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NMR Study of the Molecular Order in a Liquid Crystal with Peculiar Smectic Phases

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We present a NMR study of the molecular order in a compound presenting three bilayer smectic mesophases: S_{A2}: S_{C2} and $S_{C?}$ anticlinic-like). Two different models are proposed for the interpretation of the angular dependence of experimental dipolar splittings observed for the S_{C2} and $S_{C?}$, respectively. The results presented here are in agreement with the model initially proposed in the literature for the $S_{C?}$ mesophase. In particular we present here the estimation of the two tilt angles associated with the structure of the $S_{C?}$ phase.

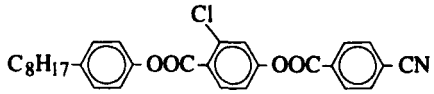
Keywords: molecular order; smectic C; anticlinic; NMR

INTRODUCTION

It is known that it is possible to observe different types of smectic A (S_A) and smectic C (S_C) mesophases, namely monolayer, bilayer and others in systems composed of molecules with a strong polar terminal group[1, 2, 3]. In particular, both tilted and non-tilted bilayer molecular arrangements have been observed in this kind of systems[4, 5]. Nuclear magnetic resonance (NMR) techniques have been used to successfully study the molecular order and the structural details in these mesophases, in particular the

smectic A and C phases[6, 7, 8].

In this work we present some results of a molecular order study by proton NMR of the octylphenyl-2-chloro-4-(p-cyano-benzoyloxy) benzoate, DB_8Cl for short[5, 9].



Cr 100°C $S_{C?}$ 107 °C S_{C2} 117°C S_{A2} 155°C N 168°C I

This compound presents a very interesting polymorphism since besides the nematic mesophase it presents three smectic bilayer mesophases: S_{A2}, S_{C2} and $S_{C?}$[5]. In these mesophases the molecules are associated in a head-on dimers as schematically shown in fig. 1. A anticlinic type of order was proposed for the $S_{C?}$ based in X-ray and dielectric measurements[10], fig. 1. The purpose of this work was to use angular dependent NMR proton

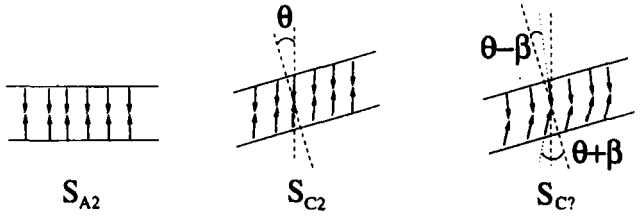


FIGURE 1 Representation of the smectic structures of DB_8Cl.

spectra to test the proposed model for the $S_{C?}$ mesophase in comparison with the results obtained for the other two smectic mesophases.

EXPERIMENTAL RESULTS

All experimental results were obtained in a Bruker SXP 4-100 MHz spectrometer using a $(\pi/2)_x$-$(\pi/2)_y$ pulse sequence with phase cycling for suppression of DC bias. Proton NMR spectra were collected as a function of the sample's orientation Δ in the magnetic field of 1.4 T, in all smectic

mesophases of DB_8Cl. All spectra were collected after slowly cooling the sample ($\leq 1°C/min$) from the isotropic phase to the desired mesophase, in the presence of the magnetic field. The temperature was controlled within $\pm 0.5°C$. The sample was rotated with the help of a step motor to achieve an angular resolution of 0.6°.

In fig. 2 we present the angular dependence of the reduced dipolar splittings $\Delta\nu_r = \Delta\nu(\Delta)/\Delta\nu(0)$ of the spectra in all smectic phases of the DB_8Cl.

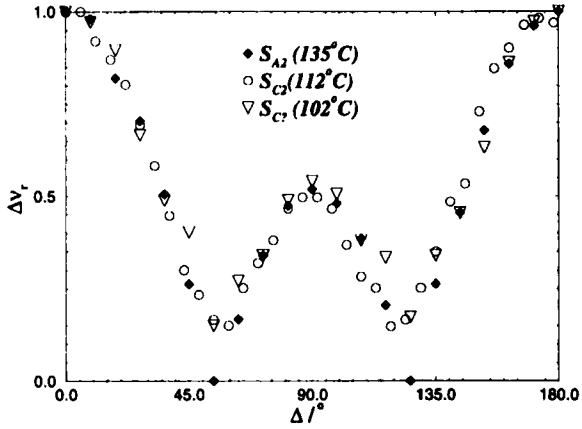


FIGURE 2 Experimental reduced dipolar splittings obtained for DB_8Cl.

