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Molecular conformational changes in the smectic C, smectic A and nematic phases of TBBA (*)

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Abstract. The relative temperature dependence of several DMR splittings in the smectic C, smectic A and nematic phases of TBBA is discussed quantitatively in terms of internal rotations and changes of the most probable molecular conformation. It is shown that in these phases, the conformation is not planar. The mean dihedral angles between some rigid molecular fragments are estimated and compared with theoretical calculations. A discussion in terms of two order parameters is also made in the Appendix.

1. Introduction. — This paper concerns the temperature dependence of deuterium magnetic resonance (DMR) splittings in thermotropic liquid crystals. The experimental result which need to be explained is the observation that the splittings corresponding to deuterons at different sites of the molecules are not proportional to one another when the tempe- rature is varied. Two extreme explanations have been proposed to explain this result [1, 2]: (i) the most probable conformation changes with tempe- rature [2] and (ii) the most probable conformation does not change with temperature, but more than one order parameter is needed to describe the molecular orientational order [1]. Recently, explanation (ii) has become very popular among some researchers, based on the finding that for a number of uniaxial phases, if we call \( \Delta \nu_i \), \( \Delta \nu_j \), \( \Delta \nu_k \) the splittings corresponding to deuterons sites i, j, k on the molecules, then the ratio plot \( \Delta \nu_i \) versus \( \Delta \nu_j \) is a straight line within experimental accuracy [3, 4]. Such a result is indeed consistent with explanation (ii) with two order parameters. From symmetry arguments, it has been argued that the uniaxial phases are characterized by the two order parameters \( S_{xx0} \) and \( S_{xy0} - S_{yz0} \) and for the biaxial phases a third one, namely \( S_{yx0} \) is also needed [3]. These results have been criticized by us [5] and other authors [6]. These criticisms are:

(i) These symmetry arguments are irrelevant for the calculation of DMR splittings when the director is aligned along the magnetic field; so that they cannot be used to prove that some order parameters are zero in certain phases [5].

(ii) This latter point is supported experimentally by counter examples where some ratio plots are found to be discontinuous where they should not and not discontinuous where they should [6].

(iii) Finally, even if \( S_{xx0} - S_{yy0} \) were non zero in the SmC, SmA and nematic phases of TBBA, it is too small (by a factor we estimate to be of the order of 10-100) to explain the observed temperature dependence of some splitting ratios [5]. In the Appendix, we detail this point.

Using the results of our previous work concerning the molecular orientational order [7], we show in this...
paper that explanation (i) in terms of changes of the most probable conformation may explain qualitatively and quantitatively the observed temperature dependence of three independent such ratios associated with the aromatic core of TBBA, in the SmC, SmA and nematic phases. The problem of the ratios associated with the butyl chains will be treated in a forthcoming paper devoted to the chain ordering in TBBA [8].

2. The TBBA molecule and existing DMR data concerning the aromatic core. — The TBBA molecule is sketched in figure 1 in its planar trans-conformation. The published DMR data which will be considered in this paper are:

(i) the splitting $\Delta v_{\text{met}}$ of the azomethine group [9],
(ii) the splitting $\Delta v_{\text{c.r.}}$ of the central phenyl ring [9],
(iii) the splitting $\Delta v_{\text{e.r.}}$ of the external phenyl rings [10, 2, 11],
(iv) the dipolar splitting $\Delta v_{\text{dp}}$ between H and D on the external ring (cf. Fig. 1) [10, 2, 11],
(v) the splitting $\Delta v_{\beta}$ of the first methylene group of the butyl chains [10, 2, 11].

For evident reasons, we can only consider ratios of splittings measured on the same spectra. In the present case, we can form three independent such ratios.

For convenience, we choose $R_1 = |\Delta v_{\text{met}}|/|\Delta v_{\text{e.r.}}|$, $R_2 = \Delta v_{\text{c.r.}}/\Delta v_{\text{dp}}$, and $R_3 = |\Delta v_{\beta}|/|\Delta v_{\text{e.r.}}|$. These three ratios are presented in figures 2, 4 and 5.

It is observed that, despite the experimental uncertainties, those ratios are not constant with temperature, but vary by an amount of ~10% throughout the SmC, SmA and nematic phases, with a discontinuity for $R_1$ (and probably for $R_2$) at the SmA-nematic transition.

