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^{2}H NMR spectra of 2-(*p*-heptylbenzoyloxy)-5-(*p*-heptylbenzenazo)tropone

A new sigmatropic liquid crystal

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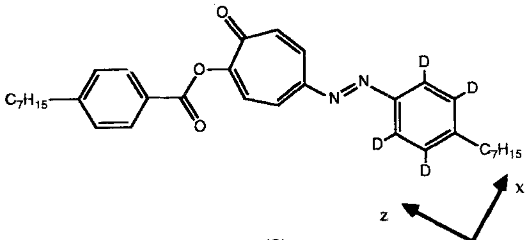
Liquid crystals incorporating in their molecular framework a seven-membered ring are still relatively rare [1]. Recently the synthesis and thermal behaviour of a series of liquid crystal materials having a tropone moiety in their mesogenic core have been reported [2–4]. These mesogens, based on a 2-(acyloxy)tropone core structure, show intramolecular migration of the acyl substituents between the two oxygen atoms at C–1 and C–2, an effect already known for simple 2-(acyloxy)tropones in their isotropic solutions [5]. This migration involves a concerted [1, 9]-sigmatropic rearrangement [2]. This rearrangement could play a major role in determining the properties of the mesophases: it has been suggested in fact that, because of this rearrangement, the mesogenic molecules acquire a mean rod-like shape which can sustain the mesophase formation [2].

In order to study the influence of the acyl migration on the liquid crystalline properties of the tropone class of liquid crystals, specifically from the point of view of the molecular orientational ordering, we have synthesized both 2-(*p*-heptylbenzoyloxy)-5-(*p*-heptylbenzenazo)tropone (**1**) and its partially deuteriated analogue **2**:



(**2**)

The synthesis of 2-(*p*-heptylbenzoyloxy)-5-(*p*-heptylbenzenazo)tropone (**1**) was carried out in a similar way to previously described procedures [5]. 2-Hydroxy-5-(*p*-heptylbenzenazo)tropone [6] (0·304 g, 0·94 mmol) was added to 4-heptylbenzoyl chloride (0·224 g, 0·94 mmol) in dry pyridine (8 ml) in the presence of a few crystals of DMAP. The mixture was stirred overnight at room temperature, then added to water

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and the product extracted into $CHCl_3$. The residue after evaporation was subjected to SiO_2 TLC with C_6H_6. The R_f 0·42 fraction was collected to give **1** as orange red crystals (0·410 g, 0·78 mmol, 83 per cent).

^1H NMR ($CDCl_3$) 20°C δ_{TMS} 8·10 (d, $J = 8{\cdot}32$ Hz 2 H) 7·91 (broad signal, 2 H) 7·85 (d, $J = 8{\cdot}3$ Hz, 2 H) 7·43 (broad d, 2 H) 7·33 (d, $J = 8{\cdot}3$ Hz, 2 H) 7·30 (d, $J = 8{\cdot}32$ Hz, 2 H) 2·71 (broad t, $J = 7{\cdot}4$ Hz, 4 H) 1·65 (m, 4 H) 1·29 (m, 16H) 0·83 t, $J = 7{\cdot}4$ Hz, 6 H). On heating to 51°C the broad signal at δ 7·91 appeared as a doublet ($J = 12$ Hz) and the broad doublet at δ 7·43 became a sharp doublet ($J = 12$ Hz).

The deuteriated analogue **2** was prepared by a similar procedure starting from 2-hydroxytropone and tetradeuteriated p-heptylaniline. In the ^1H NMR spectrum of **2**, the AA'BB' system (at δ 7·33 and 7·85) was lacking.

The phase transition temperatures were determined by differential scanning calorimetry, optical microscopy and nuclear magnetic resonance. Compound **1** gives on heating one enantiotropic nematic (N) mesophase (melting temperature 95°C) extending over a very broad temperature range ($T_{N-I} = 142$°C) and with enthalpy and entropy values at the N–I transition of $\Delta H_{N-I} = 1{\cdot}2\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S_{N-I} = 2{\cdot}9\ \mathrm{J\,mol\,K)^{-1}}$, respectively. On cooling, a monotropic smectic C (S_C) mesophase occurs at 86°C. There is no detectable enthalpy associated with this N–S_C transition which appears, therefore, to be second order in character. In contrast, the transition was easily detected by microscopy, by the appearance of the typical banded pattern with transition bars. The observed change with temperature of the birefringence colours of the schlieren texture of the S_C phase suggested that the tilt angle increases with decreasing temperature. On further cooling, another mesophase formed at 80°C. This mesophase was tentatively identified as smectic I (S_I) by observation of its paramorphotic schlieren texture that showed typical brushes arising from point singularities as obtained on cooling to obtain the schlieren texture of the S_C phase. The S_C–S_I transition is rather common and for instance, occurs in standard materials exhibiting the S_I phase for miscibility studies, for example, TBDA and 8OSI [7]. However, the N–S_C–S_I sequence appears to be more unusual, an example being that of N,N'-bis-(4-*n*-heptyloxybenzylidene)1,4-phenylenediamine [7]. Finally, the onset of an additional mesophase was observed at about 62°C, but its nature could not be decided due to concomitant crystallization.

