

NUCLEAR SPIN-LATTICE RELAXATION IN THE COLUMNAR AND ISOTROPIC PHASES OF A DISCOTIC LIQUID CRYSTAL (H8.OTP). STRONG FREQUENCY DEPENDENT EFFECTS IN THE ISOTROPIC PHASE (*).

A. F. MARTINS and A. C. RIBEIRO

Centro de Física da Matéria Condensada (INIC)
Av. Prof. Gama Pinto, 2 - 1699 Lisboa Codex, Portugal

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ABSTRACT—The dynamics of disc-like molecules in the isotropic and mesomorphic (columnar) states is studied by the NMR technique. The proton spin-lattice relaxation rate $1/T_1$ has been measured as a function of Larmor frequency between 10 and 90 MHz, and as a function of temperature over the whole mesomorphic state of hexa-n-octyloxytriphenilene (H8.OTP) and in the isotropic phase up to 90K above the clearing point T_{DI} . No discontinuity of $1/T_1$ is observed at T_{DI} , which reflects the incapacity of the lateral aliphatic chains to become significantly ordered on going from the isotropic to the mesomorphic state. $1/T_1$ is strongly dependent on the Larmor frequency over the whole range of temperatures covered. The frequency dependence of $1/T_1$ in the isotropic phase remains unchanged over more than 100K above T_{DI} and is shown to agree qualitatively with the predictions of available theories, but not quantitatively. The temperature dependence of $1/T_1$ is of the Arrhenius type, with an activation energy $W = 4.4$ kcal/mole.

(*) The results in this work were first presented in an oral communication at the Second National Conference of the Portuguese Physical Society (Porto, 16-18 April, 1980).

1 — INTRODUCTION

A rapidly growing interest on discotic liquid crystals has arisen since the appearance, three years ago, of the first report on the synthesis of a disc-like molecule capable of thermotropic mesomorphism [1].

Most of the papers published up to now describe the synthesis of new mesogens and the molecular arrangement, the optical, and thermodynamic properties of this new mesomorphic state [2].

The dynamics of disc-like molecules in the isotropic and mesomorphic states is also of considerable interest but has naturally received less attention so far. We have approached this problem by nuclear magnetic resonance (NMR) techniques, and we give here a set of results obtained from systematic measurements of the proton spin-lattice relaxation time T_1 , as a function of temperature T and Larmor frequency ω , in the mesomorphic (columnar) and isotropic phases of hexa-*n*-octyloxytriphenylene (hereafter abbreviated to H8.OTP). In this work, we comment on the whole set of results obtained but concentrate the discussion on the subset of results relative to the isotropic phase.

As it will appear below, the proton spin-lattice relaxation in the isotropic phase of H8.OTP shows a peculiar behaviour which is not common to the isotropic phases of usual liquid crystals (i.e. those composed of rod-like molecules).

In section 2 we mention the techniques used in this work. In section 3 we give a brief analysis of the whole experimental data obtained, with particular reference to the columnar phase and the columnar-isotropic transition. In section 4 we contrast the experimental data relative to the isotropic phase to those theoretical models so far proposed for the nuclear spin-lattice relaxation in isotropic liquids which can account for a frequency-dependent relaxation time. The results so obtained are discussed in section 5. Finally, in section 6 we present our conclusions.

An extension of this research including the full presentation and discussion of the results obtained for the columnar phase will be presented in a forthcoming paper [3].

2—EXPERIMENTAL TECHNIQUES

The synthesis of hexa-*n*-octyloxytriphenilene was described elsewhere [4]. Its molecular structure is given in figure 1.

After purification, the sample (0.5 cm³) used in our NMR experiments was degassed and sealed in an evacuated glass tube ($\phi=10$ mm). The degassing pressure was less than 10⁻⁴ mbar.

The clearing point of H8.OTP is $T_{D1}=358.8$ K, and the crystal-discotic transition is $T_{KD}=340$ K.