3. Model for the motions and calculation of the splittings. — The concept which is useful for the present purpose is that of the most probable molecule. The most probable molecule is the conformation such that all the dihedral angles between rigid molecular fragments, linked between themselves by single covalent bonds, correspond to minima of the potentials hindering the rotations around these bonds. The height of these potentials is generally low (a few kJ/mole, i.e. a few $k_B T$ with $T$ around or above room temperature [2]). Consequently, rotations around these bonds are expected to occur frequently on the time scale of DMR ($\sim 10^{-6}$ s). On the other hand, since the molecules are elongated objects, it is natural to define a molecular frame $O_x O_y O_z$ attached to the most probable molecule such that $O_z$ is the long molecular axis. The overall rotational motion of the molecule with respect to $H_0$ is thus conveniently described by its rotation around $O_z$ and by angular fluctuations of $O_z$ with respect to $H_0$.

To calculate the DMR splitting $\Delta v_1$ of a deuteron $\beta$ attached to a given rigid fragment (m) which can rotate around some axis within the most probable molecule (e.g. a phenyl ring around its para-axis), we decompose the motion of the CD bond with respect to the magnetic field $H_0$ into a motion of the CD bond with respect to the $O_x O_y O_z$ frame (internal motion) and a motion of the $O_x O_y O_z$ frame with respect to $H_0$ (external motion). The problem of the external motions in the mesophases of TBBA was treated in detail in reference [7]. The main result is that in the SmC, SmA and nematic phases the
molecules rotate practically uniformly around their long axes, the deviation from the perfect uniformity being very small [5] and will be neglected in the present calculation (cf. the Appendix for details).

In this case, the expression of $\Delta V_i$ is very simple and we have, assuming that (i) the e.f.g. acting on the deuterons has cylindrical symmetry around the CD$_i$ bond and (ii) that the external and internal motions are not coupled [5] :

$$\Delta V_i = \frac{3}{2} c_i S \langle P_2(\cos \theta_i, \Omega_{0z}) \rangle.$$  \hspace{1cm} (1)

In this expression, $c_i = e^2 q_i q_h$ is the quadrupolar coupling constant of deuteron $i$, $S = S_{\omega=0}$ is the nematic order parameter and the brackets stand for an average over the internal motions.

To calculate this average, we proceed as follows : we assume that the rigid fragment has at least one plane of symmetry and we define a frame Oxyz attached to this fragment such that Ox is in this plane of symmetry and Oz along the internal rotation axis. We call $u_i$ and $\varphi_i$ the polar and azimuthal angles of the CD$_i$ bond in this frame. Then we introduce the frame Ox$_m$ y$_m$ z$_m$ with Oz$_m$ == Oz attached to the most probable orientation of the fragment. The angle $\varphi' = (Ox, Ox_m)$ which defines the Oxyz frame with respect to the Ox$_m$ y$_m$ z$_m$ frame describes the rotation of the rigid fragment in the most probable molecule. Finally we introduce the polar and azimuthal angles $e$ and $\phi$ of the Oz$_0$ long axis in the Ox$_m$ y$_m$ z$_m$ frame. With these ingredients, standard algebra leads to the relation :

$$P_2(\cos (\theta_i, \Omega_{0z})) =$$
$$= \sum_{m=-2}^{2} e^{-im\varphi'} e^{-im\varphi} d_{m0}^2(u_i) d_{m0}^2(e) \hspace{1cm} (2)$$

where the $d_{m0}^2$ are the matrix elements of the reduced Wigner matrices of order 2 [12]. The average over the internal motions corresponds to an average over $\varphi'$. If we assume that the potential $V(\varphi')$ has $C_2$ symmetry (this will be the case for the internal rotation considered in this paper), then

$$\langle \cos \varphi' \rangle = \langle \sin \varphi' \rangle = \langle \sin 2 \varphi' \rangle = 0 ,$$

and we obtain, replacing the $d_{m0}^2$ by their explicit expression [12]

$$\langle P_2[\cos (CD_i, \Omega_{0z})] \rangle = P_2(\cos \theta_1 \cos \theta_2) +$$
$$+ \frac{1}{2} \sin^2 u_1 \sin^2 e \langle \cos 2 \varphi' \rangle \cos 2(\theta_1 - \theta_2). \hspace{1cm} (3)$$

