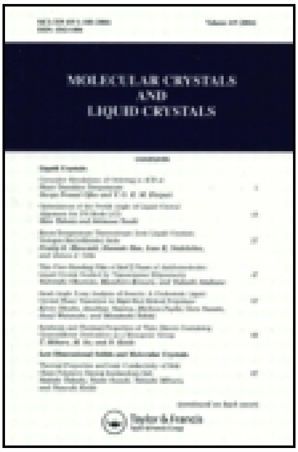

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NMR Study of Molecular Order in a Liquid Crystal with Smectic A_d and Reentrant Nematic Mesophases. A Comparative Study with Models for the S_{Ad} Phase

J. L. Figueirinhas [a] , C. Cruzi [a] , A. C. Ribeiro [a] & Nguyen Huu Tinh [b]

[a] Centro de Física da Matéria Condensada, Av. Prof. Gama Pinto, 2, 1699, Lisboa Codex, Portugal

[b] Centre de Recherche, Paul Pascal Domaine Universitaire, 33405, Talence, France

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NMR STUDY OF MOLECULAR ORDER IN A LIQUID CRYSTAL WITH SMECTIC A_d AND REENTRANT NEMATIC MESOPHASES. A COMPARATIVE STUDY WITH MODELS FOR THE S_{Ad} PHASE.

J. L. FIGUEIRINHAS[#], C. CRUZ[#], A. C. RIBEIRO[#], NGUYEN HUU TINH[*]
[#] Centro de Física da Matéria Condensada
Av. Prof. Gama Pinto, 2, 1699 Lisboa Codex, Portugal
[*] Centre de Recherche Paul Pascal
Domaine Universitaire, 33405 Talence, France

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Abstract The orientational order of a compound exhibiting nematic, S_{Ad} and reentrant nematic mesophases was studied through the analysis of proton spectra of the molecular core and deuterium spectra of the chain. The results are compared with the different theoretical models for the S_{Ad} phase. Simulations of the proton spectra yield the molecular core order parameters and rule out some of the models proposed, favoring others. Dynamical information regarding the life times of the different molecular aggregates proposed to exist in the S_{Ad} phase is obtained from the deuterium spectra of the chain.

Keywords: molecules, order, NMR, smectics, reentrant, phases

INTRODUCTION

In the large majority of condensed matter systems an increase in temperature leads to states of higher disorder. However, there are several systems, in particular some liquid crystals, where this trend is inverted.

The phenomenon of reentrancy in liquid crystals was first observed by P. Cladis [1] for the nematic phase in a mixture of two compounds with molecules which have a strong terminal dipole. This phenomenon was later observed also in the S_A phase and was detected both in mixtures and pure compounds, with molecules which have a strong terminal dipole (groups CN and NO_2) [2]. Multiple reentrancy of the nematic and smectic A type polymorphisms were also observed [2]. Smectic A phases with different layer spacings can also be found in this type of materials, namely S_{A1} (monolayer), S_{Ad} (partial bilayer), S_{A2} (bilayer) and the antiphase $S_{\tilde{A}}$ [2]. Several models were presented in the literature to address the phenomenon of reentrancy and the rich polymorphism observed in Liquid Crystals with a strong polar terminal group [3-9]. In particular these models try to describe the structure of the S_{Ad} phase where a layer thickness of about 1.4 l was found from

X-ray studies. In this work the molecular orientational order in the compound "C_8D_{17}-O-ϕ-COO-ϕ-ϕ-CN" is analyzed in light of the different microscopic models proposed for the S_{Ad} phase [3-9]. Proton spectra of the molecular core and deuterium spectra of the chains were recorded as a function of temperature in the high temperature nematic, the smectic A_d and the reentrant nematic phases. This compound exhibits the following transition temperatures:

$$K \ 97^oC \ N_{Re} \ 120^oC \ S_{Ad} \ 201^oC \ N \ 240^oC \ I$$

EXPERIMENTAL RESULTS

I - Proton spectra of the molecular core

Typical proton spectra in the different mesophases are presented in figure 1.

