Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Deuterium NMR investigation of a new class of macrocyclic columnar liquid crystal

L. Abis[a]; V. Arrighi[a]; G. Cometti[a]; E. Dalcanale[ab]; A. Du Vosel[a]
[a] Istituto G. Donegani, Novara, ITALY [b] Istituto di Chimica Organica, Università di Parma, Parma, ITALY

To cite this Article Abis, L. , Arrighi, V. , Cometti, G. , Dalcanale, E. and Vosel, A. Du(1991) 'Deuterium NMR investigation of a new class of macrocyclic columnar liquid crystal', Liquid Crystals, 9: 2, 277 — 284
To link to this Article: DOI: 10.1080/02678299108035505
URL: http://dx.doi.org/10.1080/02678299108035505

LIQUID CRYSTALS, 1991, VOL. 9, NO. 2, 277–284

Deuterium NMR investigation of a new class of macrocyclic columnar liquid crystal

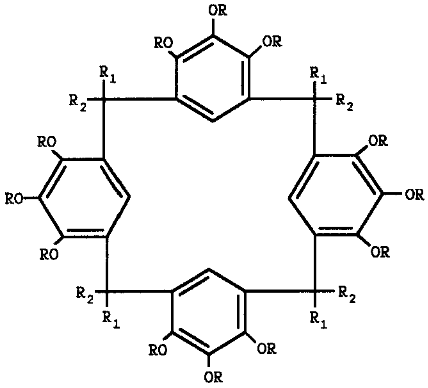
by L. ABIS, V. ARRIGHI†, G. COMETTI,
E. DALCANALE‡ and A. DU VOSEL
Istituto G. Donegani, Via Fauser 4,
I-28100 Novara, Italy

(*Received 5 February 1990; accepted 3 September 1990*)

Deuterium NMR spectroscopy of C_6D_6, added as a probe to compound **1**, shows the formation of an uniaxial columnar mesophase, with domain directors perpendicular to the magnetic field. Spectral patterns at various temperatures are interpreted in terms of slow equilibrium between two solvent sites placed respectively between the cores and among the lateral chains. Deuterium NMR spectra of the deuteriated derivative **2** confirm this model, allow the evaluation of the molecular order parameter, S_{zz}, and exclude the presence of fast rotational diffusion around the main molecular axis.

1. Introduction

Recently a new class of columnar liquid crystals, having bowl-shaped mesogenic cores, has been discovered [1–4]. The specific physico-chemical properties of the resulting mesophases are of particular interest, because of their potential ferroelectric behaviour [5]. In this paper we report deuterium NMR investigations of the structure and dynamics of the mesophase generated by molecules with the general structure I. The liquid crystal properties of these materials have already been characterized by



1: $R=COC_{13}H_{27}$; $R_1=CH_3$; $R_2=H$
2: $R=COC_{13}H_{27}$; $R_1=CD_3$; $R_2=D$

Structure I.

---

† Ph.D. student at Imperial College, London, supported by Istituto G. Donegani.

‡ Present address: Istituto di Chimica Organica, Università di Parma, Via delle Scienze, I-43100 Parma, Italy.

optical, thermal and X-ray diffraction studies [4]. This last technique classified the mesophase as D_{ho}, i.e. a hexagonal columnar phase in which the molecules have a well-defined order within the columns. The measurements were conducted on deuteriated benzene dissolved as a probe in the mesophase of **1** [6] and in the deuteriated derivative **2**.

2. Experimental

Compound **1** was prepared according to a published procedure [4, 7]. Compound **2**, selectively deuteriated in the CH–CH_3 positions, was synthesized by the same procedure,§ using 1,1-diethoxyethane-d_4. This deuteriated reagent was prepared by treatment of acetaldehyde-d_4 99 per cent D with ethanol under acidic conditions: 2 g of CD_3CDO, 5 g of highly acidic resin (Amberlite 200) and 10 ml of ethanol were stirred at room temperature in a sealed bottle. After 4 hours (95 per cent of conversion by GC) 4·8 g of reagent in ethanolic solution were ready to be used for the synthesis of the deuteriated macrocyclic core. No D/H exchange was observed throughout the synthetic sequence. The transition temperatures for compounds **1** and **2** are given in the table.