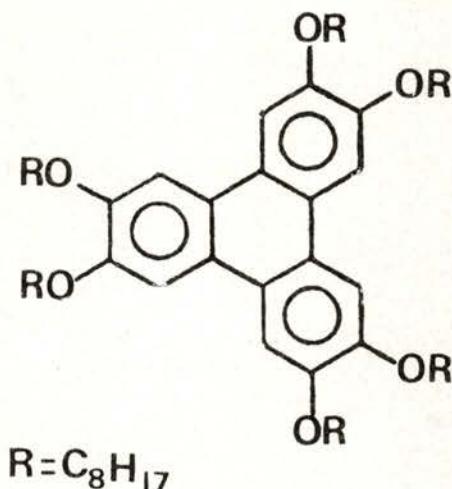


Fig. 1 — Structure of the hexa-*n*-octyloxytriphenilene (H8.OTP) molecule. Note its disc-like shape.

Measurements of the proton spin-lattice relaxation time T_1 were performed at eight different frequencies between 10 and 90 MHz. In each case the temperature was varied over the whole discotic (columnar) range and at least up to 10 K above the clearing point. In two cases, in fact, the isotropic phase was spanned up to 90 K above the clearing point (see below). T_1 was measured by the π - τ - $\pi/2$ pulse sequence with a Bruker SXP/4-100 spectrometer. The temperature of the sample was automatically controlled to within ± 0.3 K, and the estimated error in the absolute values of T was less than 1 K.

3—EXPERIMENTAL DATA AND GENERAL COMMENTS

The X-ray experiments of Levelut [5] suggest that the mesophase of H8.OTP is of the columnar type with regular stacking of molecules in the columns, their planes being normal to the columnar axis. The packing of the columns follows a two-dimensional hexagonal lattice. There is no correlation between molecular positions in neighbouring columns (longitudinal disorder).

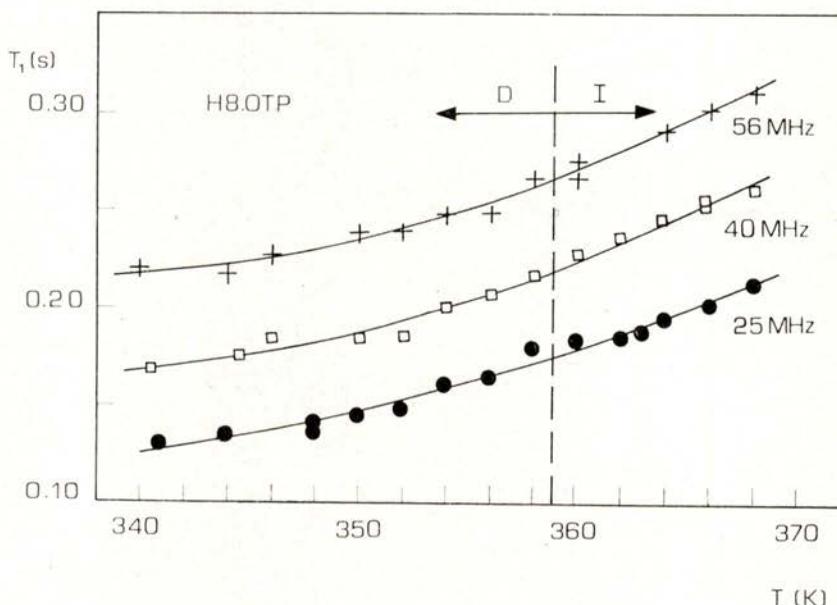


Fig. 2 — Observed temperature dependence of T_1 in the columnar (D) and isotropic (I) phase of H8.OTP, at 25, 40, and 56 MHz. The curves shown are simply guides to the eye, they have not a theoretical origin.

The results of our measurements of T_1 as a function of temperature are displayed in fig. 2 for three working frequencies. The results obtained at five other frequencies are omitted in this figure for the sake of clarity; they partially reappear in figures 4 and 5 (for one temperature). The subset of results referring to the isotropic

phase are best represented by figure 3, where $Lg(1/T_1)$ at 25 and 56 MHz is plotted as a function of $1/T$ over a much larger temperature range (from T_{DI} to $T_{DI} + 90$ K).

