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# Polymorphism and dynamics of MBBA as studied by NMR

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We report proton NMR experiments on the liquid crystal material *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA) at 100 MHz in the temperature range 110–350 K. The phase diagram was investigated by means of second moment and spin-lattice relaxation measurements in order to establish connections between dynamics and phase transitions. The results show that in a slow cooling experiment, two processes contribute to the relaxation, a slow ethyl group motion together with reorientation of the methyl groups. For the glassy nematic state, as well as for the phases observed after reheating a quenched sample, only methyl rotation is observed. The correlation times of these various mechanisms were determined and the results compared with those obtained by previous NMR and dielectric analysis.

## 1. Introduction

Nuclear spin-lattice measurements have proven to be one of the most useful techniques in studying molecular motions in liquid crystals [1]. The main effort in these studies has been devoted to observing nuclear magnetic relaxation times for nematogens and smectic liquid crystal materials. In the phases of these materials, the relaxation mechanism for protons were found to be due to order director fluctuations, self-diffusion and rotational motions and the discussion involved was based on the frequency and temperature dependence of the relaxation rates [2].

A classical object of such analysis is [*N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline] (MBBA) which forms a nematic phase at room temperature and is considered as a model compound for liquid crystal studies. A schematic picture of MBBA is shown in figure 1. On cooling, MBBA exhibits a large variety of solid polymorphic modifications. In particular it has been demonstrated that the nematic phase of MBBA can be quenched-in by rapid cooling leading to a glassy nematic-like liquid crystal with a glass transition temperature  $T_g = 205$  K. By a slow reheating of this glassy state, the occurrence

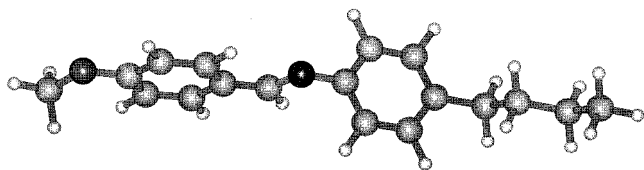


Figure 1. A schematic picture of MBBA:  $\text{CH}_3\text{-O-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-C}_4\text{H}_9$ .

of a variety of successive phases has been demonstrated by X-ray, DSC, Raman, and dielectric experiments [3–6]. The resulting phase diagram at atmospheric pressure is represented in figure 2.

In the present paper we have used proton NMR in order to investigate the polymorphism and the dynamics of the low temperature phases of MBBA. The sensitivity of NMR to molecular motions affords a useful probe into the dynamics of liquid crystals by the analysis of

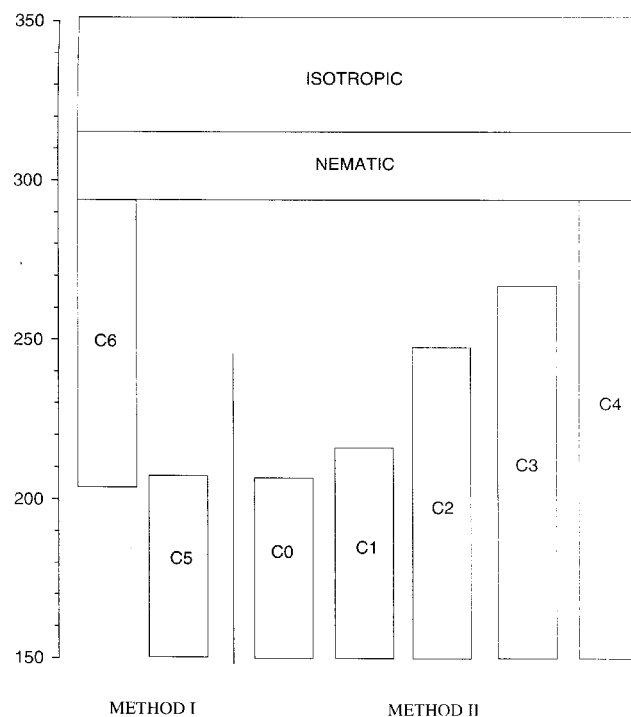


Figure 2. Phase diagram of MBBA.

