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Temperature Dependence of DMR Splittings in Nematic PAA: A Quantitative Interpretation in Terms of Changes in the Molecular Conformation—Comparison with Other Models*

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It is shown that the deuterium magnetic resonance data of Emsley *et al.* (Mol. Phys. **37**, 959 (1979)) on nematic PAA, can be quantitatively explained in terms of a single order parameter model which permits changes in the most probable conformation. The question of straight line plots of ratios of splittings introduced by Bos and Doane (Phys. Rev. Lett. **40**, 1030 (1978)) in the framework of a two order parameter model, is discussed in detail. In the case of PAA, it is shown that the single order parameter model also predicts such plots, and a simple geometrical interpretation of this result is given for this particular case. Comments on other approaches to the same data are also made.

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1 INTRODUCTION

In a previous paper,[1] two of us have proposed a model which explains quantitatively the relative temperature dependence of DMR splittings in the smectic C, smectic A and nematic phases of TBBA, and which is consistent with other data, in particular ^{14}N NQR data.[2,3] In this model, the molecules rotate practically uniformly around their long axis and in addition (i) the rigid fragments reorient around single covalent bonds and (ii) the most probable conformation changes with temperature. These changes correspond to changes in the mean dihedral angles between the various rigid fragments. They are possible because the internal potentials hindering the rotation around single bonds have rather shallow minima and the height of these potentials is of the same magnitude as the intermolecular forces existing in these fluid phases.[4,5] Thus, relatively small changes of these intermolecular forces may reasonably shift the position of the minima (i.e. change the mean dihedral angles) in such a way that they tend to the value in the gas phase, as the temperature raises, i.e. as the free volume per molecule increases.

The other two presently available models used to approach this problem are to assume that the most probable molecule does not change with temperature,[6,7] or that it changes in a very peculiar constrained manner,[8] and that the molecules do not rotate uniformly around their long axis, i.e. several order parameters (instead of only one in the previous model) are necessary to describe the complete molecular orientational order. The first of these latter models has been used to analyze DMR data in various systems,[7,9] but has never been proved independently in the corresponding cases. It turns out that in the very few cases where these other order parameters have been estimated directly[10,11] they have been found to be extremely small. In particular, they are too small to explain the observed effects in TBBA.[1] Thus, this interpretation in terms of several order parameters may be considered as questionable and it seems of interest to see if the above mentioned single order parameter model also gives reasonable quantitative results in another and more typical case. For this test we have chosen the very standard system nematic PAA, for which a complete and rather accurate set of DMR data is now available in the literature.[12–14] In Section 2, we detail the model and give the theoretical expression for the splittings. In Section 3, we analyze the DMR data of Ref. 14 in terms of this model and in Section 4 we discuss the meaning of the values found for the various parameters. In Section 5, we discuss the same data in terms of the two order parameter model and we consider the question of straight line ratio plots[7,8] for this particular case. Finally, we comment on the approaches used in the literature to interpret the same or similar data in PAA.

2 THE MODEL AND EXPRESSION OF THE SPLITTINGS

A scaled picture of the PAA molecule deduced from X-ray data in the solid phase[15] is shown in Figure 1. The two anizole fragments have been drawn coplanar for the sake of clarity. In reality, the dihedral angle α between them is 22.6°. It is interesting to note the distorted character of this molecule which is at variance with the more symmetric picture found usually in the literature [e.g. Ref. 13, 14]. The model we propose for the molecular motions in the nematic phase is the following:

We define the most probable molecule as the conformation such that all the dihedral angles between the various rigid fragments of the molecule linked between themselves by single covalent bonds correspond to minima of the potentials hindering the rotation around these bonds.[1] We associate a molecular frame $Ox_0y_0z_0$ to this most probable molecule with Oz_0 along the long axis. The main assumption of the model is that we can decompose the overall motion of a CD bond into internal motions, mainly rotations in the $Ox_0y_0z_0$ frame, and external motions, i.e. motions of the $Ox_0y_0z_0$ frame with respect to H_0. Moreover these motions are assumed to be not coupled. More specifically, these motions are, in the case of PAA:

i) reorientation of the methyl groups around their threefold axis. This rotation has been indeed found to be extremely rapid even in the solid phase, with a correlation time of $\sim 10^{-11}$ s.[16]

ii) each anizole fragment rotate around the N $-$ ϕ linkage and exchange between two equivalent planar conformations. We got evidence for such an exchange from a careful analysis of high resolution proton magnetic resonance on PAA with completely deuterated phenyl rings. This complex motion is

