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Observing molecular motions of a fluorinated ferroelectric liquid crystal using fluorine-19 NMR

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Fluorine-19 NMR spectra have been recorded for both the phases (cholesteric and smectic C*) of the ferroelectric liquid crystal 2,3-difluoro-4-octyloxybiphenyl-4′(-4″-oxycarbonyl-(*S*)-1-chloro-3-methylbutyl)benzoate, using a conventional high-resolution NMR probe. The magnitude of the dipolar coupling constant, D_{FF}, was found to increase with decreasing temperature in the cholesteric phase with a sudden increase (of approximately 1 000 Hz) at the cholesteric–smectic C* transition, whereafter a more gradual change was observed. The order parameter, S_{FF}, was subsequently calculated for each temperature.

1. Introduction

There is considerable current interest in methods which could contribute to an understanding of the correlation between the physical properties and the molecular structure of a liquid crystal. A variety of methods have been used to study molecular motion in liquid crystalline phases. In this respect, NMR spectroscopy has been used quite successfully as it is excellently suited as a probe on the molecular level. The selective incorporation of deuterium into a specific part of a molecule therefore resulted in the development of techniques from which information on orientational properties of a liquid crystal could be obtained [1–4]. The synthesis of partially deuterated liquid crystals does however, remain expensive and involves considerable synthetic effort. Alternatively, the study of partially fluorinated liquid crystalline compounds using ^{19}F NMR has not received much attention, partly due to instrumental restrictions [5], but mainly as a result of the lack of suitably fluorinated compounds. The recent development of much improved synthetic routes resulted in selectively fluorinated mesogens becoming readily accessible [6]. Apart from the much enhanced sensitivity of the ^{19}F nucleus relative to that of ^{2}H, the incorporation of fluorine has the added advantage of reducing the melting point of a liquid crystal, suppressing the formation of the more ordered smectic phases and most importantly stabilizing tilted phases, such as smectic C.

The work presented here represents the first ^{19}F NMR study of a liquid crystal with a chiral smectic C (S_C^*) phase (i.e. ferroelectric) and we show that it is possible to obtain well-resolved spectra using a conventional high-resolution probe.

2. Experimental

For the purpose of our work, a liquid crystal, 2,3-difluoro-4-octyloxybiphenyl-4′-(4″-oxycarbonyl-(*S*)-1-chloro-3-methylbutyl)benzoate **1**, which contains two fluorine

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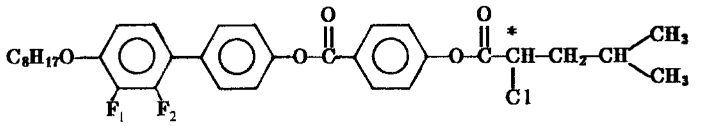

1

$$C \underset{321\,K}{\overset{347\,K}{\rightleftarrows}} S_C^* \xrightarrow{380\,K} Ch \xrightarrow{390\,K} I$$

Figure 1. Structure and phase transitions (K) of 1. Crystal (C), smectic C* (S_C^*), cholesteric (Ch) and isotropic (I).

atoms *ortho* with respect to one another on the aromatic core and a chiral chlorinated terminal chain was synthesized. The compound has a favourable temperature range and a phase sequence which, when submitted to cooling in the presence of the superconducting magnet, results in good alignment in the S_C^* phase. Compound **1** was synthesized by treating 2,3-difluoro-4-octyl-oxybiphenyl-4′-(4″-hydroxy)benzoate [7] with (*S*)-2-chloro-4-methylpentanoic acid (prepared by treating the diazonium salt of *S*-leucine with hydrogen chloride). The structure of the product was confirmed with ^{1}H, ^{13}C and ^{19}F NMR (as a solution in $CDCl_3$) as well as IR and mass spectroscopy. Liquid crystalline phases (see figure 1) were identified with polarizing microscopy and confirmed with DSC.