Two paramount features of our results are apparent in fig. 2, namely the absence of a discontinuity in $T_1(T)$ at the mesomorphic-isotropic transition temperature T_{DI} (up to the experimental

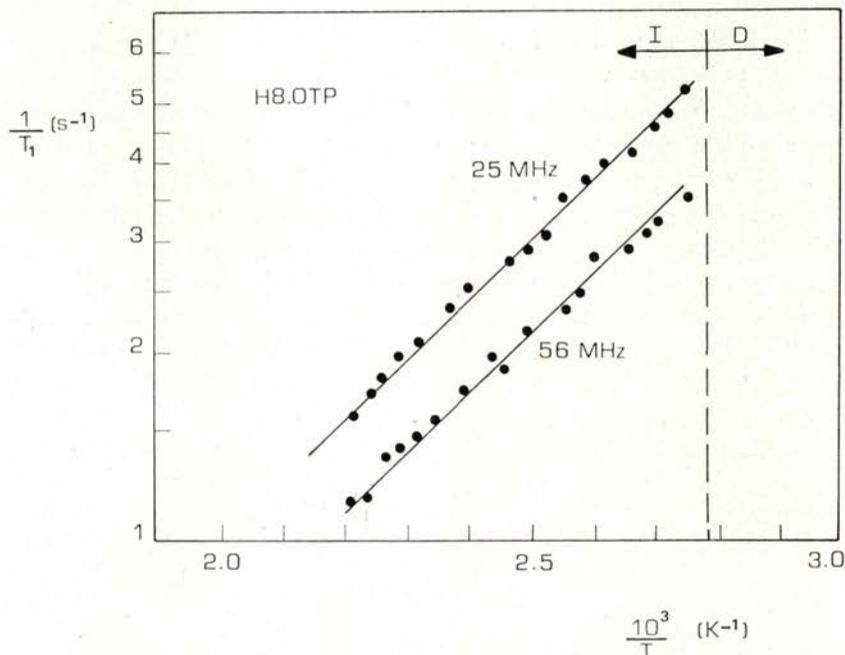


Fig. 3 — Arrhenius-type representation of the values of $1/T_1$ measured at 25 and 56 MHz, as a function of temperature, in the isotropic phase of H8.OTP. The activation energy is $W = 4.4$ Kcal/mole.

accuracy of our measurements), and the rather similar behaviour of $T_1(\omega)$ in both phases. The continuity of $T_1(T)$ at the isotropic-mesomorphic transition is in strong contrast to what is observed in liquid crystals composed of rod-like molecules [6].

We shall see [3] that the frequency behaviour of T_1 is only apparently similar in both phases. A quantitative analysis shows that we have $T_1^{-1} \sim \omega^{1/2}$ in the isotropic phase, as discussed in the

next section of this paper, and a different and more complex behaviour in the columnar phase. In this phase the overall behaviour at low temperatures is dominated by a new contribution of the type $T_1^{-1} \sim \omega^{-1/2}$, but our results [3] suggest that the previous one remains active. These two contributions may be explained in terms of molecular diffusion (section 4 below and ref. [3]) and thermal bending of the columns (long wave-length modes, see ref. [3]). Internal motions also play a role but do not contribute appreciably to the dispersion of the relaxation rate.

To understand the apparent continuity of $T_1(T)$ across T_{DI} we first note that we have measured the overall relaxation of a system of 108 proton spins, of which 102 belong to the lateral chains of the disc-like molecule and only 6 belong to the central core. If there is some short range order of the cores in the isotropic phase and the (dis)order of the chains does not change drastically at the transition, we indeed expect a quasi continuity of $T_1(T)$ at T_{DI} . Within the previous assumptions, only the contributions to the overall T_1 from the protons in the core are expected to change significantly at the transition, due to the onset of long range order, but these contributions will not affect the overall T_1 by more than a few percent. To be quantitative we expect, at T_{DI} :

$$\delta \left(\frac{1}{T_1} \right)_{\text{all}} = \frac{6}{108} \delta \left(\frac{1}{T_1} \right)_{\text{core}} + \frac{102}{108} \delta \left(\frac{1}{T_1} \right)_{\text{ch.}} \quad (1)$$

With $\delta(1/T_1)_{\text{ch}} \simeq 0$ and $\delta(1/T_1)_{\text{core}} \simeq -1$ the measured discontinuity in T_1 would be $\delta T_1 \simeq 0.056 T_1^2$, on going from the isotropic to the mesomorphic phase. Such a discontinuity could only be observed, within the accuracy of our present data, if $T_1 > 1$ s. As seen from fig. 2, this is not the case in the frequency range considered in this work.