In fact, this is not the final result. The reason is that we have so far assumed that we have only one most probable molecule. For a molecule like TBBA where all the rigid fragments have a plane of symmetry, it is clear that if we define the most probable conformation by the set of values $\{e, \phi\}$ with respect to all the fragments, then the conformation $\{e, -\phi\}$ is energetically equivalent. This means, that there are in fact two most probable conformations which necessarily exchange rapidly on the DMR time scale. Consequently, equation (3) should be further averaged for the two values $\phi$ and $-\phi$. Performing this average and combining the result with equation (1) yields

$$\Delta V_i = \frac{3}{2} c_i S \left[ P_2(\cos u_i) P_2(\cos e) +$$
$$+ \frac{1}{2} \sin^2 u_i \sin^2 e \langle \cos 2 \varphi' \rangle \cos 2(\theta - \varphi) \right]. \hspace{1cm} (4)$$

The introduction of the two equivalent most probable conformations is only relevant when $\varphi_i \neq 0$, i.e. when the CD$_i$ bond is not in the plane of symmetry of the fragment. In the particular case of the methylene groups attached to the rings which contain two CD$_i$ bonds with $\varphi_i \approx \pm 115^\circ$, this exchange is sufficient to insure that the two deuterons are magnetically equivalent. Without this exchange, the equivalence would occur only for $\phi = m\pi$. There is no reason that this is the situation for all the liquid crystalline mesophases especially those made up of short chain molecules : there is no known DMR experiment on the fluid mesophases of thermotropic or lyotropic liquid crystals where the two deuterons on a methylene group are not found to be equivalent (1).

Let us discuss equation (4). It contains three kinds of parameters, namely the structural parameters $c_i$, $u_i$, $\varphi_i$, the conformational parameters $e$ and $\phi$, and the dynamical parameters $S$ and $\langle \cos 2 \varphi' \rangle$.

The structural parameters can be estimated from X-rays studies of the solid phase [13] and DMR data on similar systems, essentially on smaller but similar molecules. They are expected to be practically independent of temperature. The conformational parameters depend upon the most probable molecular conformation. The latter is essentially determined by the shape of the potentials $V(\varphi')$ hindering the rotation around the single bonds, in particular the position of the minima. These potentials are mainly determined by the electronic distribution within the bond (intramolecular contribution), but also by the intermolecular forces, whose changes with temperature may shift the minima, i.e. change the mean dihedral angle between fragments. This phenomenon is particularly plausible for TBBA if we consider the theoretical calculations performed on the parent benzilidene-aniline molecule [14a] and more recently on the TBBA molecule itself [14b]. It is indeed found that the minima of these potentials are very flat and their height of the order of one or a few kcal/mole.

(1) A counter-example seems to have been found by Seelig et al. (Biochim. Biophys. Acta 406 (1975) 1) for the first methylene group of chain 2 of dipalmitoyl-phosphatidyl choline in the L$_a$ phase. However this counter-example is not a true one since the authors explain their observation by the existence of two long lived conformations of the lipid molecule with two different orientations of chain 2. This means that if our argument were wrong, one should have observed four splittings instead of two.
i.e. typically of the order of the intermolecular potentials in a molecular solid or liquid.

We thus expect that $\phi$ changes with temperature due to changes of these intermolecular potentials. On the contrary, $\varepsilon$ should not be much affected by this phenomenon, and in fact, the analysis of reference [7] suggests that $\varepsilon$ is practically constant (within $\sim 0.2^\circ$) and equal to $7.9^\circ$ for TBBA in the SmC, SmA and nematic phases. We consider finally the dynamical quantities: the nematic order parameter $S$ is mainly determined by the intermolecular forces. It has been estimated for TBBA in reference [7]. The internal order parameter $\langle \cos 2 \phi' \rangle$ is mainly determined by the height of the potential $V_{\phi'}$ and little by the exact shape and by the temperature in the relevant temperature range. For a cosine potential of the form $V(\phi') = -\frac{V}{2} \cos 2 \phi'$, we have [15]

$$\langle \cos 2 \phi' \rangle = I_1(\gamma') I_0(\gamma') \quad \text{with} \quad \gamma' = V k_B T.$$  

Here, $I_0$ and $I_1$ are modified Bessel functions of the first kind of order 0 and 1. In TBBA, $V$ is of the order of a few kJ/mole for rotation of the rings around their para-axes [2, 14] and for rotation of the first methylene group around the bond connecting the carbon to the external ring [16]. With $V = 11$ kJ/mole and $T = 300$ K, we have $\langle \cos 2 \phi' \rangle \approx 0.7$. Since the potentials are not better known and since the influence of temperature on $\langle \cos 2 \phi' \rangle$ is relatively small, we shall take $\langle \cos 2 \phi' \rangle = \text{const.} = 0.7$ in the following numerical calculations.