^2H NMR measurements of C_6D_6 were performed on a Bruker AM 300 spectrometer operating at variable temperature. Samples were prepared in 5 mm tubes by mixing vigorously 0·4 g of **1** in the isotropic phase with 1·4 μl of C_6D_6 (3 wt.%). Deuterium spectra were taken with a solid echo–pulse sequence [8], a delay between 90° pulses of 20 μs, a spectral width of 80 kHz and 5000 scans accumulation. Spectra of **2** were obtained with a Bruker MSL 200 spectrometer using a solid echo sequence; recycle time: 100 ms (4 s for the solid phase); 90° pulse length: 2·4 μs; delay (τ) between 90° pulses: 20 μs; spectral width: 500 kHz; accumulation scans 30 000.

3. Results

3.1. *Addition of C_6D_6 to 1*

Symmetry and alignment properties of the mesophase exhibited by **1** have been investigated by ^2H NMR of C_6D_6 dissolved in it. This technique, involving a probe molecule, has been widely used to study discotic columnar liquid crystals [9–12]. With this method we cannot measure the order parameters of the mesogenic molecules in the crystalline microdomains, which would require deuteriation of specific sites in the molecule, but we can retrieve useful information on the symmetry of the mesophase and on its macroscopic alignment with respect to the magnetic field at various temperatures. Adding 3 per cent w/w of C_6D_6 to compound **1** in the isotropic phase, a uniform mixture is obtained. This amount of C_6D_6 does not alter significantly the mesophase properties of the pure compound. In fact optical and DSC measurements made both on the mixture and on the neat compound show the formation of a mesophase in a temperature range only slightly different (see the table). Furthermore these measurements together with IR spectra show a sharp phase transition from the isotropic liquid to the mesophase without evidence of an intermediate biphasic region.

Two different experiments were performed. In the first the mesophase was obtained by cooling the isotropic phase outside the magnetic field; then ^2H NMR spectra were run in the temperature range 33–60°C. The derived powder pattern has only two

---

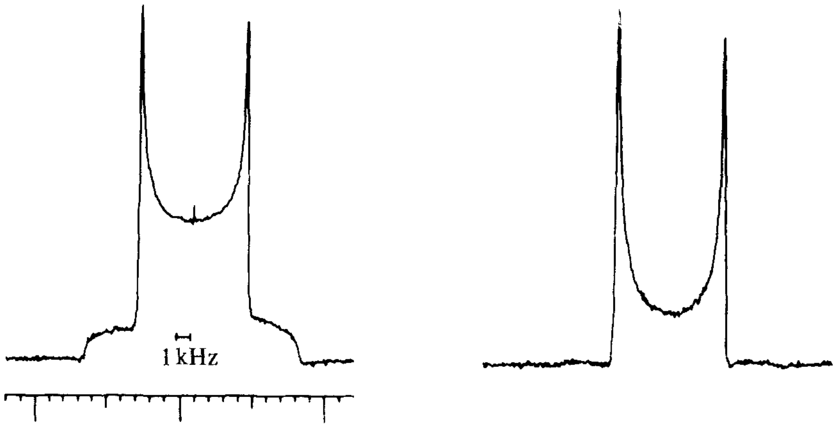
§ Compound **2** gave satisfactory analytic and spectral data.

quadrupolar interaction components: at 37°C the parallel component has $\Delta\nu_Q^{\parallel} = 15\,300$ Hz, and the perpendicular component $\Delta\nu_Q^{\perp} = 7350$ Hz (see figure 1 (*a*)). No change in the spectral shape is observed on increasing the temperature, but only an increase in the amount of isotropic benzene. In the second experiment the sample, in the isotropic phase, is put in the magnet preheated at 67°C and the spectra were recorded over the temperature range 67–30°C. In this case the deuterium spectra show a pattern which is typical of an aligned mesophase. In addition the splitting of the doublet matches the perpendicular component found in the crystalline powder pattern (see figure 1 (*b*)). These results are consistent with the presence of a uniaxial columnar mesophase, as found by X-ray diffraction, with the column director axis isotropically distributed on planes perpendicular to the magnetic field. Therefore, the diamagnetic susceptibility anisotropy is negative as observed for many discotic liquid crystals [13]. By simulating the distribution of the director axis around the perpendicular plane with a gaussian function [6] a variance *s* of 20° is found. Furthermore the doublet separation increases on decreasing the temperature with a steep gradient (see figure 2). Another important feature of the deuterium spectra is the presence of an intense isotropic peak in the upper part of the mesophase which disappears at 42°C. Spectra at 48°C (see figure 3), were recorded at different times (5, 10, 20 min): the amount of isotropic peak does not