4 — THEORETICAL ANALYSIS OF THE DATA RELATIVE TO THE ISOTROPIC PHASE

The most relevant feature of the results of our measurements of the proton spin-lattice relaxation time T_1 in the isotropic phase of HS.OTP is the rather strong Larmor frequency dependence observed

(figs. 2 and 3) over a wide temperature range above the clearing point T_{DI} . This behaviour of the relaxation time is not usual in the isotropic phases of liquid crystals formed by rod-like molecules, at least in the frequency range considered here. In the I-phases of these liquid crystals (sometimes called calamitic [2], as opposed to discotic) we only observe a significant dispersion of T_1 just above the clearing point, and this is due to collective (short range order) effects [6]. As we do not expect long-wavelength thermal modes of motion in HS.OTP over such a wide range of temperatures *above* T_{DI} , the observed behaviour is to be explained in terms of relative diffusion and internal motions of the molecules.

The basic theory of spin-lattice relaxation by translational diffusion (modulating the *intermolecular* spin-spin interactions) is due to Torrey [7]. Later on, several workers, particularly Harmon and Muller [8], and Freed [9], have introduced slight corrections to the theory of Torrey in order to incorporate, in different ways, the effects of boundary conditions (excluded volume due to a distance of minimum approach between the spin-bearing molecules) and the pair correlation function. We shall use below the theoretical expression proposed by Freed [9] for the spectral density $J(\omega)$ of molecular motion, in the isotropic jump model:

$$J(\omega) = \frac{4}{27} \frac{n}{Dd} \left[1 + \frac{3}{8} \frac{\langle r^2 \rangle}{d^2} - \frac{3}{8} \left(\frac{\omega d^2}{D} \right)^{1/2} + \right. \\ \left. + \frac{1}{2} \left(\frac{1}{9} + \frac{3}{32} \frac{\langle r^2 \rangle}{d^2} \right) \left(\frac{\omega d^2}{D} \right)^{3/2} + O(\omega^2) \right] \quad (2)$$

where n is the average number density of protons, $D = \langle r^2 \rangle / 6\tau$ is the absolute molecular diffusion coefficient, $\langle r^2 \rangle$ is the mean square jump distance, τ is the mean time between jumps, and d is the distance of closest approach.

The spin-lattice relaxation rate $1/T_1$ due to translational diffusion is related to $J(\omega)$ given above according to the following expression:

$$1/T_1 = \frac{4\pi}{5} \gamma_H^4 \hbar^2 I(I+1) [J(\omega) + 4J(2\omega)] \quad (3)$$

where γ_H is the proton gyromagnetic ratio and $I = 1/2$ is the proton spin quantum number. From (2) and (3) we get the proton relaxation rate:

$$\begin{aligned} 1/T_1 = \frac{4\pi}{9} (\gamma_H^4 h^2) \frac{n}{Dd} \left[1 + \frac{3}{8} \frac{\langle r^2 \rangle}{d^2} - \frac{3}{40} (1 + 4\sqrt{2}) \left(\frac{\omega d^2}{D} \right)^{1/2} + \right. \\ \left. + \frac{1}{90} (1 + 8\sqrt{2}) \left(1 + \frac{27}{32} \frac{\langle r^2 \rangle}{d^2} \right) \left(\frac{\omega d^2}{D} \right)^{3/2} + 0 (\omega^2) \right] \quad (4) \end{aligned}$$

To lowest order in ω , expression (4) may be written:

$$(1/T_1)_{\text{inter}} \sim \tau [1 - \alpha (\omega \tau)^{1/2}] \quad , \quad (5)$$

where α is a constant of order unity.