$$\begin{tikzcd}
C \arrow[r, "95°C"] & N \arrow[r, "142°C"] \arrow[d, "86°C"] & I \\
S_I \arrow[u, "62°C"] & S_C \arrow[l, "80°C"'] &
\end{tikzcd}$$

For the deuteriated mesogen **2**, we observed the same mesophase sequence, but with different transition temperatures. In particular, the clearing temperature ($T_{N-I} = 152$°C) was unusually higher than that of **1**.

$$\begin{tikzcd}
C \arrow[r, "92°C"] & N \arrow[r, "152°C"] \arrow[d, "85°C"] & I \\
S_I \arrow[u, "72°C"] & S_C \arrow[l, "80°C"'] &
\end{tikzcd}$$

The orientational order was investigated by ^{2}H NMR measurements using a Bruker AMX 300 spectrometer, equipped with variable temperature control, under proton decoupling conditions. The deuterium NMR spectra of compound **2**, some of which are shown in figure 1, showed a quadrupolar splitting relative to the arene deuterons of the azobenzene substituent. This temperature-dependent splitting, clearly shows a discontinuity at 85°C in agreement with optical microscopy which reveals a phase transition (N–S_C) which was not detected by DSC.

The deuterium spectra allowed us to determine the orientational order parameters of the deuteriated phenyl ring, i.e. local order parameters. The observed peaks could be analysed satisfactorily as being from pairs of deuterons with identical quadrupolar splitting and interacting via one dominant dipolar coupling. The vector $\mathbf{r}_{DD}$ between the *ortho*-deuterium nuclei is essentially parallel to the local z axis so that the dipolar coupling D_{DD} depends only on the local order parameter S^L_{zz}. The observable quadrupolar splittings $\Delta\nu_q$ were thus used to evaluate the local biaxiality $S^{L'}_{xx}-S^{L}_{yy}$ according to the following expression:

$$\Delta\nu_q=\tfrac{3}{4}q\{S^L_{zz}(3l^2_{zb}-1)+(S^L_{xx}-S^L_{yy})(1-l^2_{zb})\}.$$

Here, the asymmetry parameter η has been neglected, while q is the quadrupolar coupling constant, assumed to be 186 kHz, which is a value typical for aromatic deuterons. The direction cosine between the z axis and the C–D bond, l_{zb}, is given by the C–D bond angle with the *para*-axis and was assigned a value of 60°. The S_{zz} order parameter for the phenyl ring, shown in figure 2, increases smoothly with decreasing temperature in the nematic phase, then shows an appreciable jump at the N–S_C

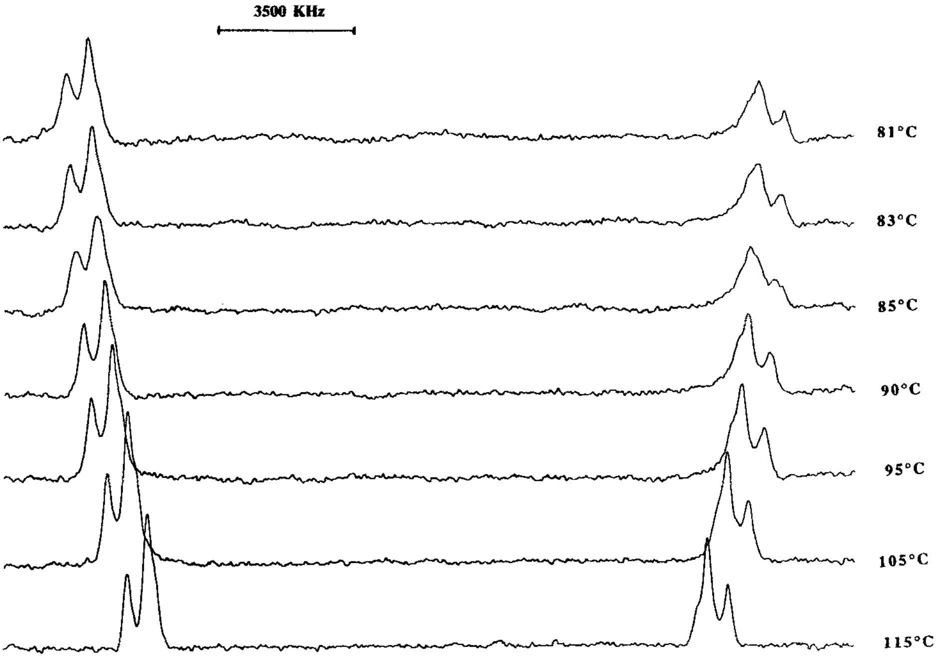

Figure 1. ^{2}H NMR spectra of compound **2** recorded on lowering the temperature from the nematic phase through the smectic C phase.