Transition temperatures for **1**–**2**†.

Compound	T_{CI}/°C	T_{KC}/°C
1	● 62·0	● 6·2 ●
1 + 3% C_6D_6	● 60·3	● 6·4 ●
2	● 67·5	● 5·9 ●
2 + 3% C_6H_6	● 61·2	● 6·6 ●

† These results refer to DSC measurements on cooling at 10°C/min; K, crystal; C, columnar mesophase; I, isotropic liquid. The transition temperatures observed in the bulk NMR samples are in some cases different (a supercooling effect is present in the DSC measurements).



(*a*) (*b*)

Figure 1. ^{2}H NMR spectra of C_6D_6 added to **1** in the mesophase region: (*a*) crystalline powder; (*b*) aligned sample.

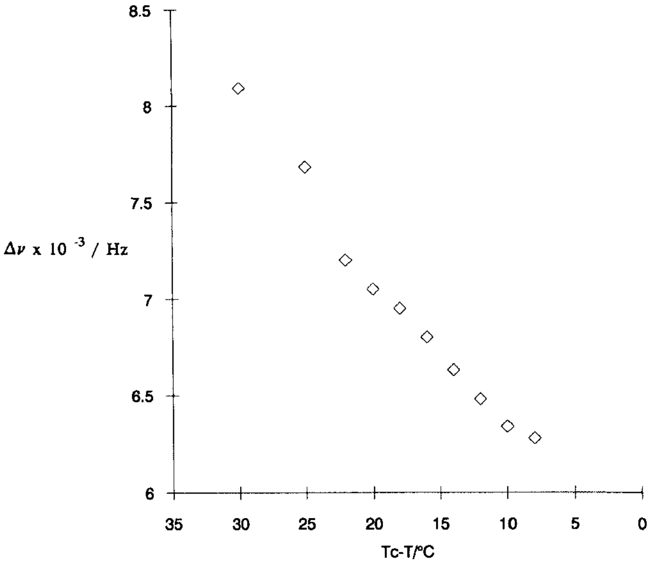


Figure 2. The doublet separation in ^{2}H NMR spectra of C_6D_6 added to **1** against the reduced temperature; T_c is the clearing temperature.