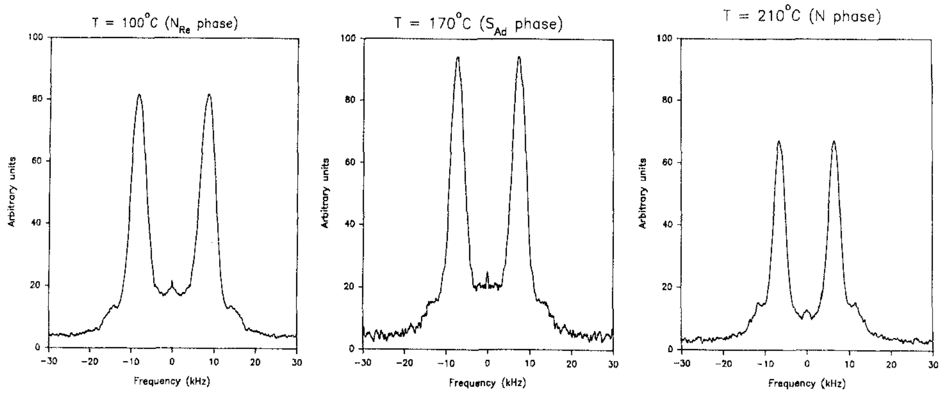

FIGURE 1- Proton Spectra in the N_{Re}, S_{Ad} and N mesophases.

The general features of the spectra are similar in the three mesophases. The spectra are dominated by the dipolar interaction between the ortho and the meta-protons of each benzene ring. The simulation of the proton spectra indicates that the molecules adopt a conformation not so different from the all-trans one, with the planes of the two neighboring benzene rings making an angle of about 24 degrees between them.

The temperature dependence of the dipolar splitting is shown in figure 2. From the dipolar splitting it is possible to obtain, with good approximation, the order parameter S_{ZZ} since the most ordered molecular axis is close to the para-axis. The dipolar splitting is given by:

$$\nu = \frac{3\mu_0}{8\pi^2} \frac{\gamma^2\hbar}{<r>^3} S_{ij} R_{ij} \qquad (1)$$

where S_{ij} is the Saupe order tensor [10] and R_{ij} is a conformation dependent tensor. In the principal frame of S_{ij} the dipolar splitting becomes:

$$\nu = \frac{3\mu_0}{8\pi^2} \frac{\gamma^2\hbar}{<r>^3} [S_{ZZ}R_{ZZ} + \frac{1}{3}(S_{XX} - S_{YY})(R_{XX} - R_{YY})] \qquad (2)$$

$$\text{with} \qquad R_{ZZ}=\frac{3}{2}\cos^2\beta - \frac{1}{2} \qquad \text{and} \qquad R_{XX}-R_{YY}=\frac{3}{2}\sin^2\beta \cos(2\alpha)$$

where β is the angle between the most ordered molecular axis and the para-axis of the benzene rings and it has a value not larger than 12 degrees. In this situation $(S_{XX}-S_{YY})(R_{XX}-R_{YY})$ is negligible compared to $S_{ZZ}R_{ZZ}$. Therefore S_{ZZ} can be obtained from the dipolar splitting. The temperature dependence of S_{ZZ} is also given in figure 2.

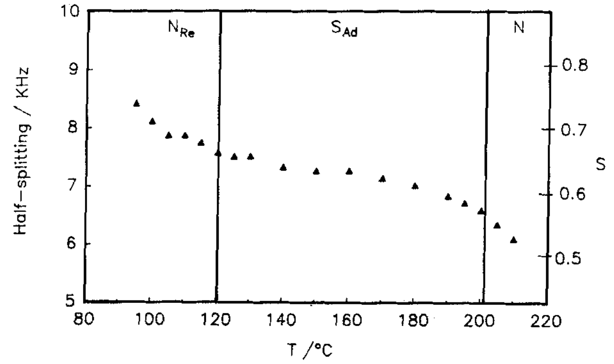

FIGURE 2- Temperature dependence of the dipolar splitting and order parameter S_{ZZ}.

