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Molecular orientational order in the mesophases of TBBA:
Results of a consistent analysis of neutron, NQR and NMR data (*)

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Abstract. Incoherent neutron quasi-elastic scattering (NQES), 14N nuclear quadrupole resonance (NQR) and deuterium nuclear magnetic resonance (DMR) data in the smectic VI, smectic H, smectic C, smectic A and nematic phases of terephtal-bis-butyl-aniline (TBBA) are analysed consistently in terms of simple rotational models allowing both orientational order around the long molecular axis and fluctuations of this axis. It is found that:

(i) In the SmVI phase, the molecules rotate around their long axis in a two fold periodic potential. The corresponding bipolar order parameter varies from ~ 1 to ~ 0.8 near the transition VI-H.

(ii) In the SmH phase, the rotation is almost uniform, but a small bipolar ordering still exists, which varies from ~ 0.15 to ~ 0.06 near the transition H-C. In addition, the long axes fluctuate about their average positions, the average amplitude of these fluctuations vary from ~ 0 to ~ 22° near the transition H-C.

(iii) In the SmC phase, the bipolar ordering is very weak (~ 0.005). As the temperature increases the long axes tend to be perpendicular to the layers. The polar fluctuations of the axis remain practically constant (~ 22°), but the azimuthal fluctuations increase rapidly and become uniform at the C-A transition. Values of corresponding order parameters are given.

(iv) In the SmA and nematic phases, the polar fluctuations increase and are as large as ~ 42° at the nematic-isotropic transition. The values of the nematic order parameter are given.

All these results seem to rule out definitely the Meyer-MacMillan [1] and Meyer [2] theories for the tilted phases of TBBA.

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1. Introduction. — In the field of liquid crystals, the knowledge of the molecular order is of prime importance to test the various microscopic theories which have been developed to describe these systems. Among the several methods which can be used for such a purpose, high resolution incoherent neutron quasi-elastic scattering (NQES) and nuclear magnetic resonance (NMR) of well chosen nuclei are very powerful since they are practically sensitive to molecular properties only. However, the interpretation of the data obtained by one of these methods alone may not be unique, and this has lead to controversies between different authors in the recent past. The most famous controversy concerns the existence or the absence (and in the former case, the nature) in the tilted smectic phases, of some orientational order of the molecules around their long axis, in connection with the Meyer-McMillan [1] (smectic C and H) and Meyer [2] (smectic H and VI) mean field theories of these phases. The main reason for this situation is that the various methods are probing different aspects of the molecular motion, and also because the actual physical situation is probably more complex than that described by the simple models used. It turns out that a significant amount of experimental data obtained by various methods is now available and it is thus time to look for descriptions which are consistent with all these data.

The purpose of this paper is to analyse quantitatively in a consistent manner most of the existing NQES [3-5], 14N nuclear quadrupolar resonance [7-8] (NQR) and deuterium magnetic resonance [9-10] (DMR) data in the smectic VI, smectic C, smectic A and nematic phases of terephtal-bis-butyl-aniline (TBBA). We shall restrict ourselves here to the data concerning the body of the molecules, leaving to a further paper those concerning the chains. In the next section, we recall briefly which quantities are measured in the three kinds of experiments mentioned and how they are linked to the molecular order and dynamics. Then, we summarize the present state of the problem concerning the various phases of TBBA. In the main part of the paper, we analyse quantitatively the existing NQES data [3-5] and 14N NQR data [7-8] in terms of rather simple models allowing both orientational order around the long axis and orientational order of this axis and deduce the relevant order parameters. This analysis is then checked using DMR data [9-10]. These DMR data are also used to extract important additional information.

2. The principles of NQES, NQR and NMR — theoretical background. — 2.1 NQES [13, 3-5]. — In a NQES experiment, the molecular motion is detected through the motion of the protons. If the molecules only move around their centre of mass (i.e. the motion is purely rotational), then the NQES spectra are composed of a sharp peak — a $\delta(\omega)$ function — superimposed on a broad component — generally Lorentzian lines centred at $\omega = 0$ if the motion is diffusive — whose width is of the order of the inverse of the rotational correlation time $\tau_R$. The ratio of the intensity of the sharp peak to the total intensity is the elastic incoherent structure factor (EISF) given by

$$\text{EISF} = \frac{1}{N} \sum_{i=1}^{N} |\langle \exp iQr_i \rangle|^2$$

(1)

where $Q$ is the neutron momentum transfer and $i$ an index which runs over the $N$ protons located at $r_i$ in the molecule. The brackets indicate an average over the motion. When the sample is in powder form, eq. (1) should be averaged further over all possible orientations of $Q$. If a model for the motion is assumed, then the averages in eq. (1) can be calculated exactly and the result compared to the experimental EISF. The limitation of the method is that the molecular motion should be sufficiently fast ($\tau_R \sim 10^{-10} - 10^{-11}$ s) so that the sharp and broad components can be sufficiently well separated from each other. Its main advantage is that one can work with both powder and aligned samples, and that even in the former case, one can obtain a great number of experimental data by merely varying the magnitude of $Q$. Moreover, the rotational correlation time(s) can be measured, from the width of the broad component.