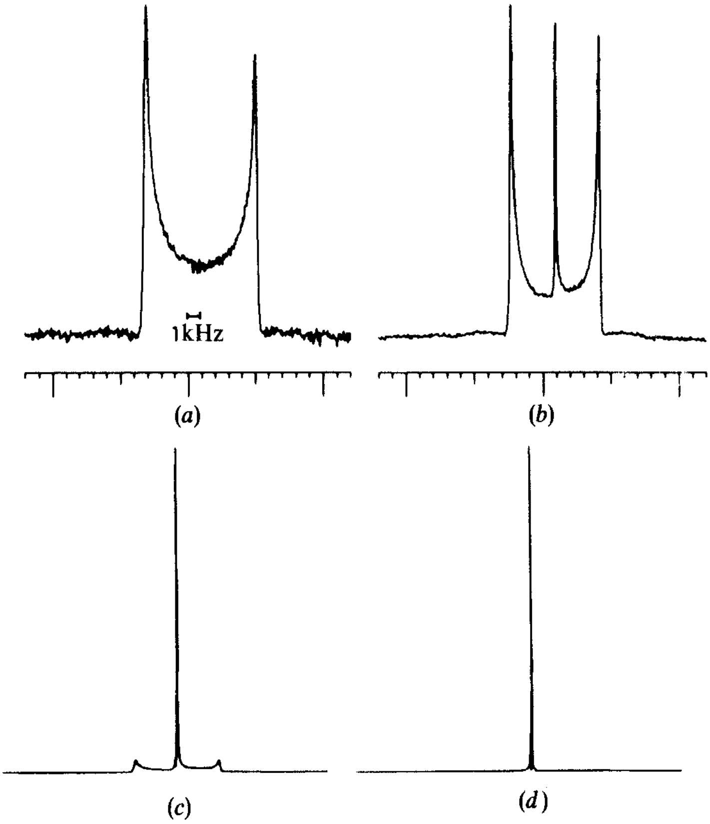


Figure 3. ^{2}H NMR spectra of **1** taken at: (*a*) 30°C; (*b*) 48°C; (*c*) 52°C; (*d*) 57°C.

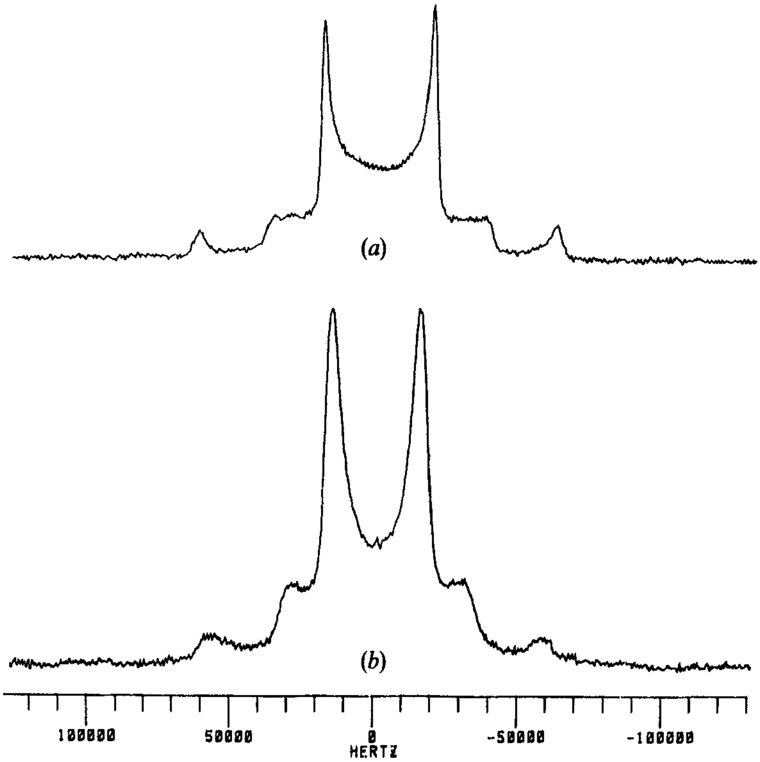


Figure 4. (*a*) ^{2}H NMR spectrum of solid crystalline **2** taken at room temperature; (*b*) ^{2}H NMR spectrum of **2** in the mesophase at room temperature.

change. Therefore, we exclude the slow formation of the mesophase and, on the basis of optical, DSC and IR measurements, the presence of two phases in equilibrium. We conclude that isotropic and ordered deuteriated benzenes are in slow equilibrium between themselves.

3.2. *Deuteriated compound 2*

Deuterium spectra of **2** were recorded adding 3 per cent of benzene to the sample in order to compare properly the results with the previous findings. The addition of benzene affected only the transition temperatures of **2** (see the table), but not the deuterium NMR spectra.

Solid crystalline **2** (see figure 4(*a*)) shows a main powder pattern due to the CD_3 groups and a less intense pattern, of which only the perpendicular component is visible, due to the CD groups. The doublet separation of the perpendicular component ($\Delta\nu_Q^{\perp}$) of the CD_3 moiety is 37·8 kHz, slightly less than expected for a fast ($\geq 10^6\,s^{-1}$) rotation around the threefold axis [14] of the C–CD_3 group. This additional reduction in $\Delta\nu$ is indicative of the presence of librational motions of the molecular axis. Instead the $\Delta\nu_Q^{\perp}$ of the CD group measures 124·5 kHz, which is consistent with a static deuterium. According to the molecular geometry determined from an X-ray crystal structure of an analogous macrocycle derivative [15], the CD_3 groups are almost collinear with the main axis of the molecule, while the CD bond axis makes an angle of about 109°.

