MOLECULAR DYNAMICS IN A COLUMNAR D_{ho} LIQUID CRYSTAL – NMR STUDY

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ABSTRACT — The proton spin-lattice relaxation time T_1 (T, ω) has been measured in the isotropic and columnar phases of hexaoctyloxytriphenilene (THE8). T_1 (T, ω) is continuous across the isotropic-columnar transition and is essentially due to the alkyl chain contribution. Data analysis suggests that the complexities of alkyl chain motions may be lumped into two simple mechanisms, namely «rigid body» chain reorientations and relatively faster internal motions. Chain motions corresponding to intercolumnar diffusion (permeation) are another effective mechanism of relaxation.

1 – INTRODUCTION

Since their discovery in 1977 [1], discotic liquid crystals have been a subject of growing interest and a large number of reports have been published on the properties of these materials [2]. Their molecular dynamics has been probed in two cases by proton spin relaxation techniques [3, 4]. We have used these techniques [3] to study the isotropic-columnar transition and the molecular dynamics in the isotropic phase of hexaoctyloxytriphenilene (THE8 for short). In this work we propose an interpretation of new and previous [3] data on the columnar phase of THE8, and revise briefly the interpretation previously given [3] to the data concerning the isotropic phase, with regard to some aspects on which an improvement is possible on the light of recently published data on some material properties.

2 – EXPERIMENTAL AND GENERAL REMARKS

The synthesis of THE8 was described in ref. [5]; it shows a single liquid crystalline phase of the columnar type D_{ho}, between 340 and 358.8 K. The molecules are regularly stacked in the columns with intermolecular distances of 3.6 Å, and the lattice arrangement of the columns is hexagonal with intercolumnar distance of 23.2 Å [6]. The sample (0.5 cm³) used in our NMR experiments was degassed and sealed under vacuum in a 10 mm diameter glass tube.

Measurements of the proton spin-lattice relaxation time T_1 were performed with a Bruker SXP/4-100 NMR spectrometer for twelve values of the Larmor frequency $\omega/2\pi$, between 4 and 90 MHz.

We have observed an apparent continuity of T_1 (T) through the isotropic to columnar transition at all working frequencies, and an apparently similar behaviour of T_1 (T, ω) in both phases, including a strong frequency dependence of T_1 in the isotropic phase over the whole range of temperatures covered in our experiments (up to 90 K above the clearing point) [3]. We also have observed vanishing angular dependence of T_1 when the sample was rotated about an axis normal to the magnetic field.

In view of the following analysis we should also keep in mind that most of the protons in each molecule belong to the aliphatic chains and only 6/108 of them belong to the triphenilene core.

3 – DATA ANALYSIS

A significant portion of our experimental data on T_1 (ω, T) for the columnar phase is displayed in Fig. 1 for T = 354 K. The curves were obtained from a computer analysis of the data, as explained below.

Four different types of molecular motions have been considered in our analysis of the data, as eventually effective mechanisms of spin-lattice relaxation:

   (i)   long-wavelength collective motions associated with bending fluctuations of the columns;

  (ii)   rotational diffusion of the molecules around the symmetry axes normal to the planes of their discs;

(iii) intercolumnar translational self-diffusion of the molecules, with components along the columnar axis ($D_{\parallel}^0$) and normal to it ($D_{\perp}^0$) due to the uncorrelated positions of adjacent columns;

(iv) intramolecular motions such as conformational changes of the aliphatic chains, etc.