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the temperature dependence of the NMR absorption spectrum and spin-lattice relaxation time  $T_1$ . Previous NMR analyses have revealed the existence of several phases, called metastable and stable [7–10]. Therefore the lack of a complete knowledge of the polymorphism of MBBA leads to an inaccurate description of molecular motions occurring in the different phases. Taking advantage of the procedure well defined by X-ray experiments, we have focused attention on understanding the dynamics parameters obtained by NMR in order to establish connections between molecular motions and phase transitions observed in MBBA.

## 2. Experimental

MBBA was synthesised in the laboratory and sealed under vacuum in glass tubes. The NMR experiments were carried out using a Bruker spectrometer operating at 100 MHz. In the experiments, the sample was first heated to 330 K, corresponding to the isotropic state, and afterwards slowly cooled into the nematic phase. Measurements were then performed as a function of temperature by two different procedures deduced from a previous analysis [3]. Method I required slow cooling of the sample from the nematic phase to the low temperature solid crystalline phases (C6 and C5). Slow cooling was accomplished by lowering the temperature in five degree intervals and waiting ten minutes for the sample to come to thermal equilibrium before each experiment. In method II, an MBBA sample was rapidly quenched from the nematic state, at maximum speed, well below the glass transition temperature ( $T_g \cong 205$  K) where the sample became amorphous (C0). According to the phase diagram depicted in figure 2, subsequent slow heating of the glassy phase above  $T_g$  produces four phases (C1, C2, C3, C4) before the nematic state is reached. As soon as a new phase formed, an annealing of several hours was carried out in order to insure complete transformation of the sample into this new state. Then the sample was cooled to the lowest temperature of the measurements (110 K) and experiments were performed on slowly increasing the temperature.

$^1\text{H}$  Zeeman spin-lattice relaxation time  $T_1$  was measured with an inversion recovery pulse sequence ( $\pi, \tau, \pi/2, D_0$ ), typically using 16–18 values of  $\tau$ , and a recycle delay  $D_0 > 5T_1$ . In all phases, the magnetization recovery was, within experimental error, exponential and could be described by one time constant. The second moment  $M_2$  was determined by using a polynomial procedure developed for the direct calculation of the second moment from the free induction decay (FID) in the time domain. Except in C2 where a rather more complex line-shape was observed leading to unreliable values of  $M_2$ , the resonance was found to be described well at all temperatures by a Gaussian function. The

precision of the NMR data lies between  $\pm 5\%$  for  $T_1$  and  $\pm 15\%$  for the second moment determination. The temperature was controlled by a conventional gas flow system over the temperature range 110–330 K, to within  $\pm 1$  K.

## 3. Results and discussion

### 3.1. Line-shape analysis

First we used proton NMR line-shape analysis in order to investigate the polymorphism diagram of MBBA. Starting from the isotropic phase, a complete assignment of the proton spectrum was made and the purity of the sample was checked. At 300 K, the proton NMR spectrum is characteristic of liquid crystal nematic phases with a central component and two wings arising, respectively, from the end chain protons and the phenyl ring protons [9]. This structure, resulting from a partial averaging of dipole–dipole interactions by molecular motion, is no longer found in the low temperature phases where a single broad line without any structural feature is observed. In order to explore the polymorphism diagram of MBBA by NMR, we have measured the second moment of the proton NMR resonance line. It is well known that, in a crystalline powder sample, molecular motion leads to a narrowing of the NMR absorption curve. The resulting variation of the second moment is characteristic of the type of motion carried out by the spins and allows a qualitative study of this motion together with an investigation of the polymorphism. The temperature variation of  $M_2$  is represented in figure 3. As shown in figure 3, the strength of  $M_2$  is different in each of the phases studied, and these can then be clearly identified by line-shape analysis.

By using method I (slow cooling), an almost linear variation of  $M_2$  with temperature is observed in the temperature range corresponding to C6. The phase transition C5–C6 is related to an important change in the slope of the curve of  $M_2$  versus  $T$  at 205 K. This value is in good agreement with previous results [3, 4]. In C5,  $M_2$  increases and then displays a plateau of about  $10.5 \text{ G}^2$  down to 120 K.