On the other hand, we expect the relaxation due to the modulation of intramolecular spin-spin interactions to be of the form

$$(1/T_1)_{\text{intra}} \sim \tau' [1 - \beta (\omega \tau')^2] \quad , \quad (6)$$

to the leading term in ω , where β is also a constant of order unity, and τ' is an appropriate correlation time [10].

Simple order of magnitude considerations allow us to expect $\omega \tau' \lesssim \omega \tau \sim 10^{-1} - 10^{-2}$ in the frequency range considered in this work. Then, it can be seen from equations (5) and (6) that the *intermolecular* relaxation will dominate the overall *frequency effect*. This is just what is suggested by our experimental data.

In fact, our data cannot be reasonably fitted to equation (6) at every temperature in the isotropic phase. On the other hand, fitting the data with equation (5), gives rather good qualitative agreement over the whole frequency range considered in this work, as shown in fig. 4 for one particular temperature ($T = 366\text{K}$). The straight line in fig. 4, as obtained by the least squares method, is given by

$$(1/T_1)_{\text{exp.}} = 7.773 - 2.372 \times 10^{-4} \omega^{1/2} \quad (7)$$

with a root mean square error

$$\varepsilon(\text{rms}) \equiv \left[(1/N) \sum_1^N (R - R_i)^2 \right]^{1/2} = 0.133 \text{ s}^{-1} \quad (8)$$

where $R \equiv 1/T_1$. So, it is clear that to lowest order in ω our data give $1/T_1 \sim \omega^{1/2}$, which is consistent with the predominance of a diffusion-controlled relaxation mechanism.

The next approximation in contrasting our data with theory is obtained by introducing a term proportional to $\omega^{3/2}$, according to eq. (4). In this case we find, by the least squares method, at $T = 366\text{ K}$:

$$(1/T_1)_{\text{exp.}} = 8.379 - 3.012 \times 10^{-4} \omega^{1/2} + 7.783 \times 10^{-14} \omega^{3/2} \quad (9)$$

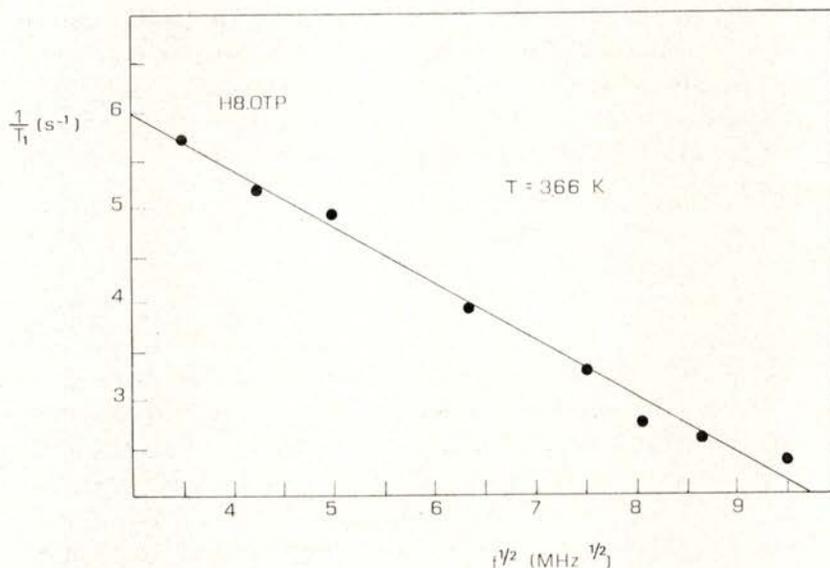


Fig. 4 — Linear least-squares fit of the data on $1/T_1$ versus $f^{1/2}$, where $f = \omega/2$; eq. (7) in the text.

with $\varepsilon(r \text{ m s}) = 0.108 \text{ s}^{-1}$. Terms of higher order in ω cannot introduce differences outside the experimental error of our measurements, in agreement with the foregoing order of magnitude considerations.