Mechanism (i) has been discarded on the basis of actual computations and the fact that no discontinuity of $T_1(T)$ is observed at the isotropic-columnar transition. Mechanism (ii) has been described by the following expression [7]:

$$\left(1/T_1\right)_R = B \left(\frac{\tau_R}{1 + \omega^2 \tau_R^2} + \frac{4\tau_R}{1 + 4\omega^2 \tau_R^2}\right). \tag{2}$$

and assumed to be independent of (iii); B has been treated as an adjustable parameter. To describe (iii), i. e., relaxation induced by molecular translational self-diffusion, the theoretical computations by Zumer and Vilfan [8] have been used. They give:

$$\left(1/T_1\right)_D = (9/8)\, \gamma^4 h^2 \left(n\tau_D/d^3\right) R_c \left(l/d, D_{\perp}^0/D_{\parallel}^0, \varepsilon, \Delta, \omega\tau_D\right) \tag{2}$$

where R_c is a dimensionless function such that expression (2) can be very well aproximated by:

$$\left(1/T_1\right)_D = C_1 \left(\frac{\tau_D}{1 + \omega^2 \tau_D^2}\right) \tag{3}$$

in the region of our measurements. The diffusion coefficients $D_{\perp}^0$ and $D_{\parallel}^0$ are given by:

$$D_{\perp}^0 = <r_{\perp}^2>/4\tau_D \quad \text{and} \quad D_{\parallel}^0 = <r_{\parallel}^2>/2\tau_D. \tag{4}$$

Finally, the motions included in (iv) have been assumed to be fast enough to contribute only with a constant term (C) to the relaxation rate.

The overall relaxation rate should then be given by the following expression:

$$\frac{1}{T_1} = B \left(\frac{\tau_R}{1 + \omega^2 \tau_R^2} + \frac{4\tau_R}{1 + 4\omega^2 \tau_R^2}\right) + C_1 \frac{\tau_D}{1 + \omega^2 \tau_D^2} + C \tag{5}$$

which was fitted to the experimental data in Fig. 1 (for T = 354 K) giving:

$$\tau_R = 1.5 \times 10^{-8} \text{ s} \qquad B = 2.72 \times 10^7 \text{ s}^{-2} \qquad C = 2.58 \text{ s}^{-1}$$

$$\tau_D = 0.9 \times 10^{-8} \text{ s} \qquad C_1 = 1.32 \times 10^9 \text{ s}^{-2}$$

Putting these values in expressions (1) to (3) and (5), curves for the overall relaxation rate $1/T_1$ and for its three components have been drawn as functions of $1/\sqrt{\omega}$, as represented in Fig. 1.
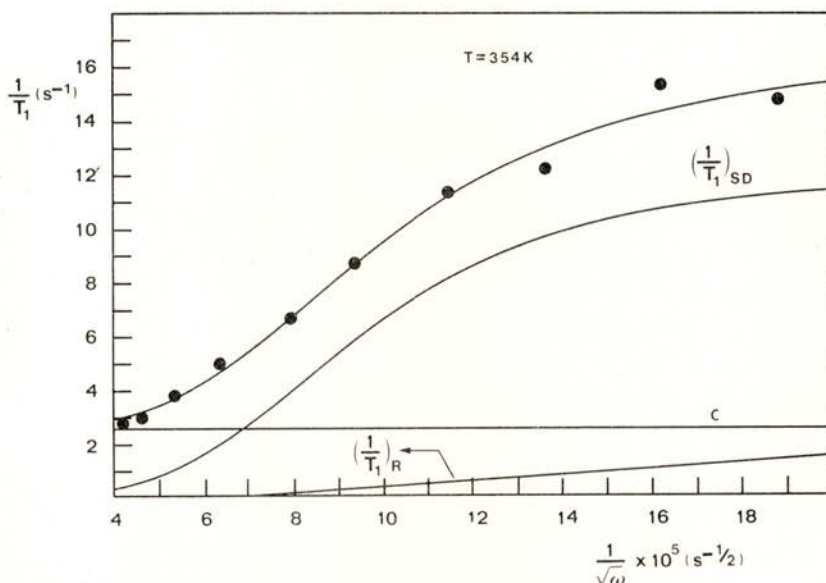

Fig. 1 — Frequency dependence of the overall and partial contributions to the relaxation rate, at T = 354 K, in the columnar phase.

