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

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Résumé. — On discute de manière quantitative la dépendance en température de plusieurs rapports de *splittings* de DMR, dans les phases smectique C, smectique A et nématique de TBBA, à l'aide d'un modèle qui prend explicitement en compte les rotations internes et les changements de la conformation moléculaire la plus probable. On montre que dans toutes les phases, cette conformation n'est pas plane. La valeur de l'angle dièdre moyen entre quelques fragments moléculaires rigides est estimée et comparée à des valeurs théoriques. Dans l'Appendice, on présente une discussion du même problème à l'aide d'un modèle à deux paramètres d'ordre orientationnels.

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 needs 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 temperature is varied. Two extreme explanations have been proposed to explain this result [1, 2]: (i) the most probable conformation changes with temperature [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 Δv_i , Δv_j , Δv_k the splittings corresponding to deuteron sites i , j , k on the molecules, then the *ratio plot* $\Delta v_i / \Delta v_k$ versus $\Delta v_j / \Delta v_k$ 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 $S_{z_0z_0}$ and $S_{x_0x_0} - S_{y_0y_0}$ and for the biaxial phases a third one, namely $S_{y_0z_0}$ 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 $S_{x_0x_0} - S_{y_0y_0}$ 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

(*) This paper has been presented as an oral communication at the Conference on « Liquid Crystals of one and two dimensional Order and their Applications », Garmisch-Partenkirchen, Germany, jan. 1980.

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 Δv_{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 Δv_{dip} between H and D on the external ring (cf. Fig. 1) [10, 2, 11],
- (v) the splitting Δv_1 of the first methylene group of the butyl chains [10, 2, 11].

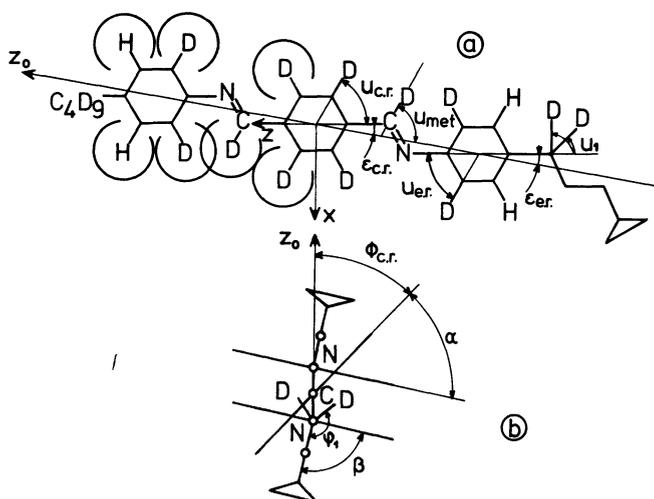


Fig. 1. — Sketch of the TBBA molecule : a) lateral view in a planar trans-conformation showing the various deuteron and proton sites discussed in the text. The circles around the nuclei indicate their Van der Waals radii. The long molecular axis Oz_0 , the internal axes Oz and the various polar angles used in the text are also shown. b) top view along the para-axes of the rings showing the long molecular axis Oz_0 and the various azimuthal angles used in the text. The two azomethine fragments have been drawn parallel only for clarity. The top view of the second most probable molecule introduced in section 3 is obtained by symmetry with respect to Oz_0 in figure 1b.

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 $R_1 = |\Delta v_{\text{met}}/\Delta v_{\text{c.r.}}|$, $R_2 = |\Delta v_{\text{e.r.}}/\Delta v_{\text{dip}}|$ and $R_3 = |\Delta v_1/\Delta v_{\text{e.r.}}|$. These three ratios are presented in figures 2, 4 and 5.

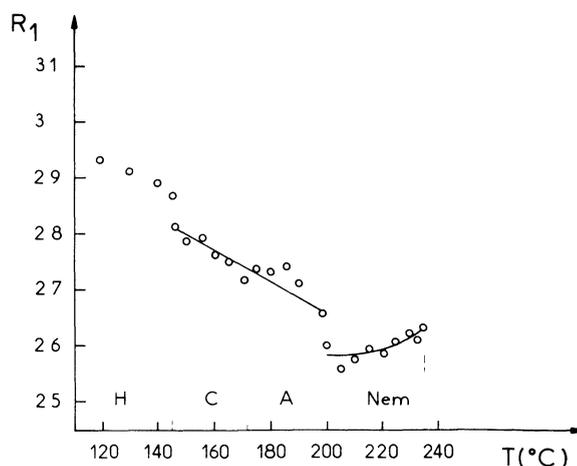


Fig. 2. — Ratio $R_1 = |\Delta v_{\text{met}}/\Delta v_{\text{c.r.}}|$ versus temperature in the SmC, SmA and nematic phases of TBBA : O : experimental points extracted from figure 4 of reference [9]. The line represents a smooth curve through the points.