Now, by equating the terms proportional to $\omega^{1/2}$ in equations (4) and (9) we find:

$$D = 1.95 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1} \quad (10)$$

Introducing this value of D in the coefficient of $\omega^{3/2}$ in eq. (4), and assuming some value for $\langle r^2 \rangle / d^2$, we find, by comparison with eq. (9),

$$d \leq 1.35 \text{ \AA} \quad (11)$$

The value of $\langle r^2 \rangle$ cannot be found because the frequency independent term in r.h.s. of eq. (9) contains both inter and intramolecular contributions, as given by the corresponding terms in equations (4) and (6) (and eventually a small contribution from other possible mechanisms of relaxation). The separation of these frequency-independent contributions to the overall relaxation rate would require measurements of T_1 on mixture samples prepared by progressively diluting completely deuterated H8.OTP with normal H8.OTP; unfortunately, deuterated samples of H8.OTP are not available at present.

5 — DISCUSSION OF RESULTS

Let us now discuss the results obtained in the previous section.

We have seen that expression (4) fits very well the experimental data. However, both the value of D , given by (10), and the value of d , given by (11), appear to be rather low. We can reasonably expect $d \approx 3 - 4 \text{ \AA}$ and $D \approx 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. This value of D is an order of magnitude higher than the value found above. Similar discrepancies were found, by several researchers, for liquid crystals formed of elongated molecules, e.g. MBBA, between the values of D extracted from NMR-T analysis and those measured by direct techniques [11-13]. No explanation for these facts has been proposed so far.

It could be argued that in the general expression for $1/T_1$ a term proportional to ω^2 as predicted by eq. (6) may be non-negligible, in spite of the considerations about orders of magnitude developed in the preceding section. We have checked this point by fitting our data to the theoretical expression as developed to order ω^2 and have found that to the accuracy of our data the influence of such a term cannot be shown up.

On the other hand we have tried to fit our data with the full expression for $1/T_1$ given by Torrey [7] (after inclusion of the

proper weighting of the spectral densities), instead of the approximations such as eq. (4) or the equivalent one suggested by Harmon and Muller [8]. Figure 5 reproduces two examples of such fittings, where we have forced $d = 3.65 \text{ \AA}$, corresponding to the distance of closest approach of the discs (molecular cores) in the mesomorphic phase, as given by X-ray measurements [5] and semi-empirical calculations [14]. In this way we can get results which are physically sounder but not yet satisfactory.

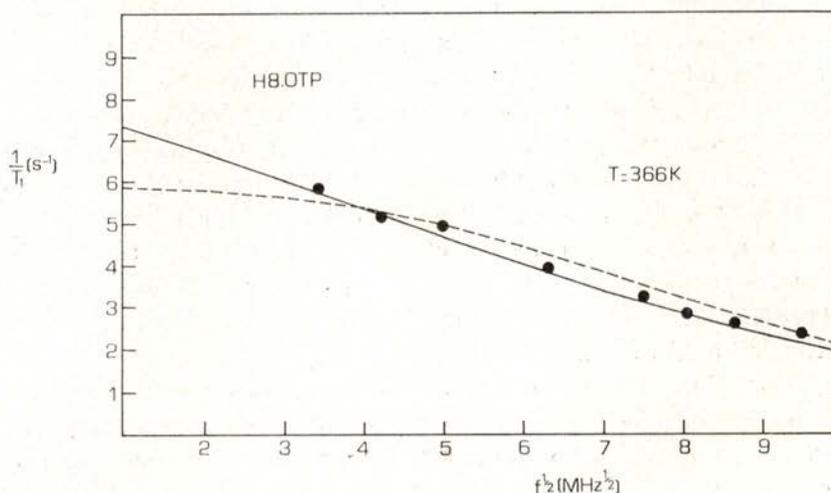


Fig. 5 — Fits of the full theoretical expression for $1/T_1$ given by Torrey [7] (corrected) with the data. Solid curve: $d^2 = \langle r^2 \rangle = (3.65 \text{ \AA})^2$, $D = 2.25 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. Dashed curve: $d = 3.65 \text{ \AA}$, $\langle r^2 \rangle = (10.9 \text{ \AA})^2$, $D = 1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The r.m.s. errors are respectively $\epsilon \text{ (rms)} = 0.157$ and 0.236 s^{-1} .