2.2 NQR [14, 7-8]. — In a pure NQR experiment, the molecular rotational motion is detected through the averaging of the electric field gradient (efg) which acts upon the nucleus studied. Let $V_{xx}$, $V_{yy}$, $V_{zz}$, defined such that $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$ be the principal values of the average efg tensor $\langle V \rangle$. Defining the coupling constant $c = |eQV_{zz}/\hbar|$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, it can be shown that for a spin 1, there are three NQR absorption frequencies $v_1$, $v_2$, $v_3$ given by

$$v_1 = \frac{3}{4} c \left( 1 + \frac{\eta}{3} \right) ; \quad v_2 = \frac{3}{4} c \left( 1 - \frac{\eta}{3} \right)$$

(2)

$$v_3 = v_1 - v_2 = \frac{1}{2} c \eta .$$

(3)

Here $Q$ is the quadrupole moment of the nucleus. If the five independent components of the efg tensor in a molecular frame are known and if a model for the molecular motion is assumed, then one can calculate all the components of the average tensor $\langle V \rangle$, deduce the principal values by diagonalization, calculate $c$, $\eta$ and the absorption frequencies and compare with the experiment. The limitations of the method are that (i) the molecular motion should be sufficiently fast ($\tau_R \ll 4 \times 10^{-8}$ s for $^{14}$N, $\tau_R \ll 10^{-6}$ s for D) and (ii) the components in the molecular frame should be known with sufficient accuracy. Its main advantage is that one can work with powder samples and that
two independent quantities related to the nature of the motion, namely \( c \) and \( \eta \), are obtained.

2.3 NMR WITH QUADRUPOLEAR INTERACTION [14, 9-10]. — In a NMR experiment with quadrupolar interaction, the rotational motion is also detected through the averaging of the efg which acts upon the nucleus studied. For a spin 1, due to the quadrupole interaction, the NMR line is split into a symmetric doublet whose spacing \( \Delta v \) is given by

\[
\Delta v = \frac{3}{2} \frac{eQ}{h} V_{H_oH_o}
\]

where \( V_{H_oH_o} \) is the component along the magnetic field \( H_o \) of the average efg tensor \( \langle V \rangle \). As for NQR, if the components of the efg tensor in a molecular frame are known and if a model is assumed, one can calculate \( \langle V \rangle \), deduce \( V_{H_oH_o} \) and the corresponding splitting, and compare with the experiment. This method is, a priori, more limited than pure NQR because only one quantity is measured and also because it is necessary to work with well aligned samples. However, if the aligned sample can be rotated with respect to \( H_o \), one can then obtain important additional information, in the case of smectics.

3. Orientational order in TBBA. The present situation. — At present, a great amount of experimental data on TBBA is available. In the NQES, NQR and DMR experiments, various partially deuterated samples have been used. In figure 1, we show the molecule

[Diagram of partially deuterated TBBA molecule]

which has been used in NQES [3-5] and some DMR [10] experiments, drawn in its trans-conformation. The angle between the line passing through the centres of the three phenyl rings and the para axis of these rings in 10.2°, as calculated from standard bond angles and lengths. The circles around the protons or deuterons indicate the van der Waals radii.

4. Orientational order in the smectic VI phase. — The NQES results obtained in the VI phase are discussed in detail in reference [5]. The model used is a bipolar model which assumes that the molecules rotate around their long axis in a potential \( V(\varphi) \propto \cos 2 \varphi \) where \( \varphi \) is the azimuthal angle, with a correlation time of \( \sim 3 \times 10^{-11} \) s. We shall use the same model to analyse the \( ^{14}N \) NQR data of reference [8]. As mentioned in section 2.2, in order to make a quantitative analysis, it is necessary to know, with sufficient accuracy, the efg tensor acting on the \( ^{14}N \) nucleus, in a molecular frame. From the measurement of \( c \) and \( \eta \) in the solid phase, it has been possible to have two independent relations between its components [7, 8]. This is clearly not sufficient. However, from symmetry considerations, one can guess where the principal axes
of this tensor are. In particular, the main principal axis is expected to be roughly in the N = C-H plane, and make an angle of about 60° with the long axis [7, 8]. However, it turns out that the exact value of this angle is very critical to test models — cf the discussion in reference [6]. Moreover the exact direction of the other axes may also be important. In spite of this it has been possible to produce approximate values of the efg tensor components \( V_{xoxo} \ldots V_{zozo} \) in a frame where \( z_0 \) is along the long axis, and \( y_0 \) is normal to the N = C-H plane (eq. (3b) of reference [8]). Since the NQR data are generally very precise, the knowledge of the exact values of these components is very important to test the models for the motion in the various phases. In the following we assume that the bipolar model for the VI phase is the true one, not only to determine the single parameter of this model, but also refine the values of the efg tensor components.

The model is a rotation around the \( z_0 \) axis. The instantaneous efg tensor can be written down as a function of \( V_{xoxo} \ldots V_{zozo} \) and of trigonometrical functions of \( \varphi \) and \( 2\varphi \) (eq. (4) of reference [8]). This tensor should be averaged over the motion. Symmetry conditions imply that

\[
\langle \sin \varphi \rangle = \langle \sin 2\varphi \rangle = \langle \cos \varphi \rangle = 0.
\]

The calculation [8] shows that the only non-zero components \( V_{xx} \ldots V_{zz} \) of the average tensor in the VI phase are

\[
\begin{align*}
V_{xx} &= -\frac{1}{2} V_{z0z0} + \frac{1}{2} (V_{x0x0} - V_{y0y0}) \langle \cos 2\varphi \rangle \quad (5a) \\
V_{yy} &= -\frac{1}{2} V_{z0z0} - \frac{1}{2} (V_{x0x0} - V_{y0y0}) \langle \cos 2\varphi \rangle \quad (5b) \\
V_{zz} &= V_{z0z0} \quad (5c) \\
V_{xy} &= V_{x0y0} \langle \cos 2\varphi \rangle. \quad (5d)
\end{align*}
\]

It is seen that these relations do not involve \( 5 \), but only 3 independent components of the efg tensor in the molecular frame, namely \( V_{x0x0}, V_{z0z0} \) and \( V_{x0y0} \).