DISCUSSION

As can be observed in fig. 2 the only clear difference appears between the dipolar splittings in the S_{A2} and $S_{C2}/S_{C?}$ mesophases. In fact the minima of the splittings is zero in the S_{A2} phase but different from zero in the $S_{C2}/S_{C?}$ phases. Moreover, the dipolar splittings minima for these mesophases are not as sharp as observed in the S_{A2} phase. In addition, the $\Delta\nu$ minimum, for the S_{C2}, seems to occur at an angle larger than the magic angle. These observations indicate that the observed dipolar

splittings for the S_{C2} and $S_{C?}$ phases are the result of an average over contributions coming from domains with different molecular orientations. This was previously reported for the S_C phase[8].

In the S_{A2} mesophase the $\Delta\nu_r$ is well interpreted in terms of a second order Legendre polynomial $P_2(\cos\Delta)$ law[6], as show in fig. 3. This means that the sample was well oriented and that, when rotated, the molecules retained their original orientation parallel to the magnetic field at $\Delta=0°$.

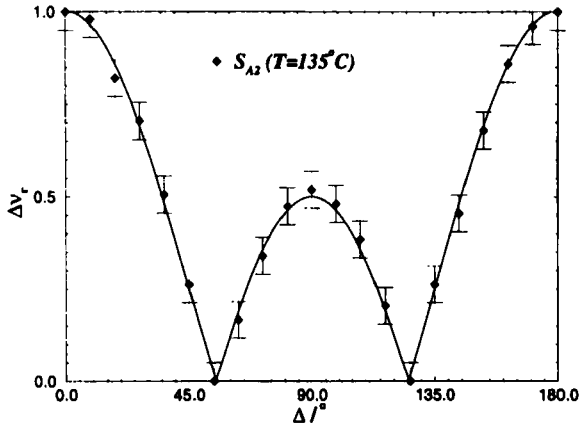


FIGURE 3 Fit of the reduced dipolar splittings as explained in the text.

In order to interpret the experimental results of both S_{C2} and $S_{C?}$ phases we first tried a structure model for the S_{C2} phase based on the assumptions initially proposed by Wise *et al.*[8]: (i) each molecule can be thought as a rod-like object with just one axis representing the preferred direction of orientation in the **B** field; (ii) when cooling from the isotropic to the S_{C2} phase in the presence of **B** the molecules remain align with the field and an uniform distribution of smectic layer normals over a cone, with opening equal to the tilt angle, θ, and axis parallel with the magnetic field, is formed (fig. 4); (iii) depending on the magnetic field intensity and elastic forces the molecules can reorient within the smectic layers in order

to remain as parallel to the field as possible, subjected to the tilt angle constraint. A particular smectic C domain is identified by its normal to

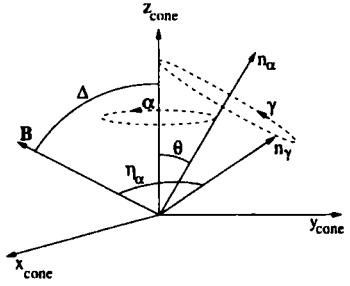


FIGURE 4 Diagram showing the axes and angles discussed in the text.

the layers, n_α, and azimuthal angle α. Within a particular smectic C domain the director orientation, n_γ, is defined by the azimuthal angle γ. η_α is the angle between a particular director n_γ and the magnetic field **B**. According to this model the reduced dipolar splitting can be calculated by

$$\frac{\Delta\nu(\Delta)}{\Delta\nu(0)} = \frac{1}{N}\sum_{i=1}^{N} P_2(\cos\eta_{\alpha_i}(\alpha_i, \gamma, \theta, \Delta)). \tag{1}$$

The η_α values can be obtained from the minimization of the reorientation energy, which can be written as the sum of a magnetic term ($E_{\text{mag.}}$) and an elastic term ($E_{\text{elas.}}$)

$$E_{\text{mag}} + E_{\text{elas}} \propto \left[\chi^{\text{mol}} B^2\right]_{lab} + R\cos(\gamma) \tag{2}$$

where χ^{mol} is the magnetic susceptibility tensor in the molecular frame and R the ratio between the two energy terms[12]. In order to write the magnetic energy in the laboratory frame, the magnetic susceptibility tensor in the molecular frame (χ^{mol}) was rotated from the molecular frame to the laboratory frame according to the Euler angles introduced in fig. 4[12]. As for the elastic energy term in eq. 2 we considered, as a first approximation, that E_{elas} is proportional to the elastic torque associated with

the orientation of the molecules within each layer with respect to their equilibrium orientations, as previously assumed for S_C^* phases[11]. Therefore, the energy will be a function of $\alpha, \gamma, \theta, \Delta$ and R, with R as a free parameter. The tilt angle θ was obtained from X-ray measurements[5].