In summary, in this model, only $S$ and the $\phi$'s are expected to significantly vary with temperature. Since all the splittings are proportional to $S$, the temperature dependence of ratios of splittings is due essentially to $\phi$. We use this result to analyse the temperature dependence of $R_1$, $R_2$ and $R_3$ in the SmC, SmA and nematic phases of TBBA.

4. Ratio $R_1 = |\Delta v_{\text{met}}/\Delta v_{\text{c.r.}}|$. — Contrary to the phenyl rings and the butyl chains, the azomethine group does not perform any specific internal rotation. The expression of $\Delta v_{\text{met}}$ is particularly simple and we have [7]

$$\Delta v_{\text{met}} = \frac{1}{2} \varepsilon_{\text{met}} SP_2(\cos \varepsilon_{\text{met}})$$  

where $\varepsilon_{\text{met}} = (\text{CD}_{\text{met}}, \text{Oz}_0)$ is the angle between the CD bond of the azomethine group and the long molecular axis $\text{Oz}_0$.

For the central ring which rotates around its para-axis [9], equation (4) applies with $\phi_i = \phi_{\text{c.r.}} = 0$ (the CD bonds are in the plane of the ring) and we have

$$\Delta v_{\text{c.r.}} = \frac{1}{2} \varepsilon_{\text{c.r.}} S [P_2(\cos \varepsilon_{\text{c.r.}}) P_2(\cos \phi_{\text{c.r.}}) +$$  

$$+ \frac{1}{2} \sin^2 \varepsilon_{\text{c.r.}} \sin^2 \phi_{\text{c.r.}} (\langle \cos 2 \phi' \rangle \cos 2 \phi_{\text{c.r.}})].$$  

It is seen that $R_1$ contains the single temperature dependent parameter $\phi_{\text{c.r.}}$.

Since $\varepsilon_{\text{met}}$ and $\varepsilon_{\text{c.r.}}$ are larger than the magic angle $54.74^\circ$ where $P_2 = 0$, it is clear that $R_1$ is minimum for $|\phi_{\text{c.r.}}| = 90^\circ$. On the other hand, inspection of figure 2 shows that the experimental minimum value of $R_1$ is $\sim 2.8$ and is obtained at $\sim 200^\circ$ C in the nematic phase. With $\varepsilon_{\text{met}} = 177$ kHz [7], $\varepsilon_{\text{c.r.}} = 185$ kHz, $\varepsilon_{\text{met}} = 67.9^\circ$ [7], $\varepsilon_{\text{c.r.}} = 7.9^\circ$ [7] and $\langle \cos 2 \phi' \rangle = 0.7$, we find that $R_1 = 2.58$ for $|\phi_{\text{c.r.}}| = 90^\circ$ and $\varepsilon_{\text{c.r.}} = 59.0^\circ$. Using these values of the parameters, we have calculated the theoretical variation of $R_1$ versus $|\phi_{\text{c.r.}}|$. The result is shown on figure 3 and it is seen that the overall theoretical variation of $R_1$ is $\sim 15\%$, significantly larger than the experimental one ($\sim 7\%$). This shows that a change of $\phi_{\text{c.r.}}$ with temperature may perfectly explain the observed variation of $R_1$. Moreover, it is seen that $\phi_{\text{c.r.}}$ increases as the temperature increases in the SmC and SmA phases and is practically constant (or slightly decreases) in the nematic phase. If we accept that $|\phi_{\text{c.r.}}| = 90^\circ$ at $\sim 200^\circ$ C in the nematic phase (minimum value of $R_1$), we can assign a value of $\phi_{\text{c.r.}}$ to each temperature as shown in figure 3. This provides a hint of how much $\phi_{\text{c.r.}}$ varies through the three fluid mesophases of TBBA, but does not mean at all that the values of $|\phi_{\text{c.r.}}|$ are precisely those indicated.