In method II (fast cooling),  $M_2$  values were found to be larger at all temperatures than those measured by the slow cooling experiments. Secondly, an increase of  $M_2$  occurred in the order C0, C1, C3. With reference to figure 3, in C0–C1, an almost linear increase of  $M_2$ , with a more steep slope of  $M_2$  versus  $T$  in C0, is observed down to 110 K where the experimental second moment is found to be similar in both phases:  $12.5 \text{ G}^2$ . In C3,  $M_2$  displays first a plateau value of  $13.5 \text{ G}^2$  up to 210 K, before diminishing on approaching the temperature range corresponding to the transition to C4 ( $T \cong 265$  K). From a dynamical point of view, this decrease corresponds to an increase in the frequency of molecular

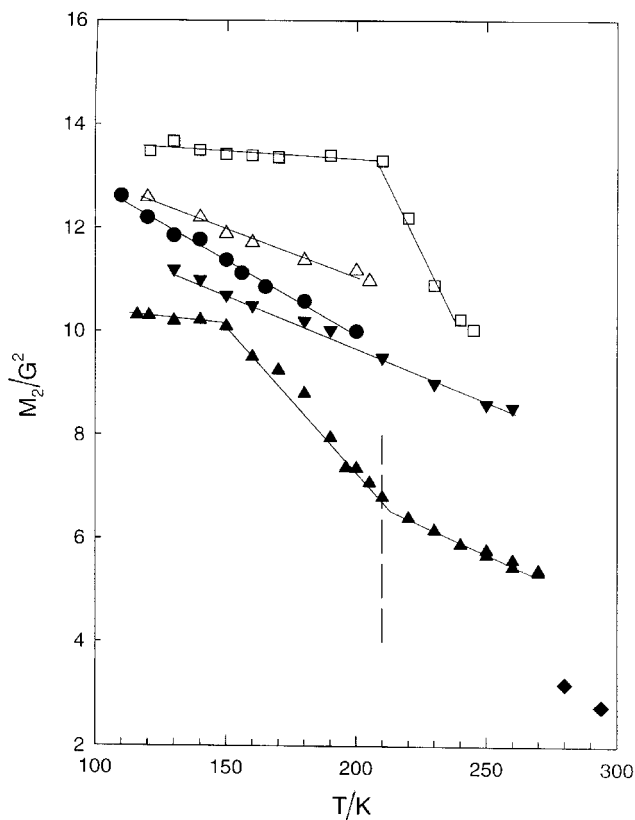


Figure 3. Second moment of the proton line versus temperature: method I (N;  $\blacklozenge$ ), (C6–C5;  $\blacktriangle$ ); method II (C0;  $\bullet$ ), (C1;  $\triangle$ ), (C3;  $\square$ ), (C4;  $\blacktriangledown$ ). Vertical dashed line indicates the transition temperature of C5–C6 at 210 K.

motions in C4, and we could suppose that on going to a higher temperature, the C3–C4 phase transition is related to release of a new motion. In C4, values obtained for  $M_2$  are intermediate between these of C0 and C5–C6. In summary, a progressive decrease of molecular disorder is observed by following the phase transition sequence: C6–C5–C0–C1–C3, before going to an intermediate disordered state in C4.

The numerical values calculated for a rigid lattice and for different possible states of internal reorientation in MBBA such as rotation of methyl groups and reorientation of the  $\text{CH}_3\text{--O}$  group are, respectively, 19.5, 15.0 and 11.7  $\text{G}^2$  [7, 11]. For a molecule that has only its molecular axis oriented,  $M_2$  was found to be 3.3  $\text{G}^2$  in good agreement with  $M_2$  results for the nematic phase. Comparison of the calculated second moment with the experimental data leads to the following conclusions. The rigid lattice condition is not yet fulfilled at 120 K. In C3, the plateau of 13.5  $\text{G}^2$  roughly agrees, within experimental error, with the theoretical value obtained when only  $\text{CH}_3$  end group rotations are present. For the glassy and reheated phases C0–C1, the experimental second moment of about 12.5  $\text{G}^2$  at 120 K should indicate that reorientation of