Fluorine-19 NMR spectra were obtained using a Bruker AC300 spectrometer equipped with a QNP probe-head and a variable temperature control unit. The liquid crystal was contained in a coaxial insert (Wilmad Glass Co.) which has an outer diameter of 2 mm. This was inserted into a standard 5 mm NMR tube containing dimethylsulphoxide-d_6 which served the dual purpose of providing a lock signal as well as to minimize temperature gradients in the sample. Proton decoupling ($\gamma B_2 = 9{\cdot}26$ kHz), without which the spectrum was broad and featureless, was accomplished by employing a WALTZ sequence. Decoupling was used only during the acquisition time of 0·19 s in order to restrict radiofrequency overheating, together with a total cycling time of 1·7 s. A decrease in linewidth was not detected when increasing the proton decoupling power, therefore total decoupling was assumed. Spectra were acquired after slowly cooling the compound from the isotropic state (1°C/min) in the magnetic field to ensure good alignment. Under these conditions a satisfactory spectrum could be obtained in 30 min.

3. Results

The isotropic melt (see figure 2 (*a*)) has the expected two doublets ($^3J_{FF} = 17{\cdot}5$ Hz) of which we assigned the low field one to F_1. Cooling of the compound below its clearing point resulted in a dramatic change in chemical shift and a spectrum of which the pattern, upon closer inspection, corresponded to that of an AB spin system (see figure 2 (*b*)). The difference in linewidth between the resonances of F_1 and F_2 became more pronounced as the sample was cooled. The cholesteric to smectic C* transition is characterized by a sudden large jump in chemical shift, together with further broadening of the two F_1 resonances (see figure 2 (*c*)). Although we are uncertain as to the possible cause for this broadening, the location of F_1 at the end of the core could either make it more susceptible to movement caused by the flexible chain or could be a result of the combined effect of chemical shift anisotropy, $\Delta\sigma_F$, and dipolar coupling, which together would give a differential broadening of the kind observed. Also, in the