II - Deuterium spectra of the molecular chain

Typical spectra obtained in the three mesophases are shown in figure 3. The spectra are similar in every mesophase denoting only an increase of the molecular order with the decreasing of temperature. The spectra are formed by seven pairs of relatively sharp lines, corresponding to the eight non-equivalent deuterated positions in the chain. Two of these positions give similar splittings and the line intensity indicates that they correspond to line "A". The temperature dependence of the quadrupolar splittings is shown in figure 4. A detailed analysis of the temperature dependence of the quadrupolar splittings reveals that, within experimental accuracy, they are compatible with the existence of a Saupe order tensor for the whole molecule, associated with an average molecular frame defined after averaging over the internal molecular motions. This statement is demonstrated by the line splittings ratio plots obtained, shown in figure 5 [11]. These ratio plots are expected if a Saupe order tensor can be associated with an average molecular frame and the temperature dependence of the splittings comes predominantly from the principal elements of the Saupe order tensor.

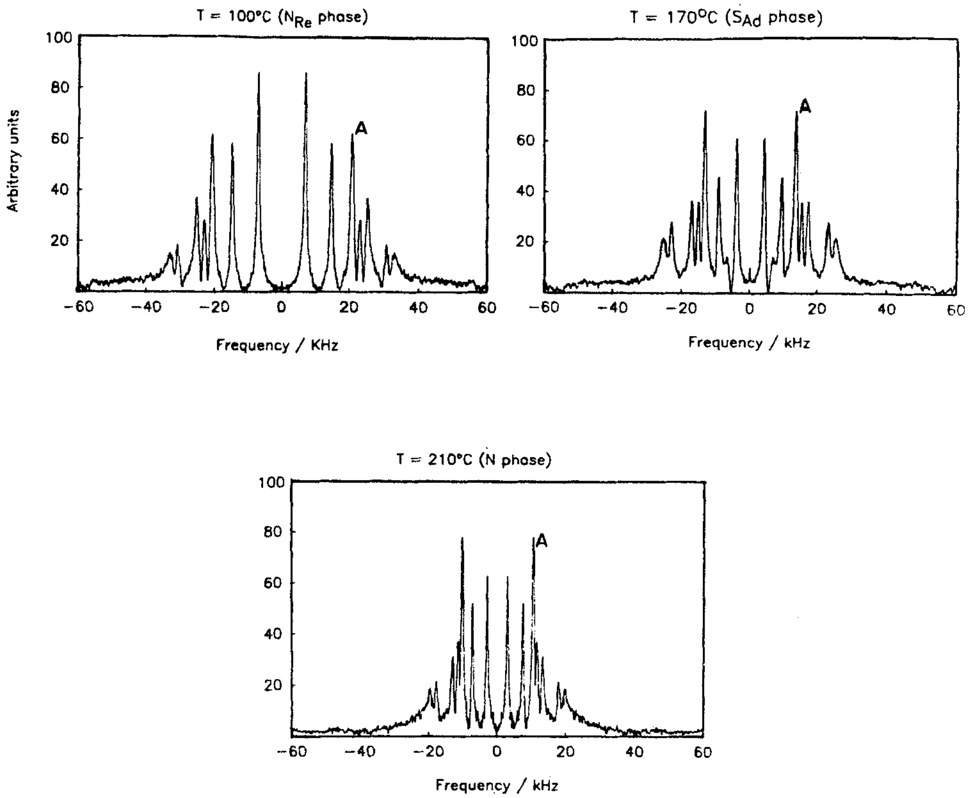

FIGURE 3-Chain Deuterium Spectra in the N_{Re}, S_{Ad} and N mesophases.

