

# DYNAMICAL BEHAVIOUR OF THE ALIPHATIC CHAINS OF 4,4'-DIHEXYLOXYAZOXYBENZENE IN THE NEMATIC PHASE. (\*)

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**ABSTRACT**—The proton spin-lattice relaxation time  $T_1$  has been measured as a function of frequency and temperature in the nematic phase of hexyloxyazoxybenzene completely deuterated on the benzene rings (6.OAB-D<sub>8</sub>). The results show that the aliphatic chains are dynamically coupled to the nematic director in a rather strong fashion ( $T_1 \sim \omega^{-1/2}$ ), and suggest that the average molecular conformation of 6.OAB-D<sub>8</sub> changes appreciably with temperature.

## 1—INTRODUCTION

Phenomenological properties of nematic liquid crystals have been extensively studied and are now rather well understood [1]. On the other hand, studies aimed to relate phenomenological properties to microscopic structure and dynamics are scarce.

In this paper, we pursue previous efforts to understand the internal order [2-4] and dynamics [5-9] of nematic materials, and concentrate our attention on the most studied homologous series of these mate-

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rials, i.e., 4,4'-dialkoxyazoxybenzenes (m.OAB, for short, where  $m=1, 2, \dots$  stands for the number of carbon atoms in the aliphatic chains).

In previous NMR studies related to the m.OAB series, only the first element (PAA, or 1.OAB) was considered, either normal or methyl-deuterated, and definite conclusions were only reached on the dynamics of the most rigid part of the molecule [6,7]. In particular, it was shown that the benzene skeleton of the molecule is strongly coupled to the long wavelength thermal fluctuations of the nematic director, which leads to a characteristic frequency dependence of the corresponding proton spin-lattice relaxation time  $T_1 \sim \omega^{1/2}$ . The dynamics of the terminal  $\text{CH}_3$  groups was indirectly considered in refs. [5] and [6], where it was concluded that the relaxation of these groups should *not* depend appreciably on the long wavelength thermal fluctuations. This conclusion has been recently confirmed by direct measurements of the proton  $T_1(T, \omega)$  on the same material, but now deuterated on the benzene rings (PAA- $\phi\text{D}_8$ , or simply PAA- $\text{D}_8$ ) so as to probe only the relaxation of the  $\text{CH}_3$  groups [9].

In this paper we will discuss a set of results obtained from systematic measurements of the proton spin-lattice relaxation time  $T_1$  as a function of Larmor frequency  $\omega$  and temperature  $T$ , over the nematic range of the element with  $m=6$ , deuterated on the benzene rings (6.OAB- $\text{D}_8$ ). This selective deuteration ensures that the measured values of  $T_1$  only contain contributions from the aliphatic chains, which are so *directly* probed.

In section 2 we give our experimental results and point out the techniques used in this work. In section 3 we discuss these results and try to answer the following questions: (i) how strong is the coupling of the flexible chains in higher homologs to the long-wavelength thermal fluctuations of the director; and (ii) can we get, from  $T_1$  measurements, some insight on the changes (if any) of the average conformation of the chains with temperature? Finally, in Section 4, we present our conclusions.

## 2 — EXPERIMENTAL RESULTS

The synthesis of 4,4'-dihexyloxyazoxybenzene- $\text{D}_8$  was carried out as follows [10]. First, by nitration of phenol- $\text{D}_6$  we got p-nitrophenol- $\text{D}_5$ , which was purified from o-nitrophenol by column chro-

matography (alumina, benzene). Addition of hexylbromide on *p*-nitrophenol in presence of potassium carbonate produced *p*-hexyloxy nitrobenzene- $D_4$ . This compound was treated by lithium aluminium hydride in dry ether at  $-70^\circ\text{C}$ . The excess of lithium aluminium hydride was then decomposed with sodium hydroxide and water. The residue was dissolved in acetic acid and after the addition of hydrogen peroxide, the solution was held at  $65^\circ\text{C}$  for 48 hours. The precipitate of 4,4'-dihexyloxyazoxybenzene- $D_8$  (yield = 75 %) was finally crystallised from ethanol giving pale yellow needles with melting point at  $81^\circ\text{C}$  and nematic-isotropic transition at  $129.5^\circ\text{C}$ .

After purification, the sample ( $\sim 0.3 \text{ cm}^3$ ) was introduced in a NMR quartz tube, degased and sealed under vacuum.

Measurements of the proton spin-lattice relaxation time  $T_1$  were performed at 25, 40, 56 and 90 MHz over the whole nematic range by using the  $\pi - \tau - \pi/2$  pulse sequence on a Bruker SXP/4-1000 spectrometer. The temperature of the sample was controlled to within  $\pm 0.3^\circ\text{C}$ , and the estimated error in the absolute value was less than  $1^\circ\text{C}$ .