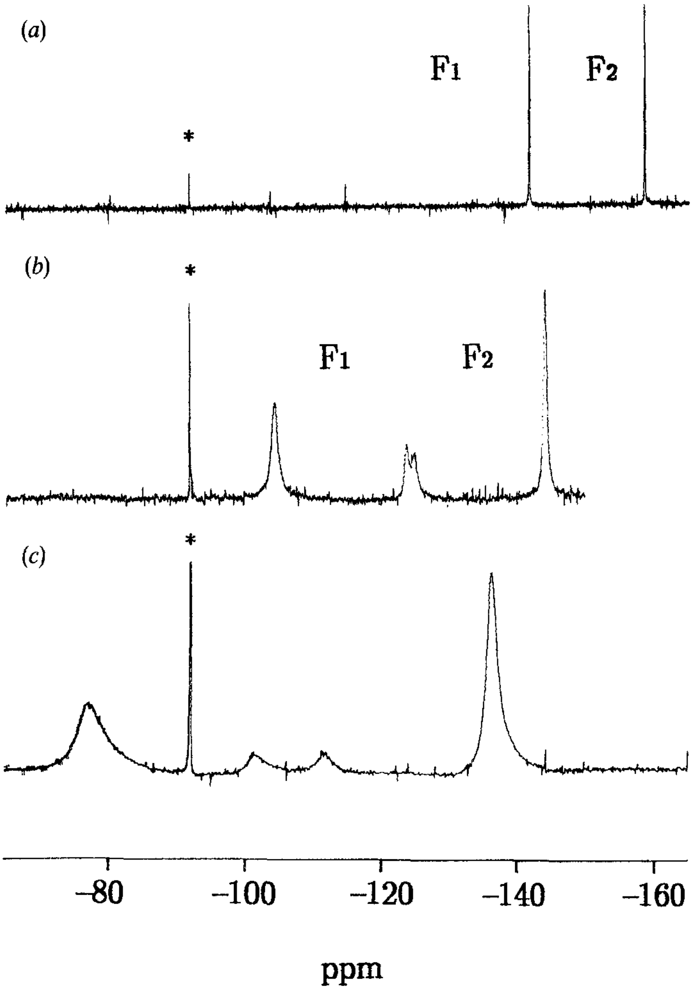

Figure 2. Proton decoupled ^{19}F NMR spectra of 1: (*a*) isotropic (391 K); (*b*) cholesteric (389 K); (*c*) smectic C* (339 K). 1-bromo-3-fluoro-4-iodobenzene was used as external reference (−91 ppm rel. $CFCl_3$) and is indicated by *.

S_C^* phase, intermolecular ^{19}F–^{19}F dipolar interaction can make a significant contribution to the linewidth. The resolution of the spectra obtained in both phases is evidential of an unwound helix. The molecular directors in the cholesteric phase align themselves with the magnetic field to form a nematic phase, a situation which is carried through into the underlying S_C^* phase which loses its chirality to become smectic C (however, the phases will hereafter be referred to as cholesteric and smectic C* to avoid confusion).

Analysis of the AB spin system according to Diehl [8] at each temperature yielded the homonuclear dipole–dipole coupling constant (D_{FF}) and the chemical shift (given in table 1). Anisotropic coupling between two *ortho* fluorines was taken to be negligibly small relative to D_{FF}. Computational iterative calculations (using PANIC software) were carried out using the resonance frequencies of the spectra shown in Figures 2 (*b*, *c*) keeping J_{FF} constant. D_{FF} values obtained were found to be in excellent agreement with

Table 1. Experimental ^{19}F–^{19}F dipole–dipole coupling constants (D_{FF}) and calculated order parameters (S_{FF}) of 1 at different temperatures.

Phase/ phase transition	T/K	D_{FF}/Hz	S_{FF}
Isotropic	393	—	—
	391	—	—
Isotropic–cholesteric	390	2670	0·453
Cholesteric	389	2940	0·499
	388	3110	0·527
	387	3090	0·524
	386	3200	0·542
	385	3270	0·555
	384	3350	0·568
	382	3460	0·587
	381	3520	0·597
Cholesteric–smectic C*	380	3580	0·607
smectic C*	378	4540	0·770
	374	4630	0·785
	369	4720	0·801
	365	4740	0·804
	361	4790	0·812
	356	4830	0·819
	352	4900	0·831
	348	4950	0·840
	339	4960	0·841

those obtained from the analysis. D_{FF} is found to increase as the temperature is lowered, with the cholesteric to smectic C* transition once again marked by a sudden change—this time an increase of approximately 1000 Hz in D_{FF}. As the two fluorine nuclei are attached to the same aromatic ring, they are conformationally fixed with respect to one another. This means that the observed large change in D_{FF} at the cholesteric to smectic C* transition cannot be ascribed to any conformational changes within the molecule, but coincides with a change in the degree of ordering of the F_1–F_2 vector. D_{FF} can be related to the order parameter, S_{FF}, for the internuclear vector by

$$D_{FF} = -1{\cdot}063 \times 10^5 \, S_{FF} \, r_{FF}^{-3},$$

where $r_{FF} = 2{\cdot}622$ Å (obtained from an X-ray structure [9]). Values calculated for S_{FF} are given in table 1 and are presented graphically in figure 3 (top). Lowering of the temperature causes the molecular movement in the cholesteric phase to become more restricted, resulting in an increase in the order parameter which in turn produces a larger D_{FF} value. In the more ordered S_C^* phase the order parameter (and therefore D_{FF}) does not change appreciably with temperature and is close to its theoretical maximum. This in turn suggests that the molecular directors, rather than the smectic plane normals, are aligned with the field.