5. Ratio $R_3 = |\Delta v_{\text{e.r.}}/\Delta v_{\text{dip}}|$. — The expression for $\Delta v_{\text{e.r.}}$ is similar to equation (6) with the index c.r. replaced by e.r. Putting $\phi_{\text{c.r.}} = \phi_{\text{e.r.}} + \alpha$ where
\( \alpha \) represents the dihedral angle between the internal and external rings, we have:

\[
\Delta v_{c.e.} = \frac{1}{2} c_{r.e.} S [P_2(\cos \alpha_{c.r.}) P_2(\cos \epsilon_{c.r.}) + \\
+ \frac{1}{2} \sin^2 \epsilon_{c.r.} \sin^2 \epsilon_{c.r.} (\cos 2 \phi') \cos 2(\phi_{c.r.} + \alpha)].
\]  

(7)

For the calculation of \( \Delta v_{\text{dip}} \) equation (4) also applies with the difference that (i) \( u_i \) and \( \phi_i \) refer to the vector \( \mathbf{r}_{HD} \) rather than to the CDi bond and (ii) \( \frac{1}{2} \phi_i \) should be replaced by \( K \phi_i \) where \( K = -\gamma_H / \pi h / 2 \pi^2 \).

Since \( \mathbf{r}_{HD} \) is practically parallel to the para-axis of the ring, we have \( u_i \approx 0 \). The second term in equation (4) drops and we have:

\[
\Delta v_{\text{dip}} = \frac{K}{\mathbf{r}_{HD}} S P_2(\cos \epsilon_{c.r.}).
\]

(8)

The single temperature dependent parameter in the expression of \( R_2 \) is \( \phi_{c.r.} + \alpha \). If we assume that the values of \( \phi_{c.r.} \) are those deduced from the preceding analysis, we can calculate \( R_2 \) as a function of temperature for various values of \( \alpha \). Theoretical curves calculated with \( \epsilon_{c.r.} = 185 \text{ kHz}, |K| = 36.89 \text{ kHz} \cdot \text{Å}^2, \mathbf{r}_{HD} = 2.54 \text{ Å}, (\cos 2 \phi') = 0.7, \epsilon_{c.r.} = 7.9^\circ [7] \) and \( u_{\epsilon_{c.r.}} = 59.25^\circ \), are shown in figure 4. It is seen that situations where \( \alpha \) is large (say 60° < \( \alpha \) < 90°) can explain the temperature dependence and the magnitude of the variation of \( R_2 \). On the contrary situations where \( \alpha \) is small (say \( \alpha < 45^\circ \)) are excluded by our model. Clearly, it is not possible to deduce the detailed temperature dependence of \( \alpha \), but it is likely that this variation is relatively small, except for a possible discontinuity at the SmA-Nem transition. For the sake of simplicity, we shall assume in the following that \( \alpha \sim 60^\circ \) in the SmC and SmA phase and \( \alpha \sim 75^\circ \) in the nematic phase. These values are indeed those which best fit the data of figure 4.

6. Ratio \( R_3 \) = \( |\Delta v_i|/\Delta v_{c.e.}| \) — As for the other splittings, we assume that the first methylene of the butyl chain reorients around the para-axis of the external ring in a potential of \( C_2 \) symmetry. In this case, equation (4) applies and we have, putting

\[
\phi_i = \phi_{c.r.} + \alpha + \beta,
\]

where \( \beta \) is the dihedral angle between the external ring and the chain in its trans-conformation:

\[
\Delta v_1 = \frac{1}{2} c_1 S [P_2(\cos u_i) P_2(\cos \epsilon_{c.r.}) + \\
+ \frac{1}{2} \sin^2 u_i \sin^2 \epsilon_{c.r.} (\cos 2 \phi') \times \cos 2(\phi_{c.r.} + \alpha + \beta) \cos 2 \phi_1].
\]

(9)

