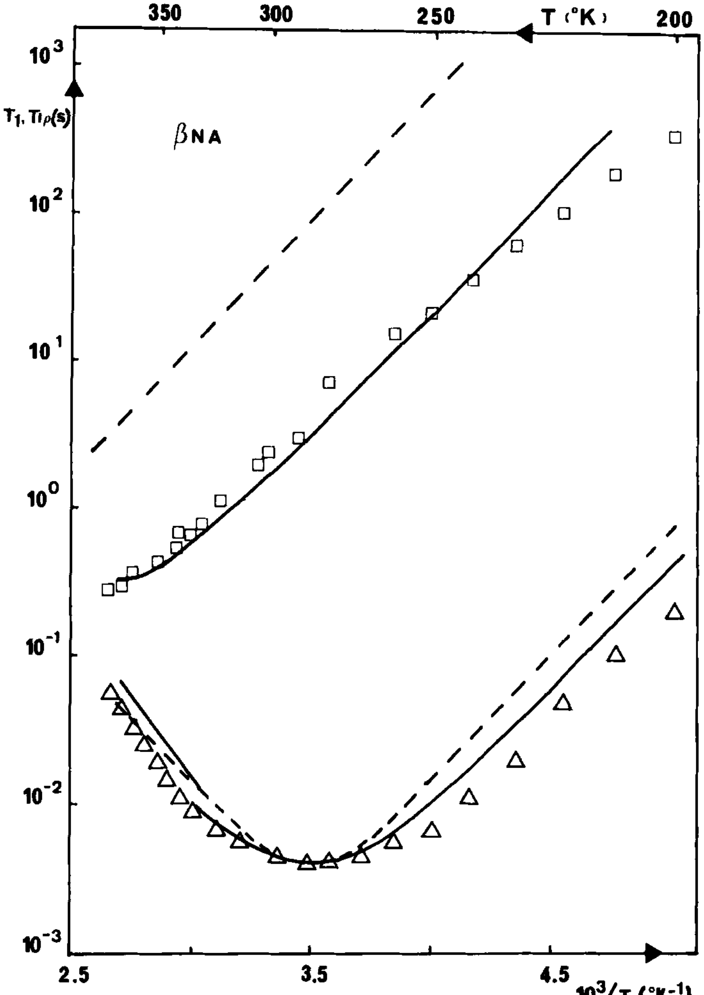

FIGURE 7 T_1 and $T_{1\rho}$ low temperature dependence in β-naphthylamine. Measured values: □, T_1 30 MHz; Δ, $T_{1\rho}$ 30 MHz; 9.4 G. The solid lines are drawn, using a Cole-Cole distribution of the correlation time $\tau_c(\alpha = 0.5$ below 330 K and $\alpha = 0.29$ above). The dotted lines are derived from the B.P.P. theory. The calculated values are fitted to the $T_{1\rho}$ minimum experimental point. (M.P. melting point).

factor greater than 2.5 to the calculated ones provided for by the B.P.P. theory, assuming a single correlation time and a single activation energy. The ratio of T_1 and $T_{1\rho}$ relaxation times is indeed given by Ref. 20a:

$$T_{1\min}/T_{1\rho\min} = 0.263\ (\omega_0/\omega_1) \qquad (5)$$

So, one should obtain, at 15 MHz, a T_1 minimum value equal to 500 ms, from the $T_{1\rho}$ minimum (#8.0 ms) for $H_1 = 14.5$ G, whereas the experimental T_1 at this resonance frequency is lower than 200 ms at the melting point, and the minimum is not still attained. This disagreement cannot be explained by a too high local field. The previous relation (5) requires a local field negligible compared to H_1. It is well satisfied ($H_{\text{local}} \simeq \sqrt{M_2/3} = 1.87$G). Besides, we obtain the same result, if we use the $T_{1\rho}$ minimum (4 à 5 ms) for $H_1 = 9.4$ G. The origin of this discrepancy could be due to the existence of two distinct motions with two different energies. A somewhat related behavior of NMR parameters T_1 and $T_{1\rho}$, on the high temperature side, has been already observed, in H_2S crystalline low temperature phase.[20b] This molecule can rotate by jumps of 90 or 180 degrees through two different potential barriers, owing to different minimum values of the potential energy. It might be that the NH_2 group is in a fairly comparable situation. However the $T_{1\rho}$ measurements below ambient temperature (Figure 7) don't show a second minimum. A single $T_{1\rho}$ minimum exists up to 200 K. This minimum is fairly broad, wider than the BPP theory provides (dotted line