We have refined the values of these three quantities and determined the order parameter \( \langle \cos 2\varphi \rangle \) for four temperatures in the VI phase, and for the lowest temperature in the H phase, where \(^{14}\text{N} \) NQR data are available. The results are summarized in figures 2a and 2b. The best values found for \( V_{x0x0}, V_{z0z0} \) and \( V_{x0y0} \) are \(-3.2, 1.17\) and \(0\) MHz respectively, to be compared with the estimated values \(-3.15, 1.20\) and \(\pm 0.15\) MHz from reference [8]. The full curves represent the theoretical values of \( \xi \) and \( \eta \) calculated from eqs. (5a)-(5d) versus \( \langle \cos 2\varphi \rangle \) using for \( V_{x0x0}, V_{z0z0} \) and \( V_{x0y0} \) the best fitted values. It is seen that the agreement is fairly good. The deduced values of \( \langle \cos 2\varphi \rangle \) are plotted versus temperature on figure 3, together with the corresponding values deduced from the NQES study [5]. The SmH-SmVI transition temperature, which was found to be between 89 and 90°C in the neutron experiment, has been renormalized, in the figure, to that found in the NQR experiment (\( \approx 85°C \)).

The agreement between the results obtained by these two very different methods is striking and is a strong support for the validity of this bipolar model. Incidentally, it can be easily shown that these NQR data are
also completely incompatible with a polar model [1, 2]. It is sufficient for this to inspect the theoretical variations of \( c \) and \( \eta \) for such model (cf. the figures of reference [6]).

In conclusion, in the smectic VI phase of TBBA, the molecular axis is fixed, but the molecules rotate around this axis in a two fold periodic potential. The corresponding bipolar order parameter is very high and varies from \( \approx 0.8 \) near the H transition to \( \approx 1 \) in the low temperature range. This corresponds to an angular fluctuation \( \Delta \phi \) in the two fold potential varying from \( \approx 20^\circ \) to \( \approx 0^\circ \) [5]. This description is in complete agreement (i) with the structure deduced from X ray studies [11, 12], and (ii) with the evolution of the DMR spectra when the sample is rotated in the magnetic field [10], but it also proves that the Meyer theory [2] is inadequate to describe the SmVI phase of TBBA [5].

5. Orientational order in the smectic H, C and A phases. — 5.1 GENERAL. — For the H, and a fortiori for the C and A phases, the NQES results show that the EISF is smaller than expected assuming purely uniaxial rotation. This was interpreted in terms of additional rotational motion, namely fluctuation of the axis about its equilibrium position [3, 5]. We believe that this interpretation is confirmed by the NQR data. The reason is that the significant decrease of the coupling constant \( c \) from 1.17 MHz at 88°C to 1.01 MHz at 139°C cannot be explained within a purely uniaxial model as the one used for the VI phase, since for \( \langle \cos^2 \phi \rangle < 0.15 \), \( c \) remains constant (cf. Fig. 2b). Consequently, the decrease of \( c \) can only be explained by an increase of the rotational disorder, namely fluctuations of the long axis. However, in this case, since the H phase is not uniaxial, these fluctuations do not have necessarily cylindrical symmetry and this may contribute to the anisotropy observed in this phase. To consistently interpret the NQR data, we should thus use a model which permits both a bipolar orientational order around the long axis and anisotropic fluctuations of this axis, as for the C phase [7, 8].

5.2 THE AVERAGE efg TENSOR AND MODEL FOR THE MOTION. — The rotation around the long axis is described by the same model as in the VI phase. To describe the axis fluctuations, we should express the efg tensor in a fixed frame. The natural frame to choose in this case is the one with \( Oz' \) along the normal to the smectic planes and \( Ox' \) along the average projection of the molecules in the planes (the C director). Let \( \theta \) and \( \phi \) be the polar and azimuthal angles of the long axis. Symmetry considerations show that \( \langle \sin \phi \rangle = \langle \sin 2 \phi \rangle = 0 \). After some algebra, we find that the only non-zero average components of the efg tensor in this frame are:

\[
V_{x'x'} = (V_{zz} - V_{xx}) \langle \sin^2 \theta \cos^2 \phi \rangle + V_{xx} \langle \cos^2 \phi \rangle + V_{yy} \langle \sin^2 \phi \rangle
\]

\[
V_{x'z'} = V_{zz} - (V_{zz} - V_{xx}) \langle \sin^2 \theta \rangle
\]

\[
V_{z'z'} = (V_{zz} - V_{xx}) \langle \sin \theta \cos \theta \phi \rangle
\]

where \( V_{xx}, V_{yy}, V_{zz} \) are given by eqs. (5a-d), with \( V_{x'x'0} = -3.2 \text{ MHz}, V_{x'x'1} = 1.17 \text{ MHz} \) and \( V_{x'x'2} = 0 \). It is seen that these formulae contain four independent order parameters which describe the ordering of the molecular axis, and one which describes the order around the long axis. Since there are only two pieces of data available, namely \( c \) and \( \eta \), it is not possible to deduce their values from the NQR data only. The approach we propose to describe the axis fluctuations is to use a model, namely the one we called model 2 in reference [3]. In this model, we assume that [3]:

