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H\textsuperscript{2}-NMR investigation of the two-dimensional smectic F and I phases*

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Abstract. — The smectic F and I phases have been reported to be quasi-two dimensional systems. The SF phase was shown to be the first tilted version of the hexatic phase whereas the SI phase was shown to exhibit a 2D solid-like order. We have studied the terephthal-bis (4-n decylaniline) (TBBA), in which the SF phase occurs at lower temperatures than the SI phase with a higher degree of positional order. To further investigate this puzzling problem we have studied the molecular behaviour by means of H\textsuperscript{2}-NMR experiments. Two deuterated samples of TBDA have been prepared so as to allow separate investigations of the aromatic core and end-chain orderings. Concerning the aromatic part the data have been interpreted in a simple model based on the reorientations of the phenyl rings about their para-axis. This analysis suggests a possible scenario for the intramolecular disordering and its influence on the intermolecular ordering through the smectic F and I phases.

1. Introduction.

Most smectic phases are known to present either a para-crystalline order (S\textsubscript{OD}, S\textsubscript{OH}, S\textsubscript{B} and S\textsubscript{D} phases) or a liquid-like order within the layers (S\textsubscript{A} and S\textsubscript{C} phases). Recently this polymorphism was shown to be even larger including intermediate structures with two-dimensional order within the layers, the smectic F and I (S\textsubscript{F} and S\textsubscript{I}) which occur in some compounds with long aliphatic end-chains. These mesophases have received increasing attention since they take place in the more general context of the two-dimensional melting. The structural investigations [1, 5] of these two phases in some homologues of the TBAA series have brought to light a surprising problem: the range of positional order is larger in the high temperature S\textsubscript{I} phase than in the S\textsubscript{F} phase which occurs at lower temperatures. Such an entropic loss at the level of the intermolecular organization is certainly to be compensated at another level. That of the intramolecular conformational states appears as the first possible candidate and the easiest to investigate with classical NMR experiments. This is the aim of the experiments reported in this work. Before describing them in detail let us first recall briefly the main structural features of these ordered smectic phases.

The S\textsubscript{OD} phase is three dimensionally ordered and consists of strongly coupled layers; within the layers, the order is of the pseudo-hexagonal type [2, 3].

In the S\textsubscript{F} phase, the layers are weakly coupled so that it can be regarded as a two-dimensional system in bulk [1]. Such a phase is the first example of a stacked tilted version of the hexatic phase predicted.

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by the 2D-melting theory \[4\] : this phase both exhibits a short-range positional order and a long range bond orientational order within the smectic planes.

The \( S_p \) phase can be also considered as a two-dimensional system \[5\] but differs from the \( S_p \) phase by the direction of the molecular tilt relative to the rectangular lattice within the smectic planes \[6\]. Moreover the positional order is quasi-long ranged whereas it is short ranged in the hexatic \( S_p \) phase \[1,7\]. At this level it should be also pointed out that another important distinctive feature exists; the molecular packing within a plane perpendicular to the long axis appears \textit{truly} hexagonal whereas it is slightly distorted from this symmetry in the \( S_p \) and \( S_0 \) phases \[8\].

We want to detect possible relationships between the structural order of the smectic F and I phases and the molecular behaviour. Among the various techniques which are sensitive to the molecular ordering, deuterium NMR (H\(^2\)-NMR) has proved to be a powerful tool for probing the local orientational anisotropy \[9,10\]. We have therefore used this technique to investigate the behaviour of labelled double Schiff's bases in their smectic phases. The experimental data will be analysed in terms of a simple model which helps to provide information on an essential feature of the intramolecular motions.