The results of the measurements of  $T_1$  as a function of temperature are displayed in Fig. 1 for three working frequencies. The

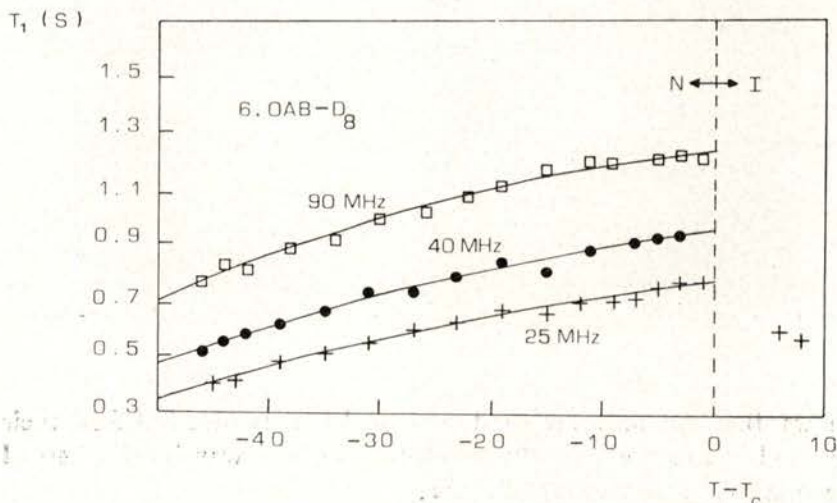


Fig. 1—Observed temperature dependence of proton spin-lattice relaxation time  $T_1$  in the nematic phase of 6.OAB- $D_8$  at 25, 40 and 90 MHz.

results obtained at 56 MHz are omitted for the sake of clarity of the figure.

An example of the frequency dependence of  $T_1$  is shown in Fig. 2, for  $T = 90$  and  $118^\circ\text{C}$ . It is seen that  $1/T_1 \sim \omega^{-1/2}$ ; this same behaviour was found at any other temperature within the nematic phase.

### 3 — DISCUSSION

The most striking feature of the results in figs. 1 and 2 is their qualitative resemblance with the results previously obtained for PAA [5]. We recall that PAA is a rather rigid molecule and that the present results strictly refer to the *aliphatic chains* of 6.OAB. The characteristic frequency dependence  $1/T_1 \sim \omega^{-1/2}$  displayed in fig. 2

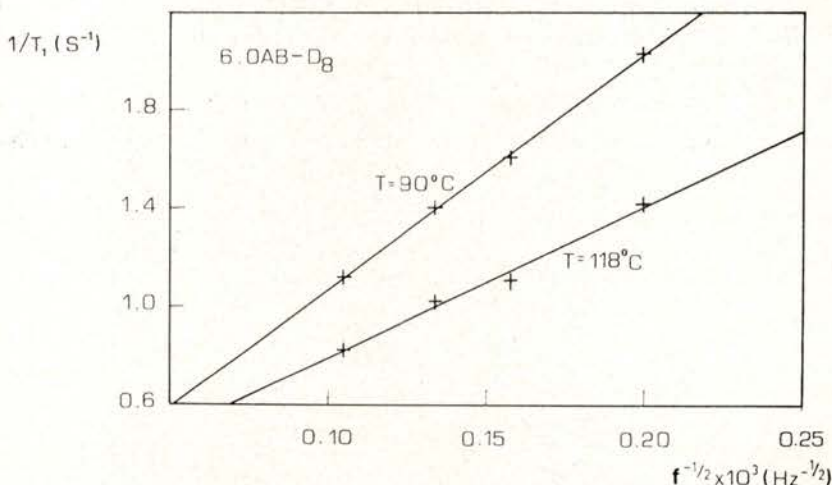


Fig. 2 — Observed frequency dependence of  $1/T_1$  in the nematic phase of 6.OAB-D<sub>8</sub>, at  $T = 90$  and  $118^\circ\text{C}$ .

shows that not only the rigid core of the molecules but also their terminal chains are strongly coupled to the long-wavelength thermal fluctuations of the nematic director.

Assuming that the frequency-dependent part of the relaxation is mainly due to the modulation of dipolar interactions, the observed behaviour may be quantitatively explored in the framework of the

theory of spin-lattice relaxation in nematics developed in ref. [6]. This treatment contains the essential features of the more sophisticated theory proposed later on by Freed [8].