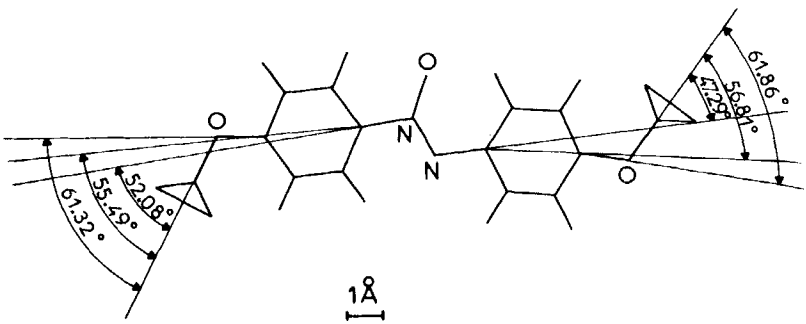

FIGURE 1 Scaled drawing of the PAA molecule in a planar conformation. The bond angles are those extracted from the structure in the solid phase.[15] The angles between the O—Methyl bond and the O—ϕ bond, the paraaxis of the ring and the N—ϕ bond are given explicitly for the anizole fragments A and B, that we cannot assign on the figure.

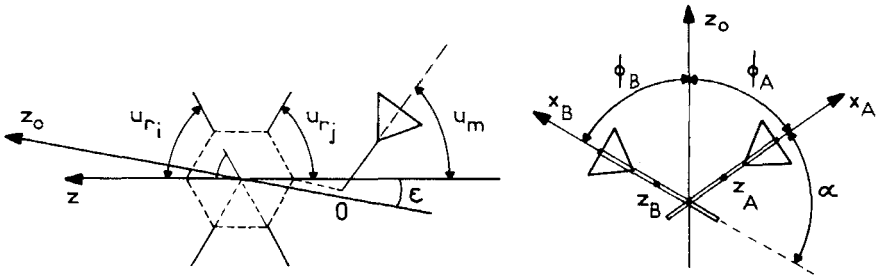

FIGURE 2 Sketch showing the definition of the various axes and angles which are useful in the calculation of the splittings. a) Lateral view of one anizole fragment, b) top view showing the most probable orientation of the two anizole fragments. Note that Oz is not an axis joining two particular atoms, but an effective rotation axis. The indexes $(i, j) = (1, 2)$ or $(2, 1)$. See the text for details.

conveniently pictured as a rotation of the phenyl ring and of the methoxy group around some common axis OZ which is between the N – ϕ and the O – ϕ bonds. However, Oz cannot be identified with one of these directions since they are not parallel, the deviation being of several degrees: 14.6° and 9.3°[15] for the two anizole fragments (cf. Figure 1). This point is important as we shall see below.

iii) the external motions are a uniform rotation around the Oz_0 axis and fluctuations of this axis about H_0.

Figure 2 pictures the angles which are useful in the calculation of the splittings. For each anizole fragment, we introduce two frames Oxyz attached one to the ring and the other to the methoxy group, with Oz along the common rotation axis and Ox in the plane of symmetry of the respective fragment. Then, we define two frames $Ox_m y_m z_m$ with $Oz_m \equiv Oz$ attached to the most probable orientation of each fragment in the most probable molecule. If we assume that the most probable conformation of the anizole moieties is the planar one, as seems to be the case in the liquid phase,[17,18] then a single $Ox_m y_m z_m$ frame is sufficient to define the most probable orientation of an anizole fragment. The angle $\varphi' = (Ox, Ox_m)$ describes the rotation of the rigid groups in the most probable molecule. This angle will be called φ'_r and φ'_m for the ring and the methoxy group, respectively. Finally, the polar and the azimuthal angles of the long molecular axis Oz_0, in the $Ox_m y_m z_m$ frame will be called ε and ϕ, respectively. Since there are two non equivalent anizole fragments in the PAA molecules, that we call A and B, all the parameters defined above will be indexed by the letter A and B, according to the case.

Each anizole fragment contains seven deuterons. Among them, the three methyl deuterons are magnetically equivalent due to the methyl rotation.