2. Experimental

The main part of this work has been carried out on TBDA the homologuous compound \((n = 10)\) of the well known terephthal-bis-[4-n-alkylaniline] series (TBAA) whose general formula is:

\[
\text{C}_\text{10H}_{\text{21}} - \text{N} = \text{CH} \quad \text{C}_\text{10H}_{\text{21}} \quad \text{CH} = \text{N} \quad \text{C}_\text{10H}_{\text{21}}
\]

This compound previously investigated by X-ray scattering, exhibits the following phase sequence:

\[
\text{Cr} \quad 23^\circ \text{C} \quad \text{S}_0 \quad 115^\circ \text{C} \quad \text{S}_F \quad 149^\circ \text{C} \quad \text{S}_1 \quad 156^\circ \text{C} \quad \text{S}_C \quad 198^\circ \text{C} \quad \text{S}_A \quad 199^\circ \text{C} \quad \text{ISO}
\]

For the purpose of the present study we prepared two TBDA samples with differently deuterated groups, using the deuteration process reported in reference \[11\]. One is specifically deuterated on the terephthalidene central group (TBDA-\(d_6\)):

\[
\text{C}_\text{10H}_{\text{21}}\text{-N} = \text{CD} \quad \text{D} \quad \text{D} \quad \text{CD} = \text{N} \quad \text{C}_\text{10H}_{\text{21}}
\]

The other is perdeuterated (TBDA-\(d_{56}\)). Note that the transition temperatures are not appreciably modified by the deuteration.

The two samples have been outgassed and then sealed under vacuum in glass ampoules. The temperature of the sample, controlled by heated air flow, as regulated to 0.15 °C and thermal gradients were of the same order. The 10 MHz H\(^2\)-NMR spectra were obtained with a home-built pulsed spectrometer after Fourier transformation of the free precession with a boxcar integrator. As for the sample configuration in the magnetic field, we know from X-ray experiments that the molecules always remain in average aligned in the field direction whereas the layer normals tilt away from this direction \[7\].

Typical H\(^2\)-NMR spectra of TBDA-\(d_6\) and TBDA-\(d_{56}\) are reported in figures 1a and 1b respectively. In both cases quadrupolar doublets are well apparent. The lack of a nematic phase prevents a good molecular alignment in the applied magnetic field so that the observed spectral resolution is weak and for instance lower than in case of the TBBA compound \((n = 4)\) previously studied with the same NMR equipment \[11-12\] and elsewhere \[13\]. The pairs of doublets in figure 1a can be easily assigned from their relative intensities and so it has been found that the doublet with the smallest splitting corresponds to the phenyl deuterons and the other to the azomethine deuterons. As in the case of TBBA the reorientation of the central ring about its para axis makes the four phenyl deuterons equivalent \[13\]. Concerning the spectrum of the TBDA-\(d_{56}\) (Fig. 1b) the azomethine and the phenyl
deuterons can be easily identified by comparison with the spectrum of the TBDA-d₆, at the same temperature. It appears that the splitting of the phenyl rings are equal within the experimental error and this means that the three phenyl rings are equivalent on the time scale of the H²-NMR. All the other doublets related to the end-chains; following the references [11] and [14] the assignment is obtained assuming a monotonic decrease of the doublet spacings along the chain form the first methylene groups towards the methyl end.

The general feature of the H²-NMR in liquid crystals have been discussed in detail in references [9, 10, 15]. Let us briefly recall that if rapid molecular anisotropic reorientations take place, the quadrupolar interaction is not averaged out and the residual coupling splits the NMR line into a doublet. In the following we shall assume that the averagings are caused by anisotropic rigid-body reorientations and by intramolecular motions and that these two types of motions are decoupled. Moreover we shall neglect the contribution to the splittings of all the other terms [16] of the order tensor S than $S = S_{x_0} \delta_0$ being the long molecular axis. This is a rather simplifying point of view but such an analysis is sufficient, in a first approximation, to discuss the essential features of the data. Under these conditions the doublet splitting of a deuteron on a chemical site (i) may be written in frequency units as:

$$\Delta v = \frac{3}{2} v_Q S \left\langle P_2(\cos(CD_i, Ox_0)) \right\rangle$$

where $v_Q$ is the quadrupolar coupling constant. According to this approach the ratio $R = \frac{\Delta v^{'}_1}{\Delta v^{'}_p}$ of splittings relative to different molecular sites depends on conformational averagings only and so provides informations about the intramolecular structure.