more than just the terminal  $\text{CH}_3$  groups is occurring in these phases. This additional motion could be a phenyl ring flipping motion or more probably, due to considerations of steric hindrance, a slow motion of the end chains, becoming progressively locked on going to the lowest temperatures. Therefore as a linear variation is observed in all these phases except C3, it is difficult to ascribe to a particular group the motions responsible for the second moment reduction. In conclusion, by means of NMR line-shape investigations we have confirmed the existence of a rather complicated polymorphism diagram for MBBA, and moreover have demonstrated that molecular motions are different in each of the low temperature phases of this compound.

### 3.2. Spin-lattice relaxation times analysis

#### 3.2.1. Slow cooling (method I)

The temperature dependence of the proton spin-lattice relaxation time  $T_1$  of MBBA obtained by method I is represented in figure 4. On cooling,  $T_1$  suddenly increases by about one order of magnitude near 290 K, which corresponds to the nematic–solid phase transition. Then

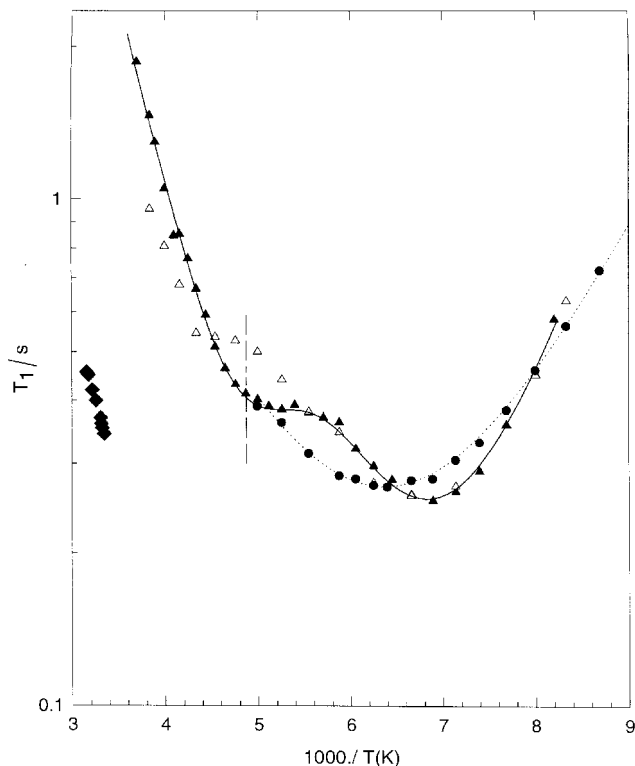


Figure 4. Variation of  $^1\text{H}$   $T_1$  versus  $10^3/T$  (K) for the phases: nematic ( $\blacklozenge$ ), C6–C5 on cooling ( $\blacktriangle$ ) [heating ( $\triangle$ )], and C0 ( $\bullet$ ). The continuous curves correspond to the refinement carried out with models described in the text for the phases: C6–C5 (—), and C0 (.....). Vertical dashed line indicates the transition temperature of C5–C6 at 210 K.

$T_1$  decreases gradually with decreasing temperature reaching a shallow unresolved minimum at  $\approx 188$  K (380 ms), while a deeper minimum is observed at  $\approx 145$  K (250 ms). No discontinuity is perceived at the temperature corresponding to the C6–C5 phase transition, which occurs with an important hysteresis.