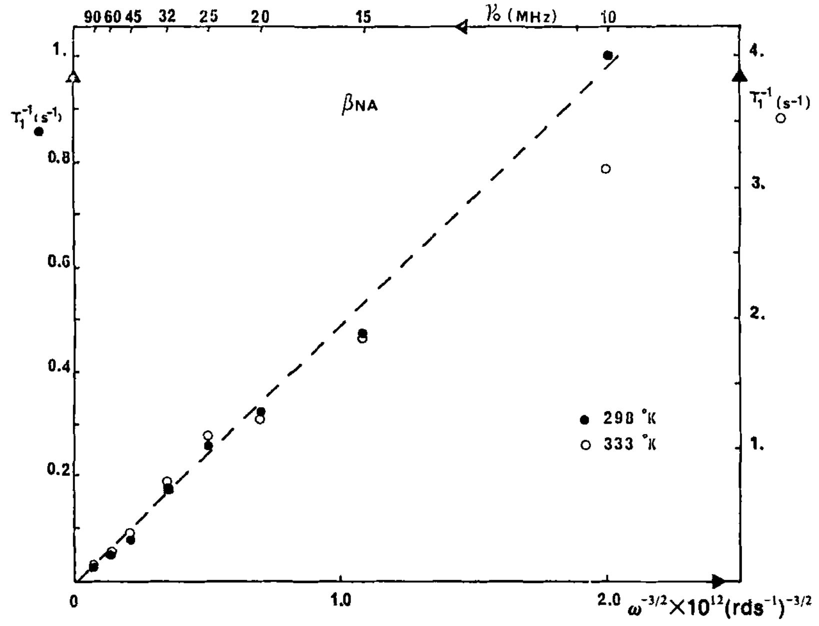

FIGURE 8 The frequency dependence of the spin-lattice relaxation rate in β-naphthylamine at 298 and 333 K.

in Figure 7). The explanation comes from a rather large distribution of the correlation times of the motion considered here.

This hypothesis is highly corroborated by the frequency dependence of the spin lattice relaxation rate at 298 and 333 K (Figure 8). We note a strict linear dependence on $\omega_0^{-1,5}$ (ω_0: resonance pulsation) at the two temperatures (however, at 333 K, this dependence is not quite verified at low frequencies, showing that the condition $\omega_0\tau_c \gg 1$ is no more satisfied). Such a variation can be explained by a Cole-Cole distribution, which provides that T_1, when $\omega_0\tau_c \gg 1$ is satisfied, varies in direct ratio[21] to $\omega_0^{2-\alpha}$. α is the parameter of the distribution ($\alpha = 0$, in absence of distribution). Here therefore $\alpha = 0.5$ at the two temperatures.

The expressions of T_1 and $T_{1\rho}$ are given by Ref. 21:

$$T_1^{-1} = \frac{C}{2\omega_0}\cos\left(\alpha\frac{\pi}{2}\right)\left|\frac{1}{\mathrm{ch}|(1-\alpha)\,\mathrm{Log}\,\omega_0\tau_c| + \sin\left(\alpha\frac{\pi}{2}\right)} + \frac{2}{\mathrm{ch}|(1-\alpha)\,\mathrm{Log}\,2\omega_0\tau_c| + \sin\left(\alpha\frac{\pi}{2}\right)}\right| \tag{6}$$