3. Results.

The temperature dependences of the quadrupolar splittings are reported in figure 2 in case of the phenyl and azomethine deuterons and in figure 3 and 4 in case of methylene and methyl deuterons. In all phases, except the S₁ phase, the splittings decrease as the temperature increases. This is the behaviour observed classically. However a most unusual and striking feature is observed in the S₁ phase: the splittings relative to the aromatic part and most of those relative to the aliphatic chains remain constant in the whole corresponding temperature range. It should be pointed out that such a behaviour is very specific of the S₁ phase since weak variations of the splittings can be easily detected, for instance just above the S₁-S₁ transition in the phenyl curve (Fig. 2). The appearance of such plateaux in the $\Delta v(T)$ curves, particularly characteristic in the phenyl case, should not only correspond to a constant order parameter but also to an average molecular conformation which is quite independent of the temperature (a compensation effect is quite improbable considering the fact that most splittings have this behaviour).

4. Discussion.

Let us first briefly comment on the case of the end-chains. With the proposed assignment, the methylene doublets (2, 3), (3, 4) and (6, 7) remain paired and, at given temperatures in the S₁, S₁, and Sₖ phases, there is a decrease of the order all along the chain towards the methyl group. Although these features are usual, the observed pairing effect on the TBDA is somewhat particular since it occurs through the whole mesomorphic range. The observation of this pairing phenomenon in the S₁ phase, in addition to the presence of real plateaux in the splitting variations $\Delta v(T)$ suggests that for this compound the first five CD₂ groups should be more correlated than is usually
Fig. 3. Temperature dependence of the quadrupolar splittings of the various methylene deuterons in TBDA-d$_{56}$. The doublet of the terminal methylene group (9) cannot be resolved except in the S$_c$ phase because of an overlap with the phenyl doublet.

Fig. 4. Temperature dependence of the quadrupolar splitting of the methyl deuterons of TBDA-d$_{56}$. This effect also visible in the other phases, might be due to a long range anchoring of the chain on the aromatic core. On the other hand the last methylene groups, and above all the methyl end group, appear much more disordered ($\frac{\Delta v}{v} \sim 30\%$ for the CD$_3$ groups in the S$_t$ range). Then the terminal part of these chains may be visualized in the S$_i$ and S$_F$ phase as a relative fluid interface which favours the sliding of the smectic layers on each others and therefore the existence of two dimensional order. We shall not discuss the chain behaviour further in the absence of any definite model. The discussion will now be focused on the behaviour of the aromatic core essentially.

Rather than discussing the variation of the phenyl and methine splittings, we propose to consider in the following their ratio $R(T)$ reported in the lower part of the figure 2. According to [1], this ratio is independent of the order parameter $S(T)$ in our first approximation.

In a first step it is useful to compare the results of the TBDA-d$_6$ (Fig. 2) with those analogous reported in figure 5 for the TBMA-d$_6$ i.e. the first member ($n = 1$) of the TBAA series [17]. The latter data are indeed characteristic of the sole aromatic core behaviour since they are devoid of any influence of the end-chains. Some strong analogies can be noticed on these two sets of curves:

(i) in the S$_C$ phase just below the transition to the next smectic phase, the respective ratios exhibit the

Fig. 5. Quadrupolar splittings of the azomethine and phenyl deuterons of TBMA-d$_6$ and their ratio as function of temperature.
same order of magnitude \((3.1 < R < 3.2)\); moreover the same is true for the splittings;

(ii) at higher temperatures, below the transition to the isotropic phase (i.e. the nematic phase of TBMA and the \(S_c\) phase of TBDA), the ratios have a nearly constant value \((R \sim 2.7)\) over a large temperature range \(\Delta T (AT \sim 20 \text{°C})\) [18].

The first point is particularly relevant since it demonstrates that in the case of TBDA the presence of end-chains does not affect strongly the orientation of the long molecule axis relative to the para-axis of the phenyl rings. In other words the direction of the long axis, along which the chains are set, should be mainly defined by the configuration of the core. This remark will help us to analyse simply the variation \(R(T)\) observed on figure 2 whereas the second point quoted above will be examined further.

The interpretation of the observed variation \(R(T)\) is based on the possibilities of intramolecular rotations within the aromatic core [12-13]. We shall use a model, initially introduced by Dianoux and Volino [19], which has been applied to the fluid phases of TBBA (\(S_A\), \(S_c\) and nematic). The angular variables which are used are defined in figure 6 and consist mainly of two conformational parameters \((\epsilon \text{ and } \phi)\) and one dynamical parameter \((\cos 2 \phi)\).