The temperature dependence of spin-lattice relaxation rate was interpreted by using a model developed for the analysis of polycrystalline ethylbenzene by Beckmann [12]. This model supposed that the main contribution to the relaxation arises from intramolecular dipole–dipole interactions modulated by reorientation of both the groups methyl(s) and ethyl(s). The corresponding expression for  $T_1$  is divided into three terms, referring to: methyl group reorientation (m), ethyl group reorientation (e) and a contribution from ethyl and methyl interaction (me):

$$\frac{1}{T_1} = \left( \frac{1}{T_1^m} + \frac{1}{T_1^e} + \frac{1}{T_1^{me}} \right). \quad (1)$$

If the orientations are characterized by the correlation times  $\tau_m$ ,  $\tau_e$  and  $\tau_{me}$ , one can find:

$$\frac{1}{T_1^m} = C_m \left[ \frac{2}{9} g(\omega, \tau_m) + \frac{2}{9} g(\omega, \tau_e) + \frac{19}{36} g(\omega, \tau_{me}) \right] \quad (2)$$

$$\frac{1}{T_1^e} = C_e [g(\omega, \tau_e)] \quad (3)$$

$$\frac{1}{T_1^{me}} = C_{me} [g(\omega, \tau_{me})] \quad (4)$$

with

$$C_m = \frac{3n}{N} \frac{6}{10} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma^4 \hbar^2}{r_m^6} \quad (5)$$

$$C_e = \frac{2n'}{N} \frac{9}{40} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma^4 \hbar^2}{r_m^6} \quad (6)$$

$$C_{me} = \frac{6n}{N} \frac{9}{20} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma^4 \hbar^2}{r_{me}^6} \quad (7)$$

where  $N$  is the number of protons in the molecule,  $n$  and  $n'$  are the number of protons in the methyl and ethyl groups, respectively, contributing to the relaxation process. The distances  $r_m$  and  $r_{me}$  are, respectively, the intramolecular proton distance in the methyl group and the distance between ethyl–methyl protons in the same molecule.

The function  $g$  is given by:

$$g(\omega, \tau_i) = \frac{\tau_i}{1 + \omega^2 \tau_i^2} + \frac{4\tau_i}{1 + 4\omega^2 \tau_i^2} \quad (8)$$

where  $\omega = \gamma_H H_0$  is the Larmor frequency. The correlation time  $\tau_{i=m,e}$  is related to the temperature by an Arrhenius relationship:

$$\tau_i = \tau_{\infty i} \exp(E_i/kT) \quad (9)$$

which introduces the activation energy  $E_i$  and the pre-exponential factor  $\tau_{\infty i}$ . The superposition correlation time  $\tau_{me}$  is given by:

$$\frac{1}{\tau_{me}} = \frac{1}{\tau_e} + \frac{1}{\tau_m}. \quad (10)$$

For MBBA, we have supposed, according to a previous NMR analysis reported for similar compounds, that the only possible motions involve one ethyl and two methyl groups. On this assumption we have performed a numerical evaluation of the coefficient  $C_i$  by using equations (5–7) with values generally admitted for the internuclear distances:  $r_m = 1.80$  Å,  $r_{me} = 2.50$  Å [12]. The best fit of experimental data, obtained by using equation (1) is shown as a solid line in figure 4, while the fitting parameters are listed in the table. As displayed in figure 4, the data were successfully fitted in this manner. Moreover, except for  $C_{me}^{\text{exp}}/C_{me}^{\text{calc}} \approx 1.2$ , the fitted ratios  $[C_i^{\text{exp}}/C_i^{\text{calc}}]_{i=m,e}$  are very close to unity as indicated in the table. This allowed us to check the validity of the dynamical model used and we conclude that only methyl groups and one ethyl group are reorienting in these solid phases. As seen in the table, the activation energy of  $9.4 \pm 0.5$  kJ mol<sup>-1</sup> found for the motion of methyl groups is consistent with the barrier of  $10.87 \pm 0.83$  kJ mol<sup>-1</sup>

Table. Activation energies ( $E$ ) and inverse frequency factors ( $\tau_{\infty}$ ) derived for the motions in different phases of MBBA from the spin relaxation studies.