The ratio plots do not show any discontinuities or changes of slope at the nematic-S_{Ad} phase transition or at the S_{Ad}-reentrant nematic one. This means that the average molecular conformation is similar in the three phases and the local molecular arrangement is not very different either.

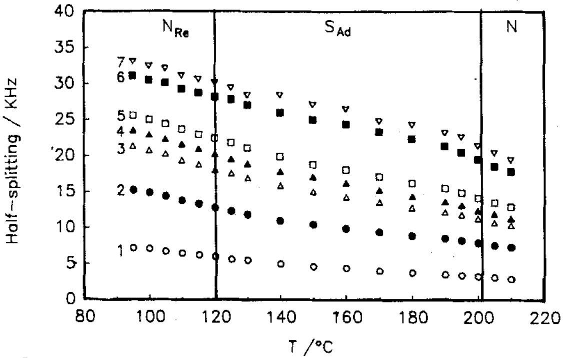

FIGURE 4- Temperature dependence of the chain quadrupolar splittings.

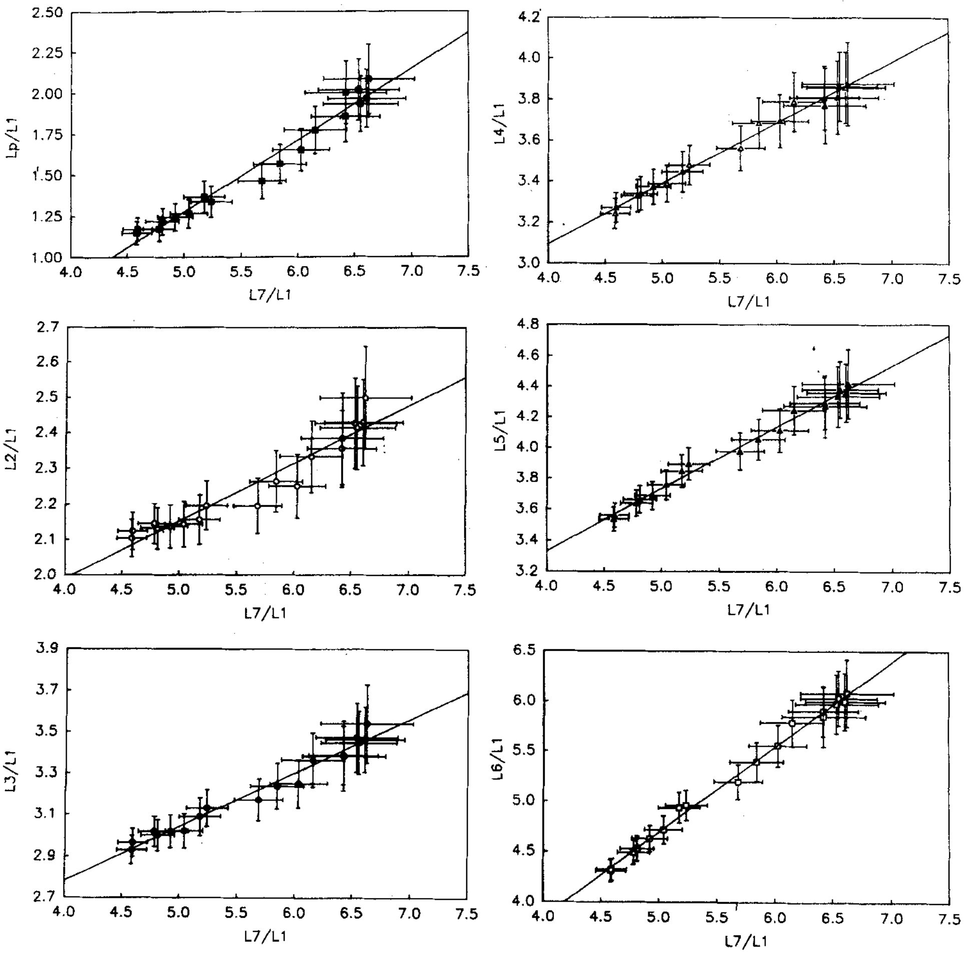

FIGURE 5- Ratio plots from the chain quadrupolar splittings and core dipolar splitting.