On the other hand, the ring rotation around the Oz axis renders equivalent the two deuterons which exchange during this motion, i.e. those which are, roughly speaking, symmetric with respect to Oz. Thus in the most general case, the model predicts at most three quadrupolar doublets whose intensities are in the ratio 2, 2, 3. If the ring is more symmetric, then the four deuterons are equivalent and we have only two doublets whose intensities are in the ratio 4 to 3. If we call u_{r_1} and u_{r_2} the angles between the corresponding ring CD bonds and Oz ($u < 90°$), the first situation is obtained with $u_{r_1} \neq u_{r_2}$ and the second one with $u_{r_1} = u_{r_2}$. Finally, we call u_m the angle between the O—C bond of the methoxy group and Oz.

With these ingredients, the expression of the splittings is readily calculated taking into account that the internal rotations necessarily occur in potentials $V(\varphi')$ which have C_{2v} symmetry: this is the symmetry imposed by the ring. Details of the calculation can be found in Ref. 1 and the result is, for anizole fragment A

$$\Delta\nu^A_{r_1} = \tfrac{3}{2}C^A_{r_1}S[P_2(\cos u^A_{r_1})P_2(\cos\varepsilon_A) + \tfrac{3}{4}\sin^2 u^A_{r_1}\sin^2\varepsilon_A\langle\cos 2\varphi'^A_r\rangle\cos 2\phi_A] \quad (1A)$$

$$\Delta\nu^A_{r_2} = \tfrac{3}{2}C^A_{r_2}S[P_2(\cos u^A_{r_2})P_2(\cos\varepsilon_A) + \tfrac{3}{4}\sin^2 u^A_{r_2}\sin^2\varepsilon_A\langle\cos 2\varphi'^A_r\rangle\cos 2\phi_A] \quad (2A)$$

$$\Delta\nu_m = -\tfrac{1}{3}\tfrac{3}{2}C^A_m S[P_2(\cos u^A_m)P_2(\cos\varepsilon_A) + \tfrac{3}{4}\sin^2 u^A_m\sin^2\varepsilon_A\langle\cos 2\varphi'^A_m\rangle\cos 2\phi_A] \quad (3A)$$

For anizole fragment B, we have exactly the same equations which we label (1B), (2B), (3B) where the index A has been replaced by B. In these equations, the e.f.g. tensor acting on the deuterons is assumed to have cylindrical symmetry around the CD bonds. The c's are the corresponding quadrupolar coupling constants, and $S = S_{z_0z_0}$ is the nematic order parameter. The factor $-\frac{1}{3} \equiv P_2[\cos(109.47°)]$ in Eqs. (3A) and (3B) comes from the partial averaging of the e.f.g. tensor acting on the methyl deuterons, due to the rotation around the threefold axis (109.47° is the tetrahedral angle).

These equations contain three kinds of quantities. The structural quantities C_i and u_i are expected to be independent of temperature. The conformational quantities ε and ϕ can vary with temperature since we permit changes in the most probable conformation. However, since these changes only concern the mean dihedral angles between rigid fragments, only ϕ is expected to vary significantly. Finally, among the dynamical quantities S and $\langle\cos 2\varphi'\rangle$, only S is expected to vary significantly with temperature (cf. the discussion in Ref. 1)].

Thus the model contains 8 constant parameters (six u and two ε) and three

temperature dependent parameters S, T_A, T_B where $T = \langle \cos 2\varphi' \rangle \cos 2\phi$ (we assume for simplicity that $\langle \cos 2\varphi'_r \rangle = \langle \cos 2\varphi'_m \rangle$). The experimental data in Table 1 of Ref. 14 correspond to six quadrupolar splittings for 12 temperatures plus one dipole-dipole splitting for 9 temperatures. Thus, there are $8 + 12 \times 3 = 44$ parameters to be determined by $6 \times 12 + 9 = 81$ pieces of data. This is a priori sufficient to test the proposed model. If the calculated splittings using the values found for the parameters are the same as the experimental one within experimental accuracy, we still have to see if the values found for the parameters are reasonable.