Phase	$\tau_{\infty}/s$	$E/\text{kJ mol}^{-1}$	$C^{\text{exp}}/C^{\text{calc}}$	Motion
C6	$(7.9 \pm 0.3) \times 10^{-14}$	$16 \pm 0.2$	1.04	Ethyl rotation
C5	$(4.3 \pm 0.2) \times 10^{-13}$	$9.4 \pm 0.5$	1.00	Methyl rotation
C0	$(8.1 \pm 0.1) \times 10^{-12}$	$6.26 \pm 0.07$	0.75	Methyl rotation
C1	$(1.1 \pm 0.13) \times 10^{-11}$	$5.95 \pm 0.04$	0.79	Methyl rotation
C2	$(6.4 \pm 0.1) \times 10^{-12}$	$6.17 \pm 0.08$	0.88	Methyl rotation
C3	$(1.12 \pm 0.2) \times 10^{-12}$	$9.3 \pm 0.2$	0.82	Methyl rotation
C4	$(1.7 \pm 0.14) \times 10^{-12}$	$8.57 \pm 0.03$	0.86	Methyl rotation

determined by NMR in solid *n*-alkanes [13]. For the ethyl group motion, the activation energy of  $16 \pm 0.2 \text{ kJ mol}^{-1}$  indicates that ethyl group reorientation is relatively hindered in the solid state of MBBA. This intra-ethyl barrier is compatible with the value of  $17.15 \text{ kJ mol}^{-1}$  deduced from entropy and heat capacity measurements on ethylbenzene [14]. Besides, these contributions are strongly dependent on molecular packaging and consequently further discussion would require a detailed structural analysis of these phases by X-ray experiments.

In summary, the correlation times obtained by NMR versus  $1000/T$  are represented in figure 6. As the temperature is decreased a progressive slowing of the ethyl group motion is observed on going through C5. The phase transition is probably related to this variation in the rotation dynamics of the end chains. However this variation, as seen in the  $M_2$  analysis where no gap is observed, is progressive and the ethyl motion is not completely frozen at the phase transition temperature. On reheating, the release of this motion is certainly responsible for the hysteresis observed in  $T_1$  values around the phase transition temperature.

### 3.2.2. Glassy nematic states and reheating of the quenched phase (method II)

The proton spin-lattice relaxation time  $T_1$  of MBBA for the glassy-nematic phase C0 is given in figure 4, the  $T_1$  values, measured on heating a rapidly quenched sample from 110 K, display a single and broad minimum. This minimum occurs at 157 K (270 ms) and can be clearly distinguished from those observed in C5. This distinct behaviour confirms the occurrence of a new phase called C0 according to the polymorphism diagram of figure 2. Moreover, as generally observed in glassy phases, a broadening of the curve  $T_1$  versus  $1000/T$  is seen, leading to a significant decrease of the activation energy of the motions involved.

The results of measurements obtained upon heating a quenched sample, and after an annealing of several hours above the phase transition temperatures determined by DSC, are presented in figure 5. In C1 the main differences from the results obtained in C0 involve firstly a small shift of the minimum reached at 163 K (260 ms) and secondly lower  $T_1$  values on the high temperature side of the minimum. For C2,  $T_1$  decreases gradually upon increasing the temperature from 110 K to 130 K (with lower values than those measured for C0–C1) reaching a minimum at 147 K (230 ms); it then increases upon heating, rejoining the results obtained in C0. In C3 and C4, a rather similar behaviour is observed, and  $T_1$  displays a single minimum at approximately the same temperature: 166 K (C3), 163 K (C4), but with different values of 250 and 237 ms, respectively.