The relaxation rate due to dipolar interactions among the chain protons may be written :

$$\frac{1}{T_1} = \frac{9\sqrt{2}}{8\pi} \gamma^4 \hbar^2 \langle \Lambda(r_{ij}, \theta_{ij}) \rangle^2 \left( \frac{k_B T S^2}{K^{3/2}} \Gamma^{1/2} \right) \omega^{-1/2} + \frac{1}{T'_1} \quad (1)$$

where  $\Lambda(r_{ij}, \theta_{ij})$  is a function of the chain configuration ( $\theta_{ij}$  is the angle made by the interproton vector  $r_{ij}$  with the molecular axis),  $S$  is the Maier-Saupe degree of order, and  $\Gamma$  and  $K$  are respectively an effective viscosity and an effective Frank elastic constant, both defined in ref. [6]. The term  $1/T'_1$ , which is frequency independent, contains all the contributions to the relaxation rate that do not couple to the long-wavelength thermal modes.

In order to facilitate the following discussion, expression (1) may be written in the form :

$$1/T_1 = A(\Delta, T) \omega^{-1/2} + 1/T'_1 \quad (2)$$

Defining  $C(K, S, \Gamma)$  as

$$C(K, S, \Gamma) = \frac{k_B T S^2}{K^{3/2}} \Gamma^{1/2} \quad (3)$$

we may write  $A \sim \langle \Lambda \rangle^2 C$ .

The coefficient  $A(\Delta, T)$  may be obtained as a function of  $T$  from the slopes of linear least squares fits of  $T_1^{-1}$  as a function  $\omega^{-1/2}$ , at different temperatures (cf. fig. 2). The resulting values are displayed in fig. 3. We see that  $A$  is strongly dependent on  $T$ , in contrast to the case of PAA, where a negligible temperature dependence was found [6]. To understand this difference, we have to go into the details of  $A(\Delta, T)$  and estimate separately the temperature dependence of  $C(K, S, \Gamma)$  and  $\langle \Lambda(r_{ij}, \theta_{ij}) \rangle$ .

The value and temperature dependence of  $C(K, S, \Gamma)$  may be estimated by taking

$$K \approx \frac{1}{3} K_{11} (1 + K_{22} / K_{11} + K_{33} / K_{11}) \quad (4)$$

(which is equivalent to assuming an isotropic distribution of the fluctuation wave-vectors) and  $\Gamma \approx \gamma_1$  [6], and quoting from the literature the values of  $S$  [11],  $K_{11}$  [12, 13],  $K_{33}/K_{11}$  [12] and  $\gamma_1$  [14], as a function of temperature. The absolute values of  $K_{22}/K_{11}$  have not been given so far for 6.0AB but we can estimate them by comparison with heptylazobenzene [12]. We find that the temperature variation of  $C$  ( $K, S, \Gamma$ ) is much stronger here than in the case of PAA [6] (see

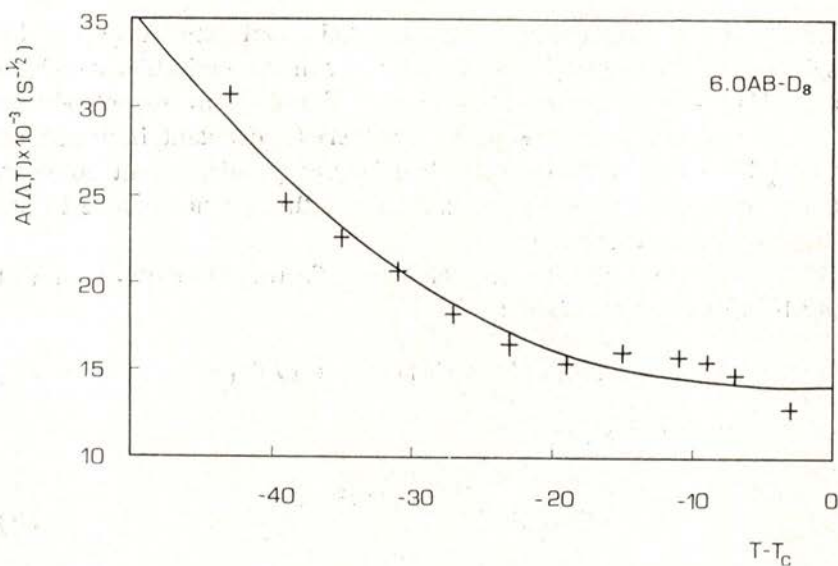


Fig. 3 — Observed temperature dependence of the function  $A(\Delta, T)$  given by eq. (2) in the text.

fig. 4). This stands on the fact that both the elastic constant  $K_{11}(T)$  and the twist viscosity  $\gamma_1(T)$  increase much more strongly with decreasing temperature in 6.0AB than in PAA [12, 14]. The order parameters have similar behaviour, and in 6.0AB both  $K_{22}/K_{11}$  and  $K_{33}/K_{11}$  are practically independent of temperature [12].