(i) \(\epsilon\) is the polar angle between the long molecular axis \((O_{zo})\) and the para-axis of the central phenyl ring.

(ii) \(\phi\) is the azimuthal angle of the long molecular axis \((O_{zo})\) in a frame \((x_m, y_m, z_m)\) related to the most probable orientation of the central phenyl ring. Let us recall that the most probable molecular configuration is such that all the dihedral angles between the rigid molecular fragments correspond to minima of the potential hindering the rotations around the various bonds [20]. In figure 6, the angle \(\phi\) corresponds to \((O_h, O_{x_m})\).

(iii) \(\varphi\) is the azimuthal angle \((O_x, O_{x_m})\) which describes the rotation of the central phenyl ring in the frame related to the most probable conformation. Then \(\langle \cos 2 \varphi \rangle\) is the dynamical parameter related to the potential \(\left( V(\varphi) = -\frac{V}{2} \cos 2 \varphi \right)\) hindering the rotation of the phenyl ring about its para-axis. For example the case \(\langle \cos 2 \varphi \rangle = 1\) corresponds to \(II\)-flips of the phenyl rings about the para-axis while \(\langle \cos 2 \varphi \rangle = 0\) corresponds to isotropic reorientations.

According to the relation (1) the expression of the splitting of the methine deuteron may be simply written as :

\[
\Delta v_{\text{meth}} = \frac{3}{2} v_{Q}^m S P_2(\cos (v + \epsilon))
\]

and for the phenyl deuterons the splittings is given by :

\[
\Delta v_{\varphi} = \frac{3}{2} v_{Q}^m S [P_2(\cos u) P_2(\cos \epsilon) + \sin^2 u \sin^2 \varphi \langle \cos 2 \varphi \rangle \cos 2 \varphi].
\]

The angle between the CD bond of interest and the para axis is \(u(59°20\text{)}\) and \(v_Q^m = 185 \text{ MHz} [19]\). Then the ratio \(R\) of the splitting may be simply expressed as :

\[
R = \frac{\Delta v_{\text{meth}}}{\Delta v_{\varphi}} = \frac{2 v_Q^m(3 \cos^2(v + \epsilon) - 1)}{v_Q^m[(3 \cos^2 u - 1)(3 \cos^2 \epsilon - 1) + 3 \sin^2 u \sin^2 \varphi \langle \cos 2 \varphi \rangle \cos 2 \varphi]}.
\]

Let us first consider the limit of planar molecular configurations. For a « cis » configuration in which the transverse components of the C = N dipoles are parallel [12], the value of the angle \(\epsilon\) is zero, so that the expression (4) for \(R\) remains always lower than 2, i.e., lower than the experimental value \(2.7 < R < 3.5\).

On the other hand the « trans » configuration, in which the transverse components of the C = N dipoles are antiparallel [21], allows to obtain the right order of magnitude for \(R\); it corresponds to \(\epsilon = 10°\) which is approximately equal to that calculated directly by using standard chemical angles and bond lengths. However it should be noted that it is impossible to fit the curve \(R(T)\) by introducing in the expression (4) a value of \(\epsilon\) which differs slightly from \(10°\) (i.e. a « trans » configuration). These remarks suggest that the resulting dipole moments of the molecules remain weak so that the dipole-dipole
interaction [22] should not be the main intermolecular effect for the ordering potential in the $S_G$, $S_F$ and $S_I$ phases.

In order to give an account for the variation $R(T)$ through the $S_G$, $S_F$ and $S_I$ phases, it is necessary to specify the temperature dependent terms in the expression (4). Of course the angles $u$ and $e$ are supposed to be constant; on the other hand, according to previous remarks, we consider that $e$ should not vary significantly and so remain equal to the value quoted above i.e. $e = 10^o$ through the $S_G$, $S_F$ and $S_I$ range. This latter point seems realistic since recent dilatometric measurements [23] on the TBDA have shown that the mean molecular area varies weakly with the temperature [24] so that each molecule may be viewed as confined in a "cage" which size is almost invariant and in which the aromatic core configuration remains "trans". Under these conditions the observed decrease of $R(T)$ implies that the product $\langle \cos 2 \varphi \rangle \cos \phi$ decreases with the increasing temperatures. Specifically, as indicated in figure 7, in order to fit the variation $R(T)$ the product has to decrease from 0.7, at the $Cr$-$S_G$ transition, to approximately 0 in the $S_I$ phase.