4. Summary

The selective fluorination of liquid crystals clearly provides a simple yet powerful method by which molecular motion in a particular liquid crystalline phase can be observed. We have shown that well-resolved spectra can be obtained in a short time

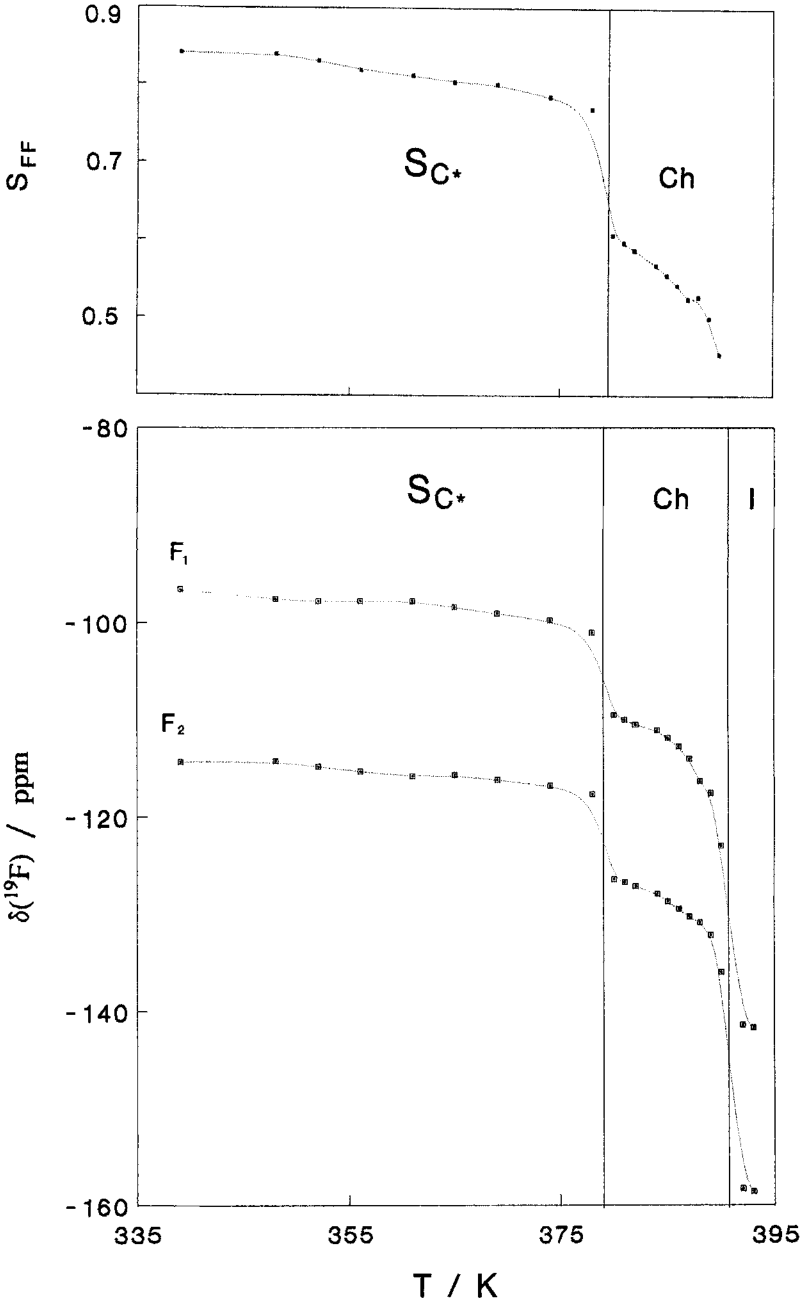

Figure 3. Temperature dependence of the order parameter, S_{FF} (top), and of $\delta(^{19}F)$ of F_1 and F_2 in the isotropic and liquid crystalline phases (the lines are intended to guide the eye).

without elaborate equipment using a conventional high resolution probe and that the simplicity of the spectra allows for instant recognition of phases and phase transitions. Hoping to extend this technique, we are presently investigating several other fluorinated liquid crystals.

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