In fig. 5 we present the best χ^2 fit of eq. 1 to the experimental results in the S_{C2} phase, obtained with $R = 2.8 \pm 0.5$ and $\theta = 27.5°$[5]. For comparison we also show the theoretical curve for $R = 0$ (no elastic term). It

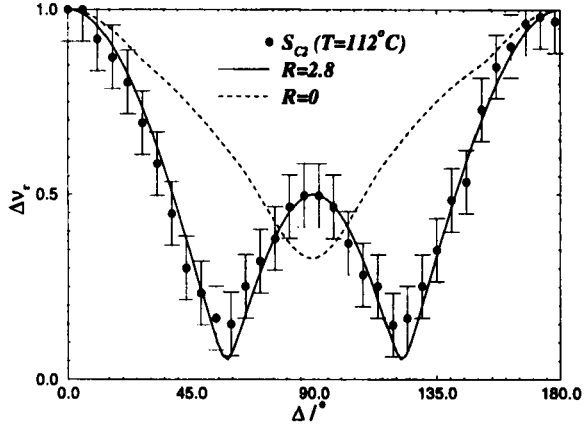


FIGURE 5 Fit of the reduced dipolar splittings as explained in the text.

is interesting to note that the introduction of an elastic term in the energy is fundamental to obtain a reasonable fit of the experimental results, as it can be observed in fig. 5. Some preliminary results obtained at a larger magnetic field confirmed our assumptions. A more detailed work will be presented elsewhere[12].

The model previously described could not be successfully applied to the interpretation of the $S_{C?}$ results. In fact the from the best fit of eq. 1 to the $S_{C?}$ results, using $\theta = 30°$[5, 9], we got $R \simeq 6$. This value, higher than the one obtained for the S_C results, sharpens and decreases the dipolar splittings minima and diminishes the fit's quality around the experimental dipolar splittings minima (see fig. 6). This could be expected in view of

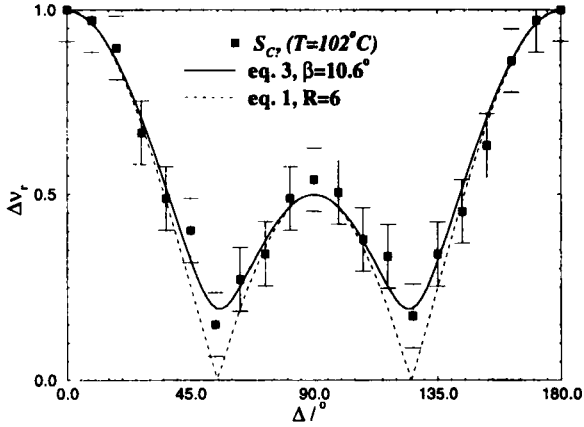


FIGURE 6 Fit of the reduced dipolar splittings as explained in the text.

the particular anticlinic-type structure proposed for the $S_{C?}$ phase, based in dielectric and X-ray measurements (see fig. 1)[10]. Therefore, we introduced some constraints in our previous model, namely: (i) the γ angle was fixed, assuming that the magnetic field was not strong enough to break the anticlinic-type of order (in consistency with an expected increase of the elastic forces with a temperature decrease); (ii) there are two different tilt angles defined as $\theta + \beta$ and $\theta - \beta$ (fig. 1), one for each smectic C? sublayer. θ can be obtained from X-ray experimental results[5, 9] but it is rather difficult to estimate β from direct measurements. Eq. 1 is then written as

$$\Delta\nu_r = \frac{1}{2N}\sum_{i=1}^{N}[P_2(\cos\eta_{\alpha_i}(\alpha_i,\gamma,\theta+\beta,\Delta)) + P_2(\cos\eta_{\alpha_i}(\alpha_i,\gamma,\theta-\beta,\Delta))] \tag{3}$$

where β is a free parameter. In fig. 6 we show the best χ^2 fit of eq. 3 to the $S_{C?}$ experimental results, using $\theta = 30°$[5, 9] and $\beta = 10.6° \pm 2.3°$. For comparison we also present the best fit of eq. 1 obtained with $R = 6$, using $\theta = 30°$[5, 9]. As it can be observed the model expressed by eq. 3 explains well the experimental results. It should be noted that the addition of

another β angle to the model fit $(\theta + \beta_1, \theta - \beta_2)$ gave also $\beta_1 \simeq \beta_2 \simeq 10°$. A more detailed work will be done in order to verify the validity of proposed model in the interpretation of dipolar splittings obtained for different magnetic fields[12].

In conclusion, we successfully interpreted our experimental results in terms of the structure models proposed in the literature for the smectic C mesophases exhibited by DB_8Cl. It was also possible to estimated the difference in tilt angles, β, between the two sublayers in the $S_{C?}$ phase. We should stress that to our knowledge this is the first experimental determination of the β parameter.

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