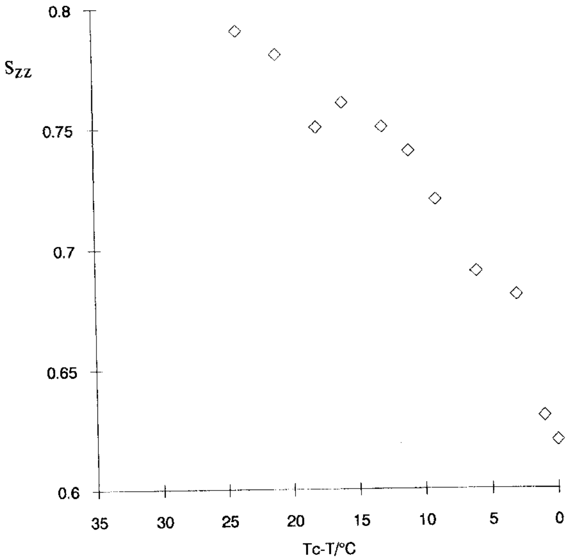


Figure 5. The ordering matrix element S_{zz} versus temperature for **2**.

Therefore the average angular excursion due to librational motions is negligible for the CD group in the solid phase. Besides all possible conformational processes involving the macrocycle ring (i.e. pseudo-rotation) do not involve the CD–CD_3 units [16].

In the lower temperature range of the mesophase (26°C) the powder pattern does not change, except for a slight decrease of the peak separation ($CD_3 = 29{\cdot}4$ kHz, CD $= 109{\cdot}0$ kHz) attributable to the onset of anisotropic motions around the director axis (see figure 4(*b*)). Therefore, a rapid diffusion around the molecular axis is excluded, since it would imply a one-third reduction of the quadrupolar coupling constant of the CD deuterium. Being the CD_3 collinear with the molecular axis, the ratio between the $\Delta\nu_Q^{\perp}$ in the mesophase and $\Delta\nu_Q^{\perp}$ in the solid gives a direct measurement of S_{zz} the ordering matrix element of the main molecular axis relative to the director axis (S_{zz} at 26°C is 0·77).

By increasing the temperature the relaxation time T_2 decreases, so a consistent part of the signal is lost in the quadrupolar echo sequence ($\tau = 20\ \mu s$). Under these conditions the background defects due to the acoustic ring phenomena overlap the spectrum and prevent a detailed analysis of the lineshape. However, since the CD doublet separation is still visible, rotational diffusion can be excluded. The CD_3 broad doublet provides the variation of the order parameter with temperature (see figure 5). At 60°C the isotropic phase begins to appear, becoming dominant at 64°C.

4. Discussion

Comparison of our ^2H NMR results for C_6D_6 dissolved in **1** with those obtained on reported D_{ho} systems such as triphenylene and truxene derivatives show consistent differences [9–12]. In fact in our case the maximum doublet separation is much higher (8000 Hz against 3700 Hz in truxene derivatives) and tend to decrease on increasing the temperature. In the reported cases an increase of the separation approaching the isotropic transition is observed, also for compounds having long alkyl chains. This behaviour has been related to the presence of a fast equilibrium between two solvation sites having order parameters of opposite sign: an intracolumnar one and an intrachain one. Furthermore we observe an isotropic C_6D_6 signal at a much lower temperature (*c.* 44°C) than the isotropic phase transition (60°C measured on the same sample by optical microscopy and DSC), which increases with the temperature, while for **2** + 3 per cent of C_6H_6 we find a narrow biphasic region (4°C) centred around the mesophase–isotropic liquid transition.

Studies carried out on hexaalkyloxytriphenylene derivatives with deuteriated chains have shown a high disorder of the side chains with a wide distribution of different conformations [17]. This is conceivably true also in our case, in the presence of even longer alkyl chains, thus providing more or less amorphous regions between the columns. Based on these considerations and on the fact that the order parameter of C_6D_6 is generally very low, we propose a model in which the long alkyl chains are not able to averagely orient C_6D_6 along a preferred direction, which is shown by the presence of an isotropic deuterium signal. Therefore, we assign the isotropic peak to the C_6D_6 which is randomly oriented in the chain region and the anisotropic one to the C_6D_6 intercalated in the core region of the columnar mesophase.