(i) The \( \theta \) and \( \phi \) motions are independent;
(ii) The \( \phi \) distribution is of the form

\[
\vartheta(\phi) = \frac{1}{2 \pi \vartheta(\gamma')} \exp(\gamma' \cos \phi).
\]

(iii) The \( \theta \) distribution is of the form

\[
f(\theta) = A_2 \exp[\gamma' \cos(\theta - \theta_M)]
\]

with

\[
A_2^{-1} = \int_0^{\pi} \exp[\gamma' \cos(\theta - \theta_M)] \sin \theta \, d\theta.
\]

We are left now with three parameters \( \gamma' \), \( \theta_M \) and \( \gamma' \) whose physical signification is simple: \( \gamma' \) or \( \gamma = \langle \cos \phi \rangle = I_1(\gamma')/I_0(\gamma') \) describes the width of the azimuthal fluctuations (motion in the smectic planes), \( \theta_M \) is the angle where the \( \theta \) distribution is peaked and \( \gamma' \) or

\[
\gamma = \langle \cos \phi \rangle = I_1(\gamma')/I_0(\gamma')
\]

describes the width of the azimuthal fluctuations (motion in the smectic planes), \( \theta_M \) is the angle where the \( \theta \) distribution is peaked and \( \gamma' \) or

\[
S = \langle P_2[\cos(\theta - \theta_M)] \rangle
\]

describes the width of the \( \theta \) distribution around \( \theta_M \) (motions outside and inside the planes). Note that for \( \gamma' = 0 \) and \( \theta_M = 0 \), \( S \) reduces to the usual nematic order parameter. Using eqs. (7) and (8) to calculate the averages in the relations (6a)-(6d), and diagonalizing this tensor, we can, at least formally, express \( c \) and \( \eta \) as a function of these three parameters. In fact, these parameters are not independent since the model should also predict the value of the tilt angle \( \theta_0 \) which has been measured by several methods [15-17]. This angle describes the average orientation of the molecular axis. It is easy to show from simple geometrical considerations, that

\[
tg \theta_0 = \langle |tg \theta| \cos \phi \rangle.
\]

Thus, using the values of \( \theta_0 \) deduced from optical [15] or neutron [16, 17] measurements, and the
values of \(c\) and \(\eta\) measured by NQR we can in principle deduce the three parameters \(\gamma', \theta_M\) and \(\delta'\) of the model. In fact, the situation is not so simple since there is a fourth parameter in the problem, namely \(\langle \cos 2 \varphi \rangle\), the bipolar order parameter around the long axis. However, this parameter does not affect the value of \(\theta_0\), and since its value is expected to be small (< 0.15), it will not significantly affect the value of \(c\) (cf. Fig. 2a). On the contrary, it is seen from figure 2b that it may strongly affect the value of \(\eta\).

To approach the problem, we have first attempted to fit the model with \(\langle \cos 2 \varphi \rangle = 0\), to the data in the H and C phases. We found that different combinations of \(\gamma', \theta_M\) and \(\delta'\) can explain the observed values of \(\theta_0\) and \(c\), but not the value of \(\eta\) which is found to be systematically smaller than the experimental result. This merely means that in both phases \(\langle \cos 2 \varphi \rangle \neq 0\). The problem is thus to find which combination of \(\gamma', \theta_M, \delta'\) is the true one. For this we assume that \(\delta'\) cannot change very much in the C phase and its value should be about 11.5. To prove this we consider the NQR data at 174 °C in the SmA phase near the smcN phase, and at 146 °C in the SmcN phase near the SmNH phase. In the A phase, we have \(\theta_M = 0, \gamma' = 0\) and we can unambiguously determine the value of \(\delta'\) from the value of \(c\). With \(c = 884 \text{ kHz} \) at 174 °C, we find \(\delta' \approx 11.2\). In the C phase at 146 °C we observe that the experimental value of \(\eta\) is very small \(\approx 0.02\). This value of \(\eta\) is caused by both the bipolar ordering around the long axis and the anisotropic fluctuations of this axis. Since both contributions add, this implies that the set \(\gamma', \theta_M, \delta', \gamma'\) which predicts the observed values of \(\theta_0\) and \(c\), should be such that the corresponding \(\eta\) is very small. This occurs for \(\gamma' \approx 3.9, \theta_M \approx 10.4°\) and \(\delta' \approx 11.5\) which predict \(\eta \approx 0.008\) for

\[
\langle \cos 2 \varphi \rangle = 0.
\]

Finally, since \(c\) is continuous through the C-H transition, \(\delta'\) should also be \(\approx 11.5\) in the H phase near the SmcN transition. The procedure we have adopted to analyse the NQR data in the H phase near the C transition and in the C phase is thus the following: we fix \(\delta' = 11.5\), assume \(\langle \cos 2 \varphi \rangle = 0\) and use the experimental values of \(\theta_0\) and \(c\) to determine \(\theta_M\) and \(\gamma'\). Then, with these values of \(\theta_M\) and \(\gamma'\) and the experimental values of \(\eta\), we determine \(\langle \cos 2 \varphi \rangle\). This analysis is then checked by recalculating \(c\) and \(\eta\) using these values of the parameters. In all cases, we have re-obtained the values chosen as input data, to an accuracy better than the experimental uncertainties, even in the H phase where \(\langle \cos 2 \varphi \rangle\) is small but significant.