Now our second basic assumption is to consider that, contrary to Dianoux and Volino [19], the decrease of the product is dominated by the average $\langle \cos 2 \varphi \rangle$. Indeed we recall that $\langle \cos 2 \varphi \rangle$ is directly related to the energy hindering the motions of the rings whereas $\cos 2 \phi$ is only a conformational parameter. Therefore the variation reported in figure 7 requires that the average $\langle \cos 2 \varphi \rangle$ decreases continuously from an undetermined value in $S_G$ to zero in $S_I$. Concerning the average conformation of the aromatic core this means that the rotation of the phenyl rings about their para-axis appears to be more and more isotropic with increasing temperatures and becomes quasi-uniform in the $S_I$ phase. Consequently the averaged symmetry of the aromatic core becomes higher as the temperature is increased from the $S_G$ and finally reaches a quasi-cylindrical state in the $S_I$ phase; under these conditions a true hexagonal packing, characteristic of this phase, may occur.

We may easily see that, when such a molecular state of high symmetry is reached, it persists at higher temperatures so that $R(T)$ remains constant as observed through the $S_I$ phase ($R = 3.0$) and through the main range of the $Sm$ $C$ phase ($R = 2.75$). The change in the constant $R$ at the $S_I-S_F$ transition may be simply explained by a slight modification of the molecular conformation around the "trans" state affecting the orientation $e$ of the long molecular axis ($e = 8.65^o$ in $S_C$ phase). Finally let us notice that there is a small increase of $R(T)$ just before the transition to the isotropic liquid. This weak effect, also observed in TBMA and TBBA, has not yet been interpreted.

5. Concluding remarks.

These present results concern the first experimental investigation of molecular ordering in the 2D-smectic F and I phases. Our study shows that the molecular behaviour of the $S_F$ phase is close to that of the $S_G$ phase while in the $S_I$ phase there is clearly a distinctive feature. Indeed, in this phase, the specific molecular state is such that the averaged conformation of the aromatic core is almost cylindrical and quite independent of temperature. Such a molecular symmetry appears to be strongly correlated to the structural properties, i.e. the true hexagonal packing and the great extension of the positional order. Finally we think interesting to quote that there might exist at least two different $S_I$ structures, the one discussed above and an hexatic version of it recently discovered in 2M4P8BC [25]. It should be also pointed out that in the case of the $S_F$ phase [26], of its tilted version $S_{II}$ [11] and of the $S_G$ phase [27] relationships between the core behaviour and the herring-bone packing have been already evidenced. These three examples illustrate that through the ordered smectic range a strong interplay occurs between the nature of the motions of the rings and the macroscopic structure.

A close comparison of NMR results on TBDA to those previously obtained on TBBA and TBMA suggests the following molecular "scenario". At low temperatures, in $S_F$ or in $S_{II}$, it has been established that the herring-bone packing characteristic of this phase is correlated to flip-flop reorientations of the phenyl rings about their para-axis. With increasing temperatures the aromatic core of homologs of the TBA series always remains close to the "trans" configuration but the reorientations of the three phenyl rings become more and more uniform. This continuous evolution is indicated by the weak decrease of the ratio $R(T)$. At higher temperatures the rotation of the rings becomes isotropic. This dynamical state in which the molecular symmetry is higher appears to be quite independent of temperature since the ratio $R(T)$ remains constant, it can be considered as the last step of the intramolecular disorder generated at the level of the phenyl rings. In the case of TBDA the ratio $R(T)$ decreases through
the $S_G$ and $S_F$ phases and becomes constant when the $S$ phase with hexagonal packing occurs (the jump at the first order $S_G$-$S_C$ transition corresponds only to a change of the mean orientation of the long axis). On the other hand, in the case of TBMA and TBBA, this molecular state, in which the rings are freely rotating, seems definitively reached for a more fluid mesophase since the corresponding ratio $R(T)$ is observed to be constant in the nematic phase only.

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References

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