$$T_{1\rho}^{-1} = \frac{C}{4}\cos\left(\alpha\frac{\pi}{2}\right)\left|\frac{3}{2\omega_1}\,\frac{1}{\mathrm{ch}|(1-\alpha)\,\mathrm{Log}\,2\omega_1\tau_c| + \sin\left(\alpha\frac{\pi}{2}\right)} + \frac{5}{\omega_0}\,\frac{1}{\mathrm{ch}|(1-\alpha)\,\mathrm{Log}\,\omega_0\tau_c| + \sin\left(\alpha\frac{\pi}{2}\right)} + \frac{1}{\omega_0}\,\frac{1}{\mathrm{ch}|(1-\alpha)\,\mathrm{Log}\,2\omega_0\tau_c| + \sin\left(\alpha\frac{\pi}{2}\right)}\right| \tag{7}$$

As $\omega_1 \ll \omega_0$, $T_{1\rho}$ is minimum for $\omega_1\tau_c = 0.5$, just like in absence of distribution, and amounts, for $\alpha = 0.5$:

$$\left(T_{1\rho\min}\right)^{-1} = 0.414\,\frac{3C}{8\omega_1}$$

From $\omega_1 = 2.5\ 10^5$ ($H_1 = 9.4$ G) and $T_{1\rho\min} = 4\ 10^{-3}\ s$, we deduce $C = 4.05\ 10^8\ s^{-2}$ and $\tau_c = 2\ 10^{-6}\ s$ at the temperature of the minimum.

It follows that the modulated part of the second moment $M_{2\mathrm{mod}}$,

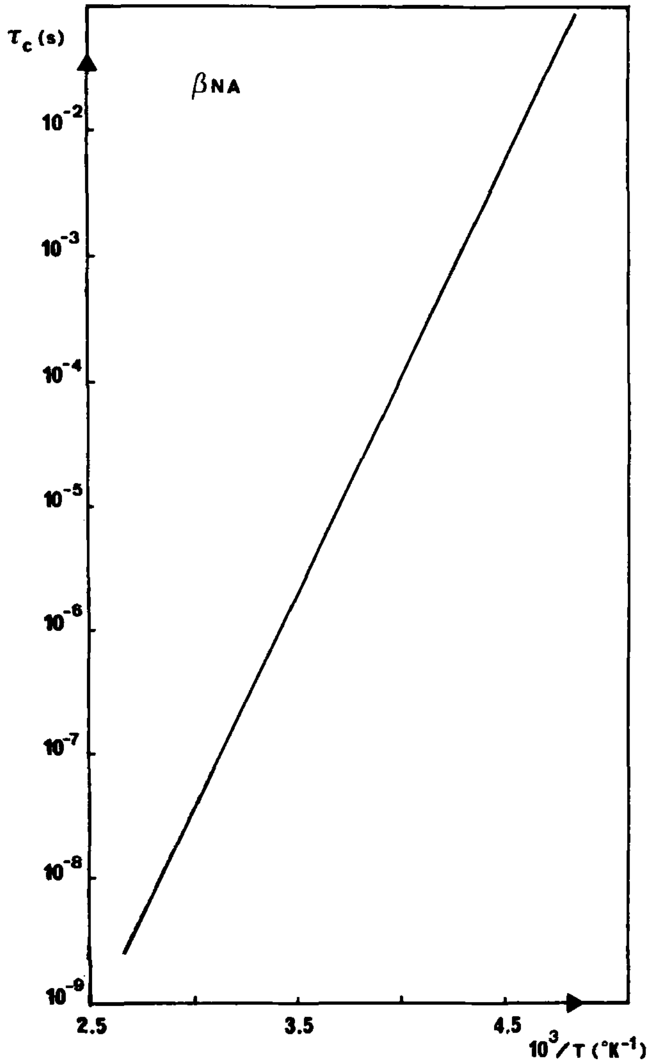

FIGURE 9 The temperature dependence of the mean correlation time for the jump of protons in the amino group of β-naphthylamine.

given by $C = \frac{2}{3}\gamma^2 M_{2\text{mod}}$, is equal to 0.85 G^2. This value is plainly too low to correspond to an amino group rotation with more than two positions (see Table II). It seems therefore that the motion considered is rather composed of jumps of 180 degrees.