We suggest that the theories proposed so far [7-9] to account for the behaviour of the nuclear spin-lattice relaxation by translational diffusion do not apply to liquids formed by strong anisometric molecules, such as liquid crystals (in the isotropic phase), both of the calamitic and of the discotic types. We intend to discuss in a future publication the corrections to be introduced in the available theories in order to render them applicable to these cases too.

Let us finally remark that the relaxation rate $1/T_1$ varies with temperature according to an Arrhenius-type law (figure 3), as expected from eq. (5), to a good approximation, where

$$\tau = \langle r^2 \rangle / 6D = \tau_0 \exp(W/kT).$$

The activation energy, extracted from the least-squares fit in figure 3, is $W = 4.4$ kcal/mole. We did not observe pretransitional effects in the temperature range just above T_{DI} .

6—CONCLUSION

This work is, to our knowledge, the first report on the dynamics of disc-like molecules, in isotropic and mesomorphic (columnar) phases, as studied by nuclear magnetic relaxation techniques. Our results were obtained from measurements on a single material, hexaoctyloxy-triphenylene (H8.OTP), but most of them are presumably of general interest. Two of these results are particularly remarkable:

(i) No discontinuity of $1/T_1$ is observed on varying the temperature across the mesomorphic-isotropic transition point, which is interpreted as a consequence of the incapacity of the aliphatic chains in the molecule to become significantly ordered on going from the isotropic to the mesomorphic state. This behaviour differs from that observed with similar chains attached to the rod-like molecules of "classic" liquid crystals [15].

(ii) The proton spin-lattice relaxation rate $1/T_1$ is strongly dependent on the Larmor frequency ω over the whole temperature range covered in our experiments (up to 90K above the clearing point T_{DI}). The theories of relaxation proposed so far [7-9] hardly account for the observed behaviour. The discrepancy should originate in the strong anisometric form of the molecules, which couples molecular rotation to translational diffusion of spins. No short range order effects are observed just above T_{DI} .

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REFERENCES

- [1] S. CHANDRASEKHAR, B. K. SADASHIVA, and K. A. SURESH, *Pramàna* **9**, 471 (1977).
- [2] For a recent review see C. DESTRADE *et al.*, in *Liquid Crystals*, S. Chandrasekhar ed (Heyden & Son Ltd, London, 1980), and

- J. BILLARD, in *Liquid Crystals of One and Two-dimensional Order*, W. Helfrich and G. Heppke eds. (Springer-Verlag, Berlin, 1980).
- [3] A. F. MARTINS and A. C. RIBEIRO, in preparation.
- [4] J. BILLARD *et al.*, *Nouveau J. de Chimie*, **2**, (1978), 535; C. DESTRADE, M. C. MONDON and J. MALTHETE, *J. Phys. (Paris)* **40**, C3-17 (1979).
- [5] A. M. LEVELUT, *J. Phys. Lett. (Paris)* **40**, 81 (1979).
- [6] A. F. MARTINS, *Molec. Cryst. Liquid Cryst.*, **14**, 85 (1971); *Portgal. Phys.* **8**, 1 (1972).
- [7] H. C. TORREY, *Phys. Rev.* **92**, 962 (1953).
- [8] J. F. HARMON and B. H. MULLER, *Phys. Rev.* **182**, 400 (1969).
- [9] J. H. FREED, *J. Chem. Phys.* **68**, 4034 (1978).
- [10] A. ABRAGAM, *The principles of nuclear magnetism* (Oxford Univ. Press, London, 1961).
- [11] M. VILFAN, R. BLINC, and J. W. DOANE, *Solid State Commun.* **11**, 1073 (1972).
- [12] R. Y. DONG, E. TOMCHUK, and E. BOCK, *Can. J. Phys.* **53**, 610 (1975).
- [13] G. ROLLMANN, K. F. REINHART, and F. NOACK, *Z. Naturforsch.* **34a**, 964 (1979).
- [14] M. PESQUER *et al.*, *J. Physique* **41**, 1039 (1980).
- [15] A. F. MARTINS, A. J. BONFIM, and A. M. GIROUD-GODQUIN, *Portgal. Phys.* **11**, 159 (1980).