It is observed that, despite the experimental uncertainties, those ratios are not constant with temperature, but vary by an amount of $\sim 10\%$ 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 $Ox_0 y_0 z_0$ attached to the most probable molecule such that Oz_0 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 Oz_0 and by angular fluctuations of Oz_0 with respect to H_0 . To calculate the DMR splitting Δv_i of a deuteron i 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_i bond with respect to the magnetic field H_0 into a motion of the CD_i bond with respect to the $Ox_0 y_0 z_0$ frame (internal motion) and a motion of the $Ox_0 y_0 z_0$ 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 Δv_i is very simple and we have, assuming that (i) the e.f.g. acting on the deuteron has cylindrical symmetry around the CD_i bond and (ii) that the external and internal motions are not coupled [5] :

$$\Delta v_i = \frac{3}{2} c_i S \langle P_2[\cos(CD_i, Oz_0)] \rangle. \quad (1)$$

In this expression, $c_i = e^2 q_i Q/h$ is the quadrupolar coupling constant of deuteron i , $S = S_{z_0z_0}$ 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 φ_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 $Oz_m \equiv Oz$ 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 ε and ϕ of the Oz_0 long axis in the $Ox_m y_m z_m$ frame. With these ingredients, standard algebra leads to the relation :

$$P_2[\cos(CD_i, Oz_0)] = \sum_{m=-2}^2 e^{-im\varphi'} e^{-im\phi - \varphi} d_{m0}^2(u_i) d_{m0}^2(\varepsilon) \quad (2)$$

where the d_{mm}^2 are the matrix elements of the reduced Wigner matrices of order 2 [12]. The average over the internal motion corresponds to an average over φ' . If we assume that the potential $V(\varphi')$ has C_{2v} 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]

$$\langle P_2[\cos(CD_i, Oz_0)] \rangle = P_2(\cos u_i) P_2(\cos \varepsilon) + \frac{3}{4} \sin^2 u_i \sin^2 \varepsilon \langle \cos 2 \varphi' \rangle \cos 2(\phi - \varphi_i). \quad (3)$$

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 $\{\varepsilon, \phi\}$ with respect to all the fragments, then the conformation $\{\varepsilon, -\phi\}$

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 ϕ and $-\phi$. Performing this average and combining the result with equation (1) yields

$$\Delta v_i = \frac{3}{2} c_i S [P_2(\cos u_i) P_2(\cos \varepsilon) + \frac{3}{4} \sin^2 u_i \sin^2 \varepsilon \langle \cos 2 \varphi' \rangle \cos 2 \phi \cos 2 \varphi_i]. \quad (4)$$

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 $\phi = n\pi$. 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 , φ_i , the conformational parameters ε and ϕ , 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_α 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 ϕ changes with temperature due to changes of these intermolecular potentials. On the contrary, ε should not be much affected by this phenomenon, and in fact, the analysis of reference [7] suggests that ε is practically constant (within $\sim 0.2^\circ$) and equal to 7.9° 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 $\langle \cos 2\varphi' \rangle$ is mainly determined by the height of the potential $V(\varphi')$ and little by the exact shape and by the temperature in the relevant temperature range. For a cosine potential of the form $V(\varphi') = -\frac{V}{2} \cos 2\varphi'$, we have [15] $\langle \cos 2\varphi' \rangle = I_1(\gamma')/I_0(\gamma')$ with $\gamma' = V/k_B T$. 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 $\langle \cos 2\varphi' \rangle \approx 0.7$. Since the potentials are not better known and since the influence of temperature on $\langle \cos 2\varphi' \rangle$ is relatively small, we shall take $\langle \cos 2\varphi' \rangle = \text{const.} = 0.7$ in the following numerical calculations.