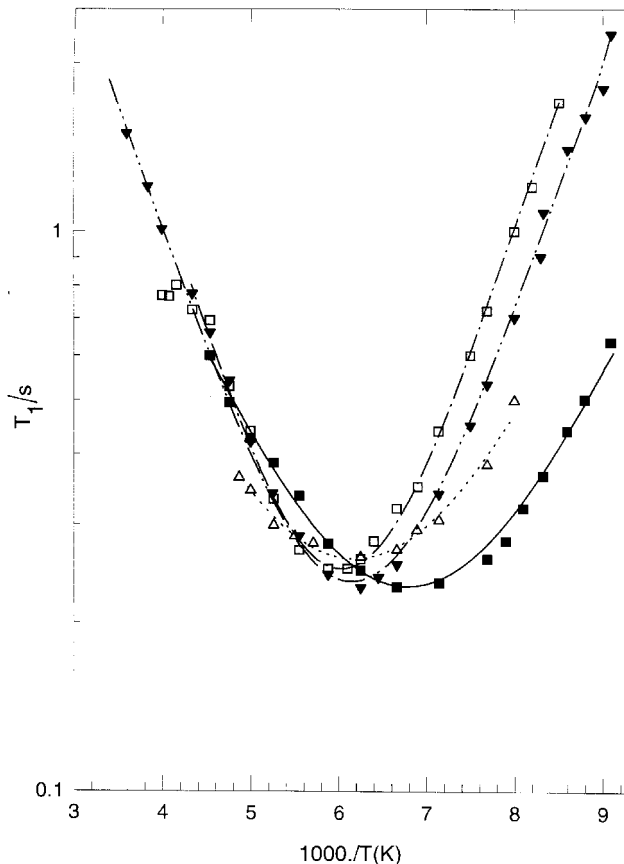


Figure 5. Variation of  $^1\text{H}$   $T_1$  versus  $10^3/T$  (K) for the phases: C1 ( $\Delta$ ), C2 ( $\blacksquare$ ), C3 ( $\square$ ), C4 ( $\blacktriangledown$ ). The continuous curves correspond to the best refinements carried out with equation (11): C1 (.....), C2 (—), C3 (— — —) and C4 (— · — ·).

In summary, for each of the phases obtained by method II, a single minimum occurs in the range  $145 \text{ K} < T < 170 \text{ K}$ . The depth of these minima, together with the symmetric V-shaped temperature dependence of  $T_1$ , indicates that the spin-lattice relaxation rates are governed by the threefold reorientation of methyl groups. In this case, if we assume that all other protons in the solid are relaxed by rapid spin exchange to and from the methyl groups, and considering that the ethyl group is fixed, we have  $\tau_e^{-1} = 0$ ,  $\tau_{me} = \tau_m$ , and equation (1) is reduced to the well known expression [15, 16]:

$$\frac{1}{T_1} = Cg(\omega, \tau_m) \quad (11)$$

with:

$$C = \frac{9}{20} \frac{n}{N} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma^4 \hbar^2}{r_m^6} \quad (12)$$

A good fit of equation (11) to the experimental data is given in figures 4 and 5, and the motional parameters characterizing the fits are listed in the table. In the whole temperature range studied, the model resulting from a threefold rotation of methyl groups fits the experimental relaxation rates very well. The deviation from unity of the ratios  $C^{\text{exp}}/C^{\text{calc}}$  implies that intermolecular interactions play a more important role in these phases. Moreover, the differences observed for the fitted values suggest a modification of the steric hindrance induced by the phase transitions. As seen in the table, the barriers for methyl reorientation are found in the range 6–9.5 KJ mol<sup>-1</sup>. The  $E_a$  values are approximately the same, within error bars, in C0, C1 and C2. This result is consistent with X-ray experiments, where it has been proposed that the local arrangement is retained during the transitions and that C1 and C2 are both smectic phases with different nature: smectic A and smectic C, respectively [3].

As shown in figure 6, the correlation times of C0 and C1 were found to be practically identical. Despite the fact, that the nature of these phases is different, NMR results confirm that the molecular packing (which governs the end chain dynamics) of the glassy nematic phase is probably conserved on going to C1. In C0 the dynamical description is consistent with a previous dielectric analysis where it has been found that the motion of the O–CH<sub>3</sub> dipole axis lies in the frequency range 1–100 kHz [15, 16]. This motion can then be considered as a very slow

motion on the NMR time scale, and it has practically no influence on our relaxation rate measurements. This result also implies, according to the fact that an anti-parallel interdipole correlation was observed, that the movements of the butyl chains are very slow, or locked, which agrees very well with our NMR  $T_1$  results, since only a single minimum related to methyl threefold motions is perceived. On the other hand, in the C2 (smectic C) phase, the tilt of the molecular principal axis tends to increase slightly the frequency of end chain motions, resulting in a shift of the minimum to a lower temperature.