5.3 RESULTS. — 5.3.1 The SmN phase. — Near the SmVI transition temperature, we have already seen that the axis fluctuations are very small and \(\langle \cos 2 \varphi \rangle \approx 0.15\). At 139 °C near the SmcN transition where we have \(\theta_0 = 28°\) [16], \(c = 1.013 \text{ MHz}\) and \(\eta = 0.20\), the best fit is found for \(\theta_M = 13.1°, \gamma' = 5.0°\) (i.e. \(\langle \cos \phi \rangle = 0.89\), \(\delta' = 11.5\) (i.e. \(S = 0.84\)) and \(\langle \cos 2 \varphi \rangle = 0.06\). It is interesting to note that with \(\langle \cos 2 \varphi \rangle = 0\), the calculated value of \(\eta\) is practically \(0 \approx 0.004\). This means that at 139 °C, and probably in the whole SmH phase, the polar and azimuthal fluctuations of the axis are, roughly speaking, the same, or in other words that the axis fluctuations have practically the uniaxial symmetry about the average molecular direction [22].

In conclusion, in the smectic H phase of TBBA, the molecules do not rotate completely uniformly around their long axis [7, 8], the corresponding bipolar order parameter \(\langle \cos 2 \varphi \rangle\) varying from \(\approx 0.06\) near the SmcN phase [8] to \(\approx 0.15\) near the SmVI phase (cf. Fig. 3). However, the long axes fluctuate about their equilibrium positions. The amplitude of these fluctuations is very small near the SmVI phase, but are about 22° near the SmcN phase [6]. In our opinion, these results resolve the controversy concerning this phase, namely that (i) the Meyer-McMillan [1] and Meyer [2] theories are inadequate to describe the SmH phase of TBBA and (ii) important fluctuations of the long axis exist, at least in the normal H phase.

5.3.2 The SmC phase. — In this case, we have seen from the general discussion that \(\delta' \approx 11.5\) i.e. that the polar fluctuations are practically constant throughout the whole SmC phase. Since \(c\) is found to decrease significantly, this means that the increasing disorder is mainly due to an increase of the azimuthal fluctuations. The parameters of the model were deduced according to the procedure mentioned above. We use the values of the tilt angle of reference [15] and the values of \(c\) and \(\eta\) that we deduced from the NQR spectra presented in figures 1 and 2 of reference [7]. The results are summarized in figures 4a-4c. Figure 4a shows the tilt angle for \(\theta_0\), together with the corresponding variation of \(\theta_0\) extracted from reference [15]. It is seen that \(\theta_0\) i.e. the maximum of the polar distribution, is always significantly smaller than the tilt angle \(\theta_0\), even when \(\theta_0\) is large (e.g. at 146 °C, \(\theta_0 \approx 25°\) but \(\theta_M\) is only \(\approx 10°\)). However their variations with temperature are very similar. Figure 4b shows the variation of \(S\) which reflects the polar fluctuations. Its variation is very small and is mainly due to the variation of \(\theta_M\) since \(\delta'\) is practically constant. Finally, figure 4c shows the variation of \(\langle \cos \phi \rangle\) which reflects the azimuthal fluctuations. Again, its variation is very similar to that of \(\theta_0\) and \(\theta_M\).

In figures 5a and 5b, we have also shown the values of \(\eta\) deduced by the model with \(\langle \cos 2 \varphi \rangle = 0\). It is seen that, although these values are smaller than the experimental values, the shape of the curve is well reproduced. This gives strong support to the analysis made, namely that the asymmetry is mainly due to the fluctuations of the long axis, and that its variation is caused by a change in the \(\phi\) fluctuations only. To raise the value of \(\eta\)
Values of the three parameters $\theta_M$, $S$ and $\langle \cos \varphi \rangle$ of the model describing the tilted smectic phases of TBBA. The open circles are the values extracted from the values of $c$, $\eta$ and $\theta_0$ assuming $\delta' = 11.5$ in the C phase. On figure 4a, we have also reported the values of the tilt angle $\theta_a$ extracted from optical ($\Delta : \text{from Ref. [15]}$) and neutron diffraction (square : \text{from Ref. [16]}) measurements. On figure 4b, is also mentioned the value of $S$ deduced independently from NQES data ($\Delta : \text{from Ref. [4]}$). It is seen that both $\theta_M$ and $\langle \cos \varphi \rangle$ go to zero at the C-A transition, as does the tilt angle $\theta_a$. Only the polar amplitude fluctuations are continuous at this transition. See text for details.

Fig. 4. — Values of the three parameters $\theta_M$, $S$ and $\langle \cos \varphi \rangle$ of the model describing the tilted smectic phases of TBBA. The open circles are the values extracted from the values of $c$, $\eta$ and $\theta_0$ assuming $\delta' = 11.5$ in the C phase. On figure 4a, we have also reported the values of the tilt angle $\theta_a$ extracted from optical ($\Delta : \text{from Ref. [15]}$) and neutron diffraction (square : \text{from Ref. [16]}) measurements. On figure 4b, is also mentioned the value of $S$ deduced independently from NQES data ($\Delta : \text{from Ref. [4]}$). It is seen that both $\theta_M$ and $\langle \cos \varphi \rangle$ go to zero at the C-A transition, as does the tilt angle $\theta_a$. Only the polar amplitude fluctuations are continuous at this transition. See text for details.