In summary, in this model, only S and the ϕ '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 ϕ . 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 Δv_{met} is particularly simple and we have [7]

$$\Delta v_{\text{met}} = \frac{3}{2} c_{\text{met}} S P_2(\cos v_{\text{met}}) \quad (5)$$

where $v_{\text{met}} = (\text{CD}_{\text{met}}, \text{Oz}_0)$ is the angle between the CD bond of the azomethine group and the long molecular axis Oz_0 .

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

$$\Delta v_{\text{c.r.}} = \frac{3}{2} c_{\text{c.r.}} S [P_2(\cos u_{\text{c.r.}}) P_2(\cos \varepsilon_{\text{c.r.}}) + \frac{3}{4} \sin^2 u_{\text{c.r.}} \sin^2 \varepsilon_{\text{c.r.}} \langle \cos 2\varphi' \rangle \cos 2\phi_{\text{c.r.}}]. \quad (6)$$

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

Since v_{met} and $u_{\text{c.r.}}$ are larger than the magic angle 54.74° 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 ~ 2.58 and is obtained at $\sim 200^\circ\text{C}$ in the nematic phase. With $c_{\text{met}} = 177$ kHz [7], $c_{\text{c.r.}} = 185$ kHz, $v_{\text{met}} = 67.9^\circ$ [7], $\varepsilon_{\text{c.r.}} = 7.9^\circ$ [7] and $\langle \cos 2\varphi' \rangle = 0.7$, we find that $R_1 = 2.58$ for $|\phi_{\text{c.r.}}| = 90^\circ$ and $u_{\text{c.r.}} = 59.0^\circ$. 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

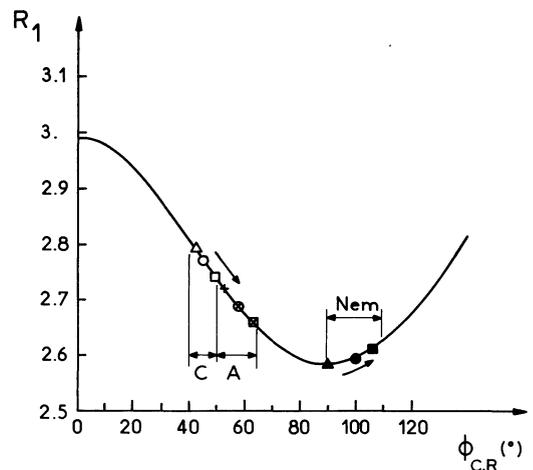


Fig. 3. — Ratio $R_1 = |\Delta v_{\text{met}}/\Delta v_{\text{c.r.}}|$ versus $\phi_{\text{c.r.}}$. The curve is the theoretical variation calculated using equations (5) and (6) and the values of the parameters given in the text (section 4). The symbols represent the values of $\phi_{\text{c.r.}}$ for various temperatures assuming that the theoretical and experimental minima coincide. Δ : 150 °C, \circ : 160 °C, \square : 170 °C, $+$: 180 °C, \times : 190 °C, \boxtimes : 200 °C (A phase), \triangle : 200 °C (nematic phase), \bullet : 220 °C, \blacksquare : 230 °C. The arrow shows the direction in which the temperature increases.

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 $\sim 200^\circ\text{C}$ 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 $R_2 = |\Delta v_{\text{e.r.}}/\Delta v_{\text{dip}}|$. — The expression for $\Delta v_{\text{e.r.}}$ is similar to equation (6) with the index c.r. replaced by e.r. Putting $\phi_{\text{e.r.}} = \phi_{\text{c.r.}} + \alpha$ where

α represents the dihedral angle between the internal and external rings, we have :

$$\Delta v_{e.r.} = \frac{3}{2} c_{e.r.} S [P_2(\cos u_{e.r.}) P_2(\cos \varepsilon_{e.r.}) + \frac{3}{4} \sin^2 u_{e.r.} \sin^2 \varepsilon_{e.r.} \langle \cos 2 \varphi' \rangle \cos 2(\phi_{c.r.} + \alpha)]. \quad (7)$$