4 — DISCUSSION

The value ~ 10^{-8} s for the correlation times derived above is quite convincing in view of the apparent dispersion of $T_1(\omega)$ shown by Fig. 1 around the corresponding frequency.

The diffusion coefficients $D_\perp^0$ and $D_\parallel^0$ are another interesting output of this research, because they can be measured inde-

pendently, thus giving a check on our data analysis. Using expression (4) with the computed value of τ_D, and taking $<r^2>^{1/2} \leq L = 3.6$ Å, where L is the intermolecular distance within one column, and $<r_\perp^2>^{1/2} = d_1 = 23.2$ Å (intercolumnar distance [6]), we find, for T = 354 K:

$$D_\perp^o = 1.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \quad \text{and} \quad D_\parallel^o \leq 7.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} .$$

Dong et al. have recently measured the diffusion coefficient $D_\perp^o$ as a function of the temperature [9]. For T = 354 K we get, from their results, $D_\perp^o = 0.6 \times 10^{-6}$ cm² s⁻¹; which has the order of magnitude of our result. The slight disagreement may be only apparent since Dong et al. [9] estimate that their absolute values of the D's may be off by as much as a factor two, due to experimental difficulties.

Small variations in the numerical values of the parameters given above do not change significantly the r. m. s. error of the fit in Fig. 1. We can, for instance, get smaller values of $D_\perp^o$ by increasing τ_D. This, however, leads to negative values of B in expression (5) (for $\tau_D \geq 10^{-8}$ s), which are unphysical. We remark that the contribution $(1/T_1)_R$ is relatively small in any case. On the other hand, $1/T_1$ as given by expression (5) may be viewed as a linear combination of three lorentzian contributions plus a constant term. We may ask whether a single lorentzian plus a constant term would reasonably fit the data. The answer is yes but if we associate that lorentzian contribution with translational diffusion we get $D_\perp^o = 1.4 \times 10^{-6}$ cm² s⁻¹, i.e., nearly the same value as before.

Similar difficulties have arisen in a reanalysis [10] of our previous interpretation of the data about the isotropic phase [3]. The addition of new experimental data, now available in the low frequency region, changed significantly the outputs of the fitting procedure in [3], which was based on the well known Torrey's theory, and suggests the need for the introduction of a second relaxation mechanism. Such a need is more evident in the isotropic phase than in the columnar phase. Depending on the value assumed for $<r^2>^{1/2}$ (certainly greater than 3.6 Å), the value of the diffusion constant which comes out from the new analysis [10] of the data is of the order of 10^{-6} cm² s⁻¹ at T = 366 K, which is consistent with the value $D^o = 1/3 (D_\parallel^o + 2D_\perp^o) = 1 \times 10^{-6}$ cm² s⁻¹, calcu-

lated from the results above for the columnar phase at $T = 354$ K (12 degrees below).

In the columnar phase the values of τ_D and τ_R are of the same order of magnitude. This suggests some coupling between molecular rotation and self-diffusion (this coupling was negelected in the analysis above). In the isotropic phase τ_D is an order of magnitude lower than τ_R [10]. The constant C is also an order of magnitude lower in the isotropic phase, thus suggesting an increased internal mobility of the alkyl chains in this phase. The correlation time for the internal motions in the isotropic phase is the order of 10^{-11} s (estimated with the interproton distance of -CH_2- groups).

5 – CONCLUSION

The proton spin-lattice relaxation rate in the columnar mesophase of hexaoctyloxytriphenilene in the 4-100 MHz region is dominated by the contribution of the protons in the alkyl chains. The data can be reasonably well rationalized on the basis of a simple model, in which the complexities of the alkyl chain motions are lumped into two main effects, namely global reorientations and relatively fast internal motions. In addition, the model considers molecular translational self-diffusion essentially as an inter-columnar permeation. A few puzzling problems arise, which suggest that more experimental studies are required, e. g. measurements at lower Larmor frequencies, to fully understand the relaxation mechanisms involved in the columnar and isotropic phases of discotic liquid crystals.

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