In the crystalline phase C3, which appears to be the less disordered phase of MBBA according to  $M_2$  analysis,  $E_a$  increases to approximately the same value as that determined for C5. However, as displayed in figure 6, the temperature dependence of the correlation times clearly indicates a slowing down of the frequencies of molecular motion in this phase. From X-ray analysis, we could suppose that C3 probably keeps a molecular packing close to that of smectic phases, the main difference being a reduction of the interlayer distance, which could be responsible for the slowing down of molecular motions by steric hindrance effects.

On going to C4, despite the fact that C4 has a completely different crystalline and textural behaviour, the correlation times were found to be almost identical to those obtained for C3 [3]. As the second moment of C4 is significantly lower than that of C3, a new motion probably takes place in this phase and according to the absence of a second minimum in the relaxation curve, this new motion still remains a slow motion on the NMR time scale. Moreover, as no relaxations were observed by dielectric analysis in the frequency range 0.3–300 kHz, we could suppose that the O–CH<sub>3</sub> axis is relatively locked in this phase [15]. However, as the dielectric experiments were performed in the absence of a reliable polymorphism diagram, it is difficult to ascribe the results of the measurements to a particular phase. More experiments (and in particular dielectric relaxation analysis of these phases) are needed in order to clarify the motional description of the low temperature phases of MBBA.

#### 4. Conclusion

The sensitivity of NMR offers an interesting method for the investigation of molecular motions in the low temperature phases of liquid crystals. In MBBA, we were able to characterize dynamically each phase previously observed by other techniques, since molecular packaging induces the existence of minima observed at different temperatures and with different magnitudes.

By a slow cooling experiment, two processes of relaxation were detected corresponding to rotations of

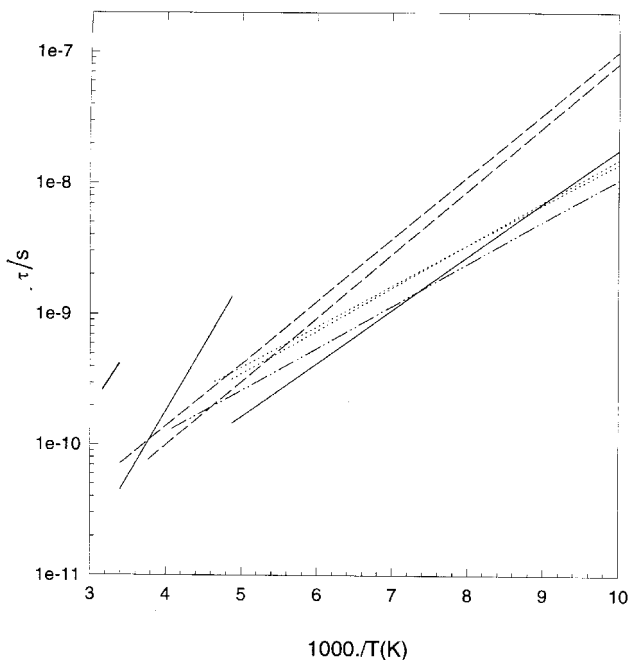


Figure 6. Temperature dependence of the correlation times obtained by NMR: method I (N–C6–C5; —); method II (C0–C1; ····), (C2; —·—·), (C3–C4; — — —).

ethyl and methyl groups. On the contrary, in the glassy nematic phase and in the phases observed after heating a quenched sample, only end group methyl rotations were detected.

From the motional parameters deduced from NMR analysis, three regions are observed:

- (1) one resulting from a slow cooling (C5–C6),
- (2) one corresponding to the glassy and nematic phases (C0–C1–C2),
- (3) one resulting from the crystalline phases (C3–C4).

However, in order to account for the second moment variation observed in some of these phases, slow motion(s) probably also exist. Therefore a distinction between the different possible motions would require more information than that available by proton NMR, and in particular experiments on partially deuteriated samples would probably give more details on the dynamics existing in these phases. To this end, further investigations, extended to involve dielectric experiments, are in progress in order to clarify the description of molecular motions in this compound.

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