For the calculation of Δv_{dip} equation (4) also applies with the difference that (i) u_i and φ_i refer to the vector \mathbf{r}_{HD} rather than to the CD_i bond and (ii) $\frac{3}{2} c_i$ should be replaced by $K r_{HD}^3$ where $K = -\gamma_H \gamma_D h/2 \pi^2$. Since \mathbf{r}_{HD} is practically parallel to the para-axis of the ring, we have $u_i \simeq 0$. The second term in equation (4) drops and we have :

$$\Delta v_{dip} = \frac{K}{r_{HD}^3} S P_2(\cos \varepsilon_{e.r.}). \quad (8)$$

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 α . Theoretical curves calculated with $c_{e.r.} = 185$ kHz, $|K| = 36.89$ kHz. \AA^3 , $r_{HD} = 2.54$ \AA , $\langle \cos 2 \varphi' \rangle = 0.7$, $\varepsilon_{e.r.} = 7.9^\circ$ [7] and $u_{e.r.} = 59.25^\circ$, are shown in figure 4. It is seen that situations where α is large (say $60^\circ < \alpha < 90^\circ$) can explain the temperature dependence and the magnitude of the variation of R_2 . On the contrary situations where α is small (say $\alpha < 45^\circ$) are excluded by our model. Clearly, it is not possible to deduce the detailed temperature dependence of α , 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 $\alpha \sim 75^\circ$

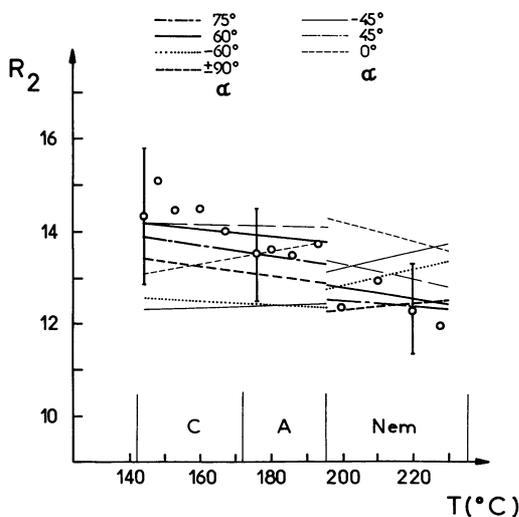


Fig. 4. — Ratio $R_2 = |\Delta v_{e.r.}/\Delta v_{dip}|$ versus temperature : \circ : experimental values deduced from figure 5 of reference [10]. They are also given in reference [11], p. 110. The lines are theoretical curves calculated from equations (7) and (8) using the values of the parameters given in the text (section 5) the values of $\phi_{c.r.}$ deduced from figures 2 and 3, for various values of α .

in the nematic phase. These values are indeed those which best fit the data of figure 4.

6. Ratio $R_3 = |\Delta v_1/\Delta v_{e.r.}|$. — 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

$$\phi_1 = \phi_{c.r.} + \alpha + \beta,$$

where β is the dihedral angle between the external ring and the chain in its trans-conformation :

$$\Delta v_1 = \frac{3}{2} c_1 S [P_2(\cos u_1) P_2(\cos \varepsilon_{e.r.}) + \frac{3}{4} \sin^2 u_1 \sin^2 \varepsilon_{e.r.} \langle \cos 2 \varphi' \rangle \cos 2(\phi_{c.r.} + \alpha + \beta) \cos 2 \phi_1]. \quad (9)$$

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 α are those deduced from the preceding analysis, we can calculate R_3 as a function of temperature for various values of β . Theoretical curves, calculated with $c_1 = 172$ kHz, $u_1 = 74.5^\circ$ [8], $|\varphi_1| = 114.28^\circ$ [8], $\varepsilon_{e.r.} = 7.9^\circ$ [7], $\langle \cos 2 \varphi' \rangle = 0.7$ for Δv_1 and the same values as in section 5 for $\Delta v_{e.r.}$ are shown in figure 5. It is seen that, in contradiction