The presence of a slow equilibrium between the two solvation sites can be justified by the fact that the mesogen forms a cavity with strong host properties toward the guest C_6D_6 [18]. The complexation properties of the mesogenic core increase the activation energy required by C_6D_6 to leave the cavity and solvate the alkyl chains considerably, and in consequence the exchange rate can be appreciably slowed down. In this way we expect a bigger $\Delta\nu_Q$ separation since the less ordered component does not contribute to the separation of the oriented ones. Consequently the decrease of $\Delta\nu_Q$ with temperature is likely to reflect a decrease of the order parameter according to the Maier–Saupe theory, as confirmed by the trend found for **2** (cf. figures 2 and 5).

^{2}H NMR on deuteriated derivative **2** allowed the direct measurement of the ordering matrix element S_{zz}, whose value (0·77) is consistent with a very ordered columnar mesophase. Fast rotational diffusion around the molecular axis is excluded, preventing any straightforward correlation between the quadrupolar splittings and the ordering matrix element difference $S_{xx} - S_{yy}$ of the molecular axes.

The authors wish to thank Professor C. Zannoni (University of Bologna, Italy) for helpful discussions and suggestions.

References

[1] Zimmermann, H., Poupko, R., Luz, Z., and Billard, J., 1985, *Z. Naturf.* (*a*), **40,** 149.

[2] Malthête, J., and Collet, A., 1985, *Nouv. J. Chim.*, **9,** 151.

[3] Zimmermann, H., Poupko, R., Luz, Z., and Billard, J., 1988, *Liq. Crystals*, **3,** 759.

[4] Cometti, G., Dalcanale, E., Du vosel, A., and Levelut, A. M., 1990, *J. chem. Soc. Chem. Commun.*, p. 163.

[5] Malthête, J., and Collet, A., 1987, *J. Am. chem. Soc.*, **109,** 7544.

[6] Goldfarb, D., Poupko, R., and Luz, Z., 1983, *J. chem. Phys.*, **79,** 4035.

[7] Bonsignore, S., Cometti, G., Dalcanale, E., and Du vosel, A., 1990, *Liq. Crystals*, **8,** 639.

[8] Davis, J. H., Jeffrey, K. R., Bloom, M., Valic, M. I., and Higgs, T. P., 1976, *Chem. Phys. Lett.*, **42,** 390.

[9] Goldfarb, D., Luz, Z., and Zimmermann, H., 1982, *J. Phys., Paris*, **43,** 421.

[10] Goldfarb, D., Luz, Z., and Zimmermann, H., 1982, *J. Phys., Paris*, **43,** 1255.

[11] Goldfarb, G., Belsky, I., Luz, Z., and Zimmermann, H., 1983, *J. chem. Phys.*, **79,** 6203.

[12] Praefcke, K., Poules, W., Scheuble, B., Poupko, R., and Luz, Z., 1984, *Z. Naturf.* (*b*), **39,** 950.

[13] RICHARDS, G. M., and DONG, R. Y., 1989, *Liq. Crystals*, **5**, 1011.
[14] ROTHGEB, T. M., and OLDFIELD, E., 1981, *J. biol. Chem.*, **256**, 1432.
[15] DALCANALE, E., and UGOZZOLI, F. (unpublished results).
[16] ABIS, L., DALCANALE, E., DU VOSEL, A., and SPERA, S., 1988, *J. org. Chem.*, **53**, 5475.
[17] GOLDFARB, D., LUZ, Z., and ZIMMERMANN, H., 1983, *J. chem. Phys.*, **78**, 7065.
[18] CRAM, D. J., KARBACH, S., KIM, H.-E., KNOBLER, C. B., MAVERICK, E. F., ERICSON, J. L., and HEGELSON, R. C., 1988, *J. Am. chem. Soc.*, **110**, 2229.