Fig. 5. — $^{14}$N quadrupolar coupling constant $c$ and asymmetry parameter $\eta$ versus temperature in the SmH, C and A phases of TBBA. O : experimental values extracted from figures 1 and 2 of reference \cite{7}; + theoretical values of $\eta$ calculated assuming $\langle \cos 2 \varphi \rangle = 0$, $\delta' = 11.5$ and using the values of $\theta_M$ and $\gamma'$ which explain the values of $c$ and $\theta_0$. Idem, except $\langle \cos 2 \varphi \rangle = 0.005$.

The full lines are guides to the eye. See text for details.

Closer to the experimental value, we should introduce a weak but finite value of $\langle \cos 2 \varphi \rangle$. The dashed curve on figure 5b are the theoretical values on $\eta$ using the value obtained in reference \cite{8}, namely $\langle \cos 2 \varphi \rangle = 0.005$. It is seen that while the agreement is good below 160 °C it worsens above 160 °C. In fact, it is not possible to obtain a value as high as $\eta \approx 0.04$ at 170 °C, i.e. at $\approx 2^\circ$C from the C-A transition. This may be beyond the scope of the model, but also may be due to the manner in which the value of $\eta$ is extracted from the NQR data. Indeed, the two lines of frequencies $\nu_1$ and $\nu_2$ are not resolved in the spectra (cf. Fig. 2 of reference \cite{7}).

In conclusion, in the smectic C phase of TBBA, the molecules rotate nearly uniformly around their long axis, the bipolar order parameter around this axis being not larger than 0.005. In addition, the long axes fluctuate about their equilibrium positions. As the temperature is increased, the angle $\theta_a$ where the polar distribution is peaked, decreases to zero and its variation roughly follows that of the tilt angle. However, the amplitude of the fluctuations around $\theta_a$ are practically constant and of the order of 22°. On the contrary, the azimuthal fluctuations increase and the azimuthal motion become uniform at the C-A transition. This description is in agreement with the usual textbook picture of this phase where the molecules are allowed to become progressively perpendicular to the smectic planes as the C-A transition is approached. It also clearly shows that the Meyer-McMillan theory \cite{1} is inadequate to describe the SmC phase of TBBA. Finally, it is worth noting that the fluctuations of the long molecular axis appear to be much less uniaxial in the C phase than in the H phase.

5.3.3 The smectic A phase. — Here the situation is much simpler than above since, as $\theta_0 = 0$ and $\eta = 0$, we have $\theta_M = 0$ and $\gamma' = 0$. The only parameter left in practice is $\delta'$ to be determined by the value of the coupling constant $c$. In fact, in this particular case, combining eqs. (6) and (5), we find that in the A phase we have, for $\langle \cos 2 \varphi \rangle \ll 1$

$$c = V_{Ez} = V_{x'x'} = V_{zz0}S \quad (10)$$

where $S = \langle P_2(\cos \theta) \rangle$ is now the usual nematic order parameter. Its value is merely given by the ratio of the actual coupling constant to the coupling constant in the H phase very near the H-VI transition. The corresponding values of $S$, deduced in this way from the NQR data are also shown in figure 4b.

As for the VI phase which could also be described by a single parameter model, it is interesting to compare these results to those obtained by NQES \cite{4}. In reference \cite{4} we have presented NQES spectra of powder TBBA at 184 °C in the SmA phase, which were analysed in terms of the EISF. At that time we did not know how to take into account the translational motions at high $Q$ so that two extreme values for $S$ were given. We know now that largest value, namely
$S = 0.70$ is the correct one. The reason is that, in a SmA phase, since the potential $V$ which maintains the molecules in the planes is rather weak ($V \approx k_B T$), the broadening of the translational component of the spectra varies like $Q^2$ up to large $Q$ values [18] and thus the analysis which has used this result is correct. This value of $S$ is also indicated in figure 4b. It is seen that, as for the VI phase, the agreement between NQR and NQES is very good. Again, this strongly supports the validity of the model, but also the approach chosen to analyse the NQES data.

In conclusion, in the smectic A phase of TBBA, the molecules are on the average normal to the planes and rotate probably uniformly around their long axes, although some (very weak) bipolar orientational order around this axis cannot be excluded. In addition, the long axes fluctuate about their equilibrium positions, with a uniaxial symmetry, the corresponding nematic order parameter $S$ being $\approx 0.70$ at 184°C. It should be also mentioned that the NQR data exclude the cone model [4] for TBBA since $\theta_0$ is always found to be smaller than $\theta_0$ in the C phase. This shows that the NQR method may be useful to test this model in other smectic A phases [19].

6. Check of the analysis in the H, C and A phases from DMR results. — 6.1 GENERAL. — The models for the VI and A phases seem to be well established since they can explain qualitatively and quantitatively both the $^{14}$N NQR and the NQES data. For the C and H phases, the available NQES data are not sufficient for a quantitative check of the models deduced from NQR. Therefore, we have used the DMR data of reference [9] concerning the deuterium of the $N = C - D$ group. These data are a priori very adequate since the deuterium, as it is in the same chemical group as the nitrogen nucleus, should feel the same motion, but may reflect it differently due to the different time scales of $^{14}$N NQR and DMR. These data, namely the splitting of the NMR line due to the quadrupolar interaction acting on the deuterium nucleus (spin 1), versus temperature, are given in figure 6.