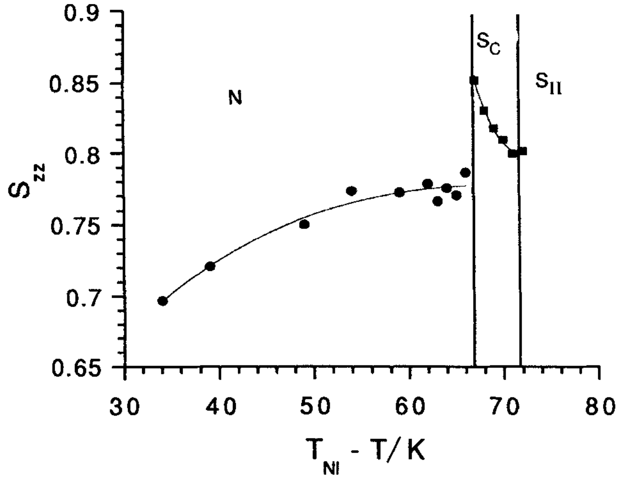

Figure 2. Local order parameter S_{zz} of the *para*-axis of the deuteriated phenyl ring of **2** as a function of temperature.

transition temperature and, finally, decreases in the smectic C phase. The local biaxiality could be evaluated to be of the order of 0·1 throughout the whole temperature range examined.

The jump in the orientational order, in contrast with the DSC measurements, suggests a first order N–S_C transition. We show below that the decrease in the local order with decreasing temperature in the smectic C phase is in agreement with the optical microscopy observations which indicate a progressive increase in the smectic C tilt angle (θ) with lowering of the temperature. A strong temperature dependence of θ is typical of a class of S_C liquid crystals, reported also as C_2 smectics [8]. In this class of smectics, θ increases with falling temperature, starting from zero at the upper temperature limit (the N–S_C phase transition in our case). As θ slowly increases, since the smectic layers are locked because of the phase viscosity, the long molecular axes tilt away from the field direction. This effect produces the decrease in the local S_{zz} order parameter: the apparent decrease in order, therefore, is not due to a decrease in orientational order, but is directly related to the increase in tilt angle. An evaluation of the order of magnitude of θ at the lowest temperature can be made by assuming that the orientational order does not change much throughout the smectic C phase range and that the variation in local order parameter is due only to variation in θ. The tilt angle thus obtained is $\theta \approx 11°$, which is a reasonable value for this type of mesophase exhibiting lower tilt angles with respect to smectic C_1 phases [8].

No deuterium signals appeared in the lower temperature smectic phases. This could be due to the high viscosity of these phases. On the other hand, a progressive increase in the linewidth was already apparent in the spectra of the smectic C phase as shown in figure 1.

It is worthwhile to discuss the role of the sigmatropic rearrangement suggested for this type of molecule on both the mesophase formation and the polymorphic behaviour of **1** and **2**. This rearrangement clearly appears in the proton spectra of isotropic solutions in $CDCl_3$, which show the effects of a dynamic process in going from 20 to 50°C. In the deuterium spectra for the liquid crystalline phases, the linewidth broadening observed in the S_C phase could be due both to the decrease in the rate of the molecular rearrangement and to the overall molecular motion becoming restricted in the more viscous phase. From the observed deuterium spectra we can conclude, therefore, that in the fast dynamic regime, the effects of the sigmatropic rearrangement cannot be evaluated from the lineshapes. Such effects can be inferred, however, from the behaviour of the orientational order as a function of temperature: at higher temperatures, in fact, a fast rearrangement can produce a mean rod-like shape of the mesogenic molecule, thus favouring a nematic phase. At lower temperatures, slower molecular rearrangement should produce a progressive asymmetrization of the mesogenic molecule and this could explain the onset of a S_C mesophase, as well as the progressive increase in θ. It should be pointed out here, however, that the apparent lowering of S_{zz} in the S_C phase does not mean that at any rate the order lowers with decreasing temperature, and simply reflects the temperature variation in tilt angle.

In order to verify and characterize the sigmatropic rearrangement, it is necessary to study the rate of such a process and its temperature dependence. We have, therefore, synthesized the same mesogenic molecular structure but with a partially deuteriated tropone moiety. This new ^{2}H NMR study is in progress.

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