IMPLICATIONS OF THE NMR DATA FOR THE DIFFERENT MODELS PRESENTED IN THE LITERATURE FOR THE S_{Ad} PHASE

Relevant implications for the different models concerning the structure of the S_{Ad} phase can be drawn from our NMR results.

Leadbetter et al. [3] proposed a model where the molecular cores are side by side with the chains alternatively disposed in opposite directions. The increase in the layer spacing would be due to the existence of a large longitudinal diffusion. The increase in specific volume implied by this model was not experimentally observed. From the NMR point of view, the enhanced longitudinal diffusion would significantly decrease the molecular order when compared to the monolayer S_{A1} phases, which is not seen.

Cladis et al. [4] proposed a model where the molecules are paired with overlapping cores and chains in opposite directions. This model has the inconvenient of requiring a high packing density of the molecular cores. The molecular area predicted by this model is substantially smaller than the value found in the crystal. From the NMR point of view the overlapping molecular cores would produce a significantly different proton spectrum, since interactions between protons of different molecules would become important.

De Jeu and Longa [5] introduced a model where a mixture of monomers and dimers similar to those proposed by P. Cladis were present in the smectic layers. From the NMR point of view the existence of such "static" dimers and monomers in the S_{Ad} phase would produce, as in the model of Cladis, a different NMR proton spectrum. A different deuterium spectrum would also be observable.

The models introduced by the Bordeaux group [6] can not be directly confronted with our data since they do not make any predictions regarding the temperature evolution of the order parameters or the existence of special molecular aggregates in the considered mesophases.

Guillon and Skoulios [7] introduced a model where two types of molecular aggregates - isolated molecules and dimers of molecules paired head to head - are present, in dynamical equilibrium, in the smectic layers. The ratio of monomers to dimers determines the layer thickness. This model predicts a molecular area compatible with the value found in the crystal. The NMR data imposes a top value for the life time, τ, of the different aggregates predicted by this model. τ must be smaller than a few microseconds as indicated by the presence of only one type of lines in the deuterium spectra.

A. N. Berker and J. O. Indekeu [8] presented a statistical mechanics model which takes into account the dipolar interaction between neighboring molecules, repulsion forces of the excluded volume type between the molecular chains and Van der Waals forces. This model considers correlations between three molecules. Minimizing the energy of the system, different possible configurations are obtained, depending on the relative strength of the interactions. The layer spacing in the S_{Ad} phase, as well as the simple and multiple reentrancy experimentally observed, are well described by this model. NMR gives some information regarding the dynamics of the configurations considered in this model, imposing a top value of a few microseconds for their life time.

N. V. Madhusudana et al. [9] performed a mean field calculation that predicts the phase sequence N - S_{Ad}- N_{Re}- S_{A1}, for a certain range of the model parameters, when the temperature is lowered. The temperature evolution of the order parameters was also calculated and a decrease in order appears in the lower part of the S_{Ad} phase when the temperature decreases. At the transition S_{Ad}- N_{Re} the order parameters are discontinuous. None of these observations regarding the temperature evolution of the order parameters is confirmed by our data, which show a monotonic increase in order with the lowering of the temperature.

CONCLUSION

The existence of only a set of lines in the deuterium spectra of the chain is compatible with the existence of more than one type of molecular aggregates (ex. single molecules and dimers) if the life times of the different aggregates are shorter than the NMR observation time.

The NMR results here presented favor the models of Guillon and Skoulios [7] and Indekeu and Berker [8] but can not draw a distinction between them. Nevertheless NMR sets a top limit of a few microseconds for the life time of the different molecular configurations predicted in those models.

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