The problem is thus to calculate the splitting $\Delta \nu$ predicted by the various models and to compare with the experimental values. For this purpose, we have to (i) express the efg tensor in the $x_D, y_D, z_D$ frame and (ii) use eqs. (6a)-(6d) to calculate $V_{H = H_0}$ and deduce $\Delta \nu$. Concerning the efg tensor the situation is much simpler for D than for $^{14}$N. It is indeed well known that this tensor is nearly uniaxial around the C-D bond and the value of the coupling constant $c_D$ lies between 170 and 200 kHz [20]. This tensor is thus completely defined. We have to express it now in the molecular frame $x_0, y_0, z_0$. Calling $v$ the angle between the C-D bond of the $N = C - D$ group and the long axis, a straightforward calculation shows that the only non zero components in this frame are :

$$V_{x_0 y_0} = -\frac{1}{2} c_D$$

$$V_{x_0 z_0} = c_D P_2(\cos v)$$

$$V_{y_0 z_0} = \frac{3}{2} c_D \sin 2v$$  

(11a)

(11b)

(11c)

(11d)

The average tensors in the $x, y, z$ and $x', y', z'$ frames are given by eqs. (5a)-(5d) and (6a)-(6d), respectively, where $V_{x_0 y_0} \ldots V_{x_0 z_0}$ are now given by eqs. (11a)-(11d).

Finally, we have to calculate $V_{H = H_0}$. If we assume that, in the DMR experiment, the long axis is always pointing along $H_0$, or in other words, that $H_0$ makes always an angle $\theta_0$ with the normal to the smectic planes, it is easy to show that we have

$$V_{H = H_0} = -\frac{1}{2} V_{y y'} +$$

$$+ \frac{1}{4} (V_{x x'} - V_{x' x'}) \cos 2\theta_0 + V_{x x'} \sin 2\theta_0$$  

(12)

The corresponding splitting is simply $3/2 |V_{H = H_0}|$ (cf. eq. (4)).

6.2 THE H PHASE. — To calculate the corresponding splitting, we need to accurately know the angle $v$. Consider figure 1. The angle $\varepsilon$ between the axis passing through the centres of the three phenyl rings and the para axis of these rings is 10.2° as calculated using standard bond lengths and angles. On the other hand, the angle between the C-D bond and the para axis lies between 59 and 64° as deduced from the structure of the TBBA molecule in the solid phase [21]. Consequently $v$ is expected to lie between 69 and 74°. For $T = 139$ °C, with $c_D = 177$ kHz, $\nu = 70.20$° (i.e. $N-C-H = 60$°) and the values of $\gamma', \theta_M, \delta'$ and $\langle \cos 2 \phi \rangle$ deduced above, we find $\Delta \nu = 75.0$ kHz, in perfect agreement with the experimental value (cf. Fig. 6). This result is not only an additional strong
support for the model, but it also gives some more precision about what is the long molecular axis in the H phase. This axis is identical to or very near (within less than 1°) the line passing through the centres of the three phenyls rings. This, in turn, shows that in this phase, the molecules always remain in their trans-conformation, at least during the time scale of DMR, namely $\sim 10^{-6}$ s.

6.3 THE C AND A PHASES. — Here, the first point to be noticed is that the experimental DMR splitting suffers a definite discontinuity at the H-C transition. However, such a discontinuity is observed neither in the $^{14}$N NQR data [7, 8], nor in the NQES data [3]. Moreover, if we try to calculate the splitting near the H transition e.g. at 146 °C, using the same values of $c_0$ and $v$ as in the H phase, we do not find the experimental value $\approx 65.5$ kHz, but 74.7 kHz, as expected if the transition were continuous (cf. Fig. 6). In our opinion, these results mean that in the C phase, DMR sees an additional motion which is not seen by $^{14}$N NQR and a fortiori by NQES. This motion is likely to be the trans-trans isomerization of the molecule via the cis-conformation [23]. In the trans-conformation, the long axis is at 10.2° from the para axis. In the cis-conformation, the long axis is nearly parallel to the para axis. If the isomerization is sufficiently rapid ($\sim 10^{-7}$ s$^{-1}$) the effective long axis will be at some angle $\langle \epsilon \rangle$ intermediate between 0 and 10.2°. Thus, the H-C transition seems to be characterized by a discontinuous change in the definition of the long axis, or equivalently by a discontinuous change in $v$ which explains the discontinuity in $\Delta v$. The new value of $v$ can be found by calculating the splitting using the known parameters of the model but taking $v$ as parameter. At $T = 146$ °C, the result is $v = 67.9°$. This means that for DMR the long axis of TBBA makes only an angle $\langle \epsilon \rangle = 7.9°$ with the para axis, in the C and in the higher temperature phases, in good agreement with the value estimated in reference [9] ($\approx 8°$).

With this new value of $v$ we can now calculate the splitting for the other temperatures in the C and A phases where the parameters of the model are known. The results are shown on figure 6 and it is seen that the agreement is again fairly good. This in turn shows that in the temperature range 146-187 °C where the NQR data exist, the angle $\langle \epsilon \rangle$ is practically constant. It is thus reasonable to assume that this is also true at higher temperature, in the A and nematic phases (see below).