The function  $\Delta(r_{ij}, \theta_{ij})$ , in expression (1), is rather complex and may only be written down completely after a dynamic model for the chain is assumed, which is not the aim of this paper. Its average value,  $\langle \Delta(r_{ij}, \theta_{ij}) \rangle$  would vanish for a completely disordered chain. So, the fact that we observe experimentally the characteristic frequency

dependence  $T_1 \sim \omega^{1/2}$  predicted by expression (1) is in agreement with direct measurements of a non-vanishing order along the chains [4].

The extent to which the chains are coupled to the director, at different temperatures and frequencies, can be evaluated by subtracting from the measured values of  $1/T_1$  the values of  $1/T'_1$  obtained from plots such as that in fig. 2. We find, e.g. at  $\omega = 2\pi \times 40$  MHz and  $T - T_c = 15^\circ\text{C}$ , that the long-wavelength contribution to the relaxation

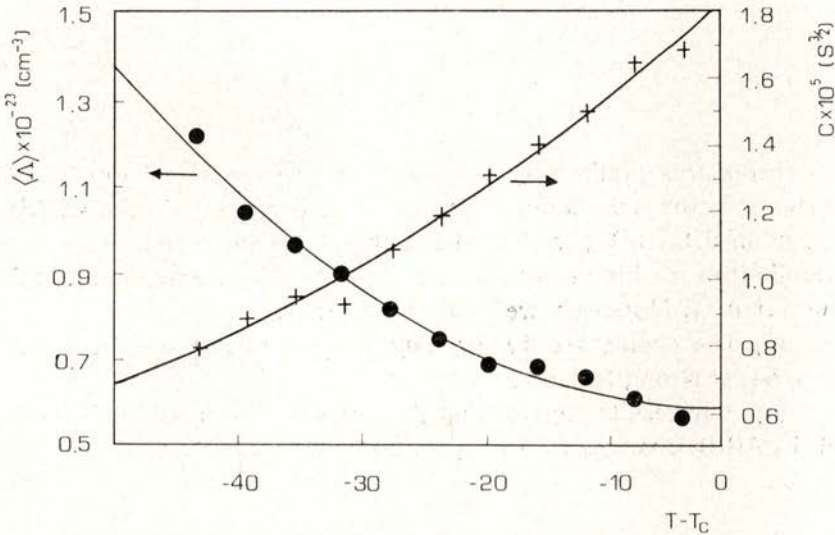


Fig. 4 — Estimated temperature dependence of the functions  $C(K, S, F)$  and  $\langle \Lambda(r_{ij}, \theta_{ij}) \rangle$  given by eqs. (3) and (5) in the text.

rate represents 83% of the total rate. This indeed reflects a strong coupling of the chains to the director, and it should be noted that this coupling increases with decreasing frequency (see expression (1)). On the other hand, as expected, it decreases as we approach the nematic to isotropic transition temperature  $T_c$ .

The temperature variation of  $\langle \Lambda(r_{ij}, \theta_{ij}) \rangle$  can be estimated now from our knowledge of  $A(\Lambda, T)$  and  $C(K, S, \Gamma)$ , through the expression

$$\langle \Lambda \rangle^2 = \frac{8\pi}{9\sqrt{2}} (\gamma^4 \hbar^2)^{-1} \cdot (A/C) \quad (5)$$

which comes directly from (1), (2) and (3). This is also shown in fig. 4, and we see that  $\langle \Lambda(r_{ij}, \theta_{ij}) \rangle$  varies by more than a factor of two, through the nematic range of 6.0AB-D<sub>8</sub>. This suggests that the average molecular conformation of 6.0AB-D<sub>8</sub> changes appreciably with temperature. Unfortunately the detailed nature of these conformation changes cannot be obtained, within this framework, before a detailed knowledge of the function  $\Lambda(r_{ij}, \theta_{ij})$  is available. This point will be discussed in future work. We feel that some aspects of the theoretical model proposed in ref. [2] by one of us may be conveniently tested by detailed research along these lines.

#### 4 — CONCLUSION

From this preliminary discussion of the results of our measurements of the spin-lattice relaxation time of protons in the aliphatic chains of 6.0AB-D<sub>8</sub>, we have been able to disclose some microscopic peculiarities of this material as compared to its lowest homolog PAA (or 1.OAB). Moreover, we have shown that:

- (i) The chains are dynamically coupled to the nematic director in a rather strong fashion;
- (ii) our results suggest that the average molecular conformation of 6.0AB-D<sub>8</sub> changes with temperature.

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