The actual activation energy associated with this motion must be equal to $33/1\text{-}\alpha = 66$ kJ mole^{-1}. This value is found again from the slopes of the T_1 dispersion curves.

For $\omega_0\tau_c \gg 1$, Eq. (6) gives:

$$T_1^{-1} = 1.707\ C\ \omega_0^{-3/2}\ \tau_c^{-1/2} \tag{9}$$

If we assume an Arrhenius law for the correlation time, $\tau_c = \tau_{c\infty} \exp(E_a/\mathrm{RT})$, the ratio of the slopes at the two temperatures 333 and 298 K, experimentally equal to 4, is given by:

$$4 = \exp \frac{E_a}{2\mathrm{R}} (0.356\ 10^{-3}) \tag{10}$$

from which, we obtain $E_a = 64.8$ kJ mole^{-1}. Therefore, we can write for the correlation time:

$$\tau_c = 1.75\ 10^{-18} \exp(66\ 10^3/\mathrm{RT}) \tag{11}$$

τ_c values given by (11) are plotted on the Figure 9. Then we can calculate the slopes of the dispersion curves: 8.65 10^{11} s^{-3} at the ambient temperature and 3.55 10^{12} s^{-3} at 333 K. The experimental values are respectively 1.0 10^{12} s^{-3} and 4 10^{12} s^{-3}. This agreement is quite good, if we consider the simplicity of the model and the relative precision of the T_1 and $T_{1\rho}$ measurements ($\simeq$10% for T_1; $\simeq$20% for $T_{1\rho}$). We have tried to fit the T_1 and $T_{1\rho}$ experimental curves using the relations (6), (7) and (11), with $\alpha = 0.5$ below 330 K and $\alpha = 0.29$ above this temperature. This last value for α is derived from the slope of $T_{1\rho}$ and T_{1D} curves in the high temperature range. The result is shown on Figure 7 by full lines. We note a good agreement for the spin lattice relaxation time. The slope of the T_1 calculated curve is almost constant, even at high temperature, because the decrease of the parameter α in this range allows to balance the approach of the T_1 minimum. For $T_{1\rho}$, the agreement is less satisfactory. However this model expresses properly the shape of the $T_{1\rho}$ curve around its minimum.

We have also plotted in this figure, by dotted lines, the "best" fit obtained with the B.P.P. model. The discordance is obvious, specially for the T_1.

Therefore, we can explain the relaxation data by a large distribution of correlation times, which narrows about forty degrees before the melting point.

CONCLUSION

For the β-naphthol compound, we have observed two transitions of the first order in the temperature range studied. The low temperature transition, around 350°K, seems correlated with the frequency independent relaxation contribution, therefore to a very fast motion (OH vibration for example) or to impurities or defects. It leaves the fast hydroxyl proton rotation unaffected, already present below the transition with a hindering energy of ~19.5 kJ mole^{-1} and mean correlation time τ_{cj} of ~5 10^{-7} s at ambient temperature. Above this first transition, a very slow motion appears with a high activation energy ~116 kJ mole^{-1}. We cannot define this motion from our results. It could be, at a very weak frequency (~20 s^{-1} at 365 K), the same molecular motion that the one observed in the high temperature phase, above the second transition (~385 K). *Even in this phase, this molecular motion is too slow to narrow* the resonance line.

For the β-naphthylamine, from 200 K up to the melting point, only one motion is observed: the rotation of the amino group around its axis, probably by jumps of 180°. The activation energy is much greater than the value given by Gupta[7] and amounts ~66 kJ mole^{-1}. A large distribution of correlation times seems present in the whole temperature range.

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