6.4. — NEMATIC ORDER PARAMETER IN THE SmA AND NEMATIC PHASES. — Since the models for the SmC and SmA phases seem to be well established, we can use the available DMR data at higher temperature to estimate $S$ in these phases. For $\theta_M = \gamma' = 0$, combining eqs. (12), (11), (6) and (5) with $\langle \cos \phi \rangle = 0$, we find

$$V_{H\mu}H_0 = c_0[P_3(\cos v) S +$$

$$+ \frac{1}{2}[1 - P_2(\cos v)][1 - S] \langle \cos 2 \varphi \rangle].$$

(13)

Since $\langle \cos 2 \varphi \rangle$ is expected to be very small if not strictly zero, and since $v$ is significantly different from the magic angle 54.74° for which $P_2 = 0$, the second term is very small and can be neglected. In this case, the splitting is given by

$$\Delta v = \frac{3}{4} c_0 P_3(\cos v) S.$$ 

(14)

With $c_0 = 177$ kHz and $v = 67.9°$, using the values of the measured splitting, we can deduce $S$. The results are shown of figure 7 where we have also reproduced the values of $S$ in the C and H phases. It is seen that $S$ decreases smoothly with temperature with a small jump at the A-Nem transition. The minimum value at the Nem-Iso transition is $S \approx 0.32$, significantly smaller than expected from the Maier-Saupe theory.

6.5 ORDERING AT THE PHENYL RING SITES. — So far we have discussed the ordering at the place of the $N = C$-D group. However, DMR data concerning deuterium nuclei on the central [9] and the external [10] phenyl rings are available. The corresponding splittings on these rings are the same within experimental uncertainties [23], but it is observed that (i) $\Delta v$ (phenyls) is significantly smaller than $\Delta v$ ($N = C$-D) and (ii) the ratio of these two splittings varies (smoothly) with temperature.

This can be explained by the fact that, in addition to the overall motions described above, (i) the phenyl rings reorient rapidly ($\gg 10^{+6}$ s$^{-1}$) around their para axis [9] and (ii) this extra-rotation occurs in a two fold periodic potential and is characterized by the internal order parameter $\langle \cos 2 \varphi' \rangle$. These points
will be detailed in a further paper together with an attempt to describe the chain ordering.

7. Conclusion. — In conclusion, we have shown that the existing NQES, \(^{14}\)N NQR and DMR data concerning the various liquid crystalline phases of TBBA now provide a rather precise, and as we believe, unambiguous description of the local orientational order in TBBA. In all the mesophases, rotational motions with a correlation time varying from \(3 \times 10^{-11} \) s in the VI phase to \(0.5 \times 10^{-11} \) s in the A phase have been measured [3-5]. These motions correspond to rotation around the long axis plus fluctuations of this axis. In the VI phase, the molecules rotate around their long axes in a two fold periodic potential, the corresponding bipolar order parameter \(\langle \cos 2\phi \rangle\) varying from \(-1.0\) to \(0.8\) near the VI-H transition. In the H phase the rotation is almost uniform, but a small bipolar ordering still exists, which varies from \(0.15\) to \(0.06\) near the C transition. In addition, the long axes fluctuate about their equilibrium positions. These fluctuations are probably nearly uniaxial and their average amplitude varies from \(0^\circ\) to \(22^\circ\) near the H-C transition. In the C phase, the bipolar ordering around the long axis is now very weak (\(< 0.005\)). As the temperature increases, the long axis tends to be perpendicular to the smectic planes. The polar fluctuations (inside and outside the planes) remain practically constant \(\approx 22^\circ\) (corresponding to an order parameter \(S \approx 0.84\)), but the azimuthal fluctuations increase rapidly and become uniform (uniaxial symmetry) at the C-A transition. The corresponding order parameter \(\cos \phi \rangle\) varies from 0.85 to 0. In the SmA and nematic phases, the polar fluctuations increase continuously with the exception of a weak discontinuity at the SmA-nematic transition, and are as large as \(\approx 42^\circ\) (corresponding to \(S \approx 0.32\)) at the nematic-isotropic transition. In addition (i) in the SmH, C, A and nematic phases, the three phenyl rings reorient around their para axis, and (ii) in the C, A and nematic phases, the whole molecules undergo the trans-trans isomerization on a time scale of \(10^{-6}\) to \(10^{-7}\) s.

Finally, we note that the weak bipolar orientational order which exists in the SmH and C phases only reflect the instantaneous lateral packing of the molecular (herringbone) arrangement which is found in SmVI phase [11, 12]. In our opinion, it is not this phenomenon which determines the tilted nature of these mesophases. It should also be said that the present results definitely show that the mean field theories of references [1] and [2] are not adequate to describe the tilted smectic phases of TBBA.

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Note added in proof. — While this paper was being written, the Ljubljana group produced more \(^{14}\)N NQR data in the VI and H phases of TBBA. Their analysis leads to conclusions which are essentially the same as those presented in this paper, for these two phases (R. Bline, J. Seliger, M. Vilfan and V. Žagar, to be published).

### References

[23] "The fact that \(\theta_m\) is about half the tilt angle \(\theta_0\) seems at first glance difficult to understand. However, this is the mathematical traduction of the fact that in the high temperature range of the SmH phase, the angular fluctuations of the long axis are important. Indeed, for no fluctuations (\(\psi' \rightarrow \infty\), \(\delta' \rightarrow \infty\)), the model gives \(\theta_m \approx \theta_0\)."