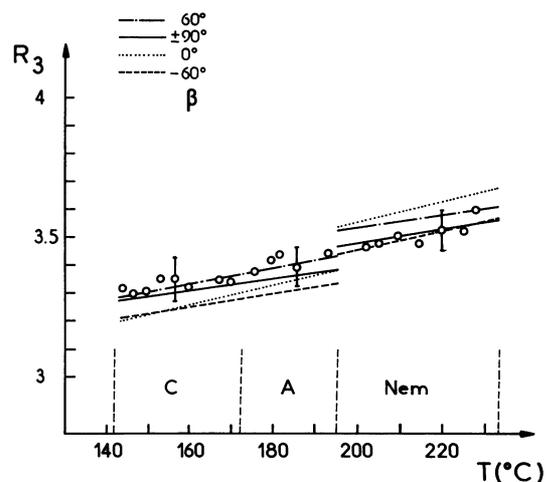


Fig. 5. — Ratio $R_3 = |\Delta v_1/\Delta v_{e.r.}|$ versus temperature : \circ : experimental points deduced partly from figure 5 of reference [10] and partly from data provided by Dr. Deloche. The lines are theoretical curves calculated from equations (9) and (7) using the values of the parameters given in the text (section 6), the values of $\phi_{c.r.}$ deduced from figures 2 and 3, α such that $\alpha = 60^\circ$ in C and A phases, $\alpha = 75^\circ$ in the nematic phase, for various values of β .

with the case of R_2 , all values of β 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 α is discontinuous at the SmA-Nem transition, then it is likely that β is also discontinuous at the same tran-

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 β , on the contrary it strongly depends on α . 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 β . Thus, it seems that the result α 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 (external ring in our notation) are about 20° , 47° and 43° in terephthal bis (4-aminofluorobenzène) [17], MBBA [18] and EBBA [19], respectively. For TBBA, 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 α between the internal and external rings. We have found that this angle is large and probably varies from ~ 60 to 75° 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° [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, α 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 $\phi_{c.r.}$. However, $\phi_{c.r.}$ 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 $\phi_{c.r.}$.

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, contrarily 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 $\Delta v_{met.}$, we simply used equation (12) of reference [7] with $v = (CD_{met.}, Oz_0) = v_{met.}$ For $\Delta v_{c.r.}$, equations (11a-d) of reference [7] have been averaged over $v = (CD_{c.r.}, Oz_0)$ 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 $d_{mm'}^2$. 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 Oz_0 , of the C_{2v} symmetry. In the framework of the model of reference [7] where rotation around Oz_0 and fluctuations of Oz_0 are independent, we have $S_{x_0x_0} - S_{y_0y_0} = (1 - S) \langle \cos 2\varphi \rangle$ [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 $\phi_{c.r.}$.

(i) $\langle \cos 2\varphi \rangle = \text{const.} = 0.005$ for all temperatures,

(ii) $\langle \cos 2\varphi \rangle$ 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 $\sim 7\%$ between 146° and 200 °C, the maximum variation being of the order of $\sim 1\%$ and is obtained for $\phi_{c,r} \sim 90^\circ$, within the somewhat unrealistic assumption that

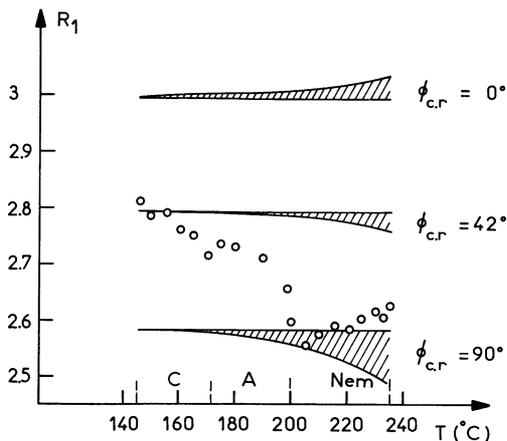


Fig. A1. — Ratio $R_1 = |\Delta v_{met}/\Delta v_{c,r}|$ versus temperature in the SmC, SmA and nematic phases of TBBA : \circ : same experimental points as in figure 2. The hatched regions delimit the possible theoretical values of R_1 due to the existence of a second order parameter and no change in the most probable conformation, for three values of $\phi_{c,r}$. (see text for details).

$\langle \cos 2\varphi \rangle$ is constant with temperature. Any decrease of $\langle \cos 2\varphi \rangle$ 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 $\sim 7\%$ is obtained assuming that $\langle \cos 2\varphi \rangle = \text{const.} = 0.04$, 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 η the asymmetry parameter, and $v = (\text{CD}_i, \text{Oz}_0)$ and λ the polar and azimuthal angles of the Oz_0 in the principal frame of the e.f.g. tensor, equation (1) should be rewritten in this case as [1] :

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

The value of η 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.

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