Combining equations (9) and (7), we can write down the expression for \( R_3 \). Its variation with temperature is more complicated than that of \( R_1 \) and \( R_2 \) since it depends on two parameters, namely \( \phi_{c.r.} + \alpha \) and \( \phi_{c.r.} + \alpha + \beta \). As above, if we assume that the values of \( \phi_{c.r.} \) and \( \alpha \) are those deduced from the preceding analysis, we can calculate \( R_3 \) as a function of temperature for various values of \( \beta \). Theoretical curves, calculated with \( c_1 = 172 \text{ kHz}, u_i = 74.5^\circ [8], |\phi_1| = 114.28^\circ [8], \epsilon_{c.r.} = 7.9^\circ [7], (\cos 2 \phi') = 0.7 \) for \( \Delta v_1 \) and the same values as in section 5 for \( \Delta v_{c.e.} \), are shown in figure 5. It is seen that, in contradiction with the case of \( R_2 \), all values of \( \beta \) predict the correct temperature dependence, the correct magnitude and the correct amplitude variation of \( R_3 \). The only thing which can be said is that if we accept that \( \alpha \) is discontinuous at the SmA-Nem transition, then it is likely that \( \beta \) is also discontinuous at the same tran-

![Fig. 4. Ratio \( R_2 = |\Delta v_{c.e.}|/|\Delta v_{\text{dip}}| \) versus temperature.](image)

![Fig. 5. Ratio \( R_3 = |\Delta v_i|/\Delta v_{c.e.}| \) versus temperature.](image)

sition, in order to explain that $R_3$ exhibits no significant discontinuity. However, a situation where $\beta \sim 90^\circ$ in all phases, which is sterically favorable for the isolated molecule [14b] and which is also the situation in the solid phase [13], is not inconsistent with the data, within the experimental accuracy. It is interesting to note also that if $R_3$ is weakly sensitive to $\beta$, on the contrary it strongly depends on $\alpha$. The calculation shows that a situation with $\alpha \sim 0^\circ$ predicts a variation of $R_3$ with temperature which is opposite to what is observed, whatever the value of $\beta$. Thus, it seems that the result $\alpha$ large (say $\alpha > 45^\circ$) is well established since it is supported by the temperature dependence of two independent ratios.

At this point it is interesting to note that the result that the Schiff base molecules in nematic phases are non planar, seems to be general. It has indeed been shown by proton NMR that the dihedral angle between the azomethine group and the aniline ring has also been shown that this angle is relatively between the azomethine group and the aniline ring. Considering the butyl chains it has also been shown that this angle is relatively large [9].

7. Discussion. — To summarize, we have shown that the temperature dependence and the magnitude of variation of three independent ratios of DMR splittings associated with the aromatic core of TBBA can be explained using the single nematic order parameter $S$, if one assumes the existence of internal rotations and changes with temperature of the most probable conformation. These changes correspond in our model to a variation of the mean dihedral angle between molecular fragments linked between themselves by single covalent bonds.

It is of interest to discuss the values of these angles and the magnitude of their variation. In fact, the only semi-quantitative information which we have obtained concerns the angle $\alpha$ between the internal and external rings. We have found that this angle is large and probably varies from $\sim 60$ to $75^\circ$ throughout the fluid mesophases. These values should be compared with those in the solid phase and in the gas phase. For the solid phase, we have $\alpha = 16.1$ and $52.9^\circ$ [13] (the two external rings are not equivalent). For the gas phase, this angle is that of the isolated molecule i.e. $\alpha \approx 90^\circ$ [14b]. We reasonably expect that in the liquid state, $\alpha$ lies between these two limits and tends towards the value for the isolated molecule as the temperature increases, i.e. as the average intermolecular forces decrease. This is precisely what is found.

The other angle on which we have obtained some information is $\phi_{e.r}$. However, $\phi_{e.r}$ is not strictly speaking a conformational angle. Its variation (Fig. 3) pictures the changes in the long molecular axis and consequently is associated with changes of all the various dihedral angles. Considering the butyl chains as individual fragments, there are not less than seven molecular fragments in the TBBA molecule. It is not unreasonable to think that a mean variation of say $\sim 10^\circ$ for each of these angles causes a variation of $\sim 50^\circ$ for $\phi_{e.r}$.

Clearly, there is no direct proof of this model, but apart from the fact that it does not seem unreasonable in view of the relative values of the intra and intermolecular potentials, it has the advantage of being not inconsistent with the present existing data, contrary to a model invoking several order parameters and no change in the most probable conformation (cf. the Appendix). In any case, it seems that, given the magnitude of the effects, any model aimed at explaining the relative temperature dependence of DMR splittings in liquid crystals cannot ignore without justification, possible changes in the most probable molecular conformation.

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Appendix. — In this Appendix, we consider the explanation of the temperature dependence of ratio $R_1$ in terms of two order parameters [1, 3], in the light of the results of reference [7]. For this purpose, we have calculated the splittings according to the method of reference [7], using equations (11) and (12) of that reference. For $\Delta_\text{met}$, we simply used equation (12) of reference [7] with $v = (CD_\text{met}, O_\alpha) = v_\text{met}$. For $\Delta_\text{e.r}$, equations (11a-d) of reference [7] have been averaged over $v = (CD_{e.r}, O_\alpha)$ according to the procedure described in the present paper, equations (3), (4) and (6). In fact, the calculation is slightly more complicated since it involves the more general Wigner matrices $d_{nm}^2$. The two order parameters describing the external motion are $S$ and $\langle \cos 2 \varphi \rangle$ [7]. The latter is the bipolar order parameter associated with the deviation from uniformity of the rotation around long axis $O_\alpha$ of the $C_{2h}$ symmetry. In the framework of the model of reference [7] where rotation around $O_\alpha$ and fluctuations of $O_\alpha$ are independent, we have $S_{\text{rot}} = S_{\text{rot}} = (1 - S) \langle \cos 2 \varphi \rangle$ [5]. In reference [7], we have deduced the absolute value of $S$ versus temperature (cf. figure 7 of reference [7]) and estimated an upper value of $\langle \cos 2 \varphi \rangle$. This upper value is 0.005 [7, 20]. To estimate the temperature dependence of $R_1$ due to the existence of a finite value of $\langle \cos 2 \varphi \rangle$, we have calculated $R_1$ for two possible extreme temperature dependences of $\langle \cos 2 \varphi \rangle$, the other parameters being fixed to the same values as in section 4 of the present paper and for three values of $\phi_{e.r}$.

(i) $\langle \cos 2 \varphi \rangle = \text{const.} = 0.005$ for all temperatures,
(ii) $\langle \cos 2 \phi \rangle$ varies smoothly from 0.005 to 0, from 146 °C to 235 °C. The results are shown in figure A1. It is seen that in all cases, it is impossible to account for a variation of $R_1$ of ~ 7% between 146° and 200 °C, the maximum variation being of the order of ~ 1°, and is obtained for $\phi_{c.t.} \sim 90^\circ$, within the somewhat unrealistic assumption that $\langle \cos 2 \phi \rangle$ is constant with temperature. Any decrease of $\langle \cos 2 \phi \rangle$ with increasing temperature (this is a realistic situation : cf. the results for the H phase [7]) diminishes correlatively the overall variation of $R_1$. In fact, we have calculated that the above mentioned variation of ~ 7% is obtained assuming that $\langle \cos 2 \phi \rangle = \text{const.} = 0.04$, i.e. about 8 times larger than the maximum estimated value. It may be argued that this result has been obtained assuming that the rotation around the long axis and fluctuations of this axis are uncoupled. It turns out that the introduction of some coupling does not change the essential result (cf. the discussion in reference [5]).

All this shows that if a (very) small contribution of the second order parameter to the temperature dependence of $R_1$ (and also of $R_2$ and $R_3$) cannot be excluded, it is necessary to introduce changes in the most conformation to account for the observed overall variation of these ratios.

Finally, we remark the following : the calculation presented in this paper has assumed that the e.f.g. tensor acting on the deuterons have cylindrical symmetry around the CD bond. In fact, a small asymmetry cannot be excluded [21]. Calling $\eta$ the asymmetry parameter, and $v = (CD, O_{z0})$ and $\lambda$ the polar and azimuthal angles of the $O_{z0}$ in the principal frame of the e.f.g. tensor, equation (1) should be rewritten in this case as [1] :

$$\Delta \eta = \frac{3}{2} S \left[ \langle P_2(\cos v) \rangle + \frac{\eta}{2} \langle \sin^2 v \cos 2 \lambda \rangle \right].$$

The value of $\eta$ usually ranges between a few per cent to zero [21]. Consequently, it can generally be neglected, except when $\langle P_2(\cos v) \rangle$ is very small i.e. $\langle v \rangle$ near the magic angle. This situation never happens for the splittings considered here so that the approximation is justified. However, in the case of very small DMR splittings, as for example for some methyl groups [1], this aspect of the problem would require a careful examination, whatever the model considered.

References