3 ANALYSIS

Before any fit can be made we have to consider two problems: The first problem concerns the assignment, i.e. which splitting corresponds to which deuteron, and the second problem concerns the sign of the $\Delta\nu_i$, since Eqs. (1A)–(3B) are algebraical expressions while the experiment gives only $|\Delta\nu|$'s. For the sake of clarity, we have reproduced in Figure 3 one DMR spectrum of completely deuterated PAA (Figure 1 of Ref. 14). It exhibits six quadrupolar doublets, two of them being superimposed. We have labelled the corresponding splittings $\Delta\nu_1$ to $\Delta\nu_6$ according to Table 1 of Ref. 14. For intensity reasons, it is clear that $\Delta\nu_1$, $\Delta\nu_2$, $\Delta\nu_4$, $\Delta\nu_5$ correspond to phenyl deuterons and $\Delta\nu_3$, $\Delta\nu_6$ correspond to methyl deuterons. The problem is to know how to share these splittings between fragments A and B. One hint may be given by the observation that some doublets are split in three well resolved lines due to dipole-dipole interaction between adjacent deuterons of the rings.[14] This is

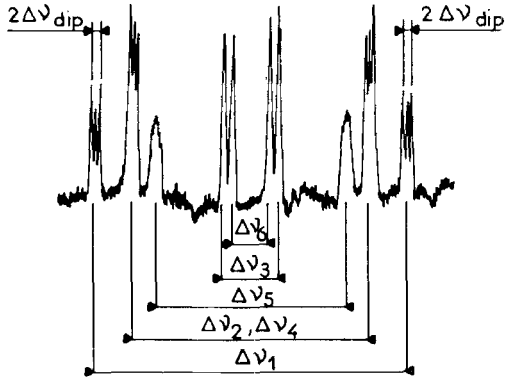

FIGURE 3 Example of DMR spectrum of completely deuterated PAA in the nematic phase (extracted from Ref. 14) showing the definition of the various splittings used in the text. This definition is the same as in Ref. 14.

TABLE I

Definition of the various assignments of the DMR doublets. Assignment 3 has been used in Refs. [12–14].

	Ass. 1	Ass. 2	Ass. 3
$\lvert\Delta\nu_{r_1}^A\rvert$	$\Delta\nu_1$	$\Delta\nu_1$	$\Delta\nu_1$
$\lvert\Delta\nu_{r_2}^A\rvert$	$\Delta\nu_5$	$\Delta\nu_5$	$\Delta\nu_2$
$\lvert\Delta\nu_m^A\rvert$	$\Delta\nu_3$	$\Delta\nu_6$	$\Delta\nu_3$
$\lvert\Delta\nu_{r_1}^B\rvert$	$\Delta\nu_2$	$\Delta\nu_2$	$\Delta\nu_4 = \Delta\nu_2$
$\lvert\Delta\nu_{r_2}^B\rvert$	$\Delta\nu_4 = \Delta\nu_2$	$\Delta\nu_4 = \Delta\nu_2$	$\Delta\nu_5$
$\lvert\Delta\nu_m^B\rvert$	$\Delta\nu_6$	$\Delta\nu_3$	$\Delta\nu_6$

the case for the doublet which is twice degenerated. The fact that the triplet is well resolved in this case strongly suggests that the two corresponding deuterons belong to the same ring. This means that for one of the two rings, the four deuterons are equivalent. Such situation also occurs for the rings in TBBA.[19,1] This assumption permits a complete assignment of the ring doublets but the uncertainty remains for the methoxy deuterons. This defines two first possible assignments for fragments *A* and *B*. A third different assignment for the ring deuterons has been considered in the previous works[12–14] namely the three largest splittings and the three smallest splittings have been associated. The idea here is that the two anizole fragments are roughly the same, but are not inclined of the same angle on the long molecular axis. We summarize these three possible assignments in Table I.

The second problem concerns the sign of the splittings. Assuming that the c's are positive, it is clear that the $\Delta\nu_r$ are always negative, since the u_r are $\sim 60°$, i.e. significantly larger than the magic angle 54.74°. On the contrary, the situation is less clear for the methyl deuterons where u_m is expected to be very near this magic angle. So, we have tried the two possible signs for $\Delta\nu_m$ in the analysis and it turned rapidly out that only the possibility where the $\Delta\nu_m$ are negative lead to reasonable results. Thus we have assumed this sign. This will be justified a posteriori in the discussion.

The fitting procedure which we have adopted is a least square fit, where we have used the $6 \times 12 = 72$ quadrupolar splittings to determine the 44 parameters. An indication of the quality of the fit is given by the quantity δ_{fit} defined as:

$$\delta_{\text{fit}} = \left[\frac{1}{72}\sum_{i=1}^{72}(\Delta\nu_{\text{cal}} - \Delta\nu_{\text{exp}})^2\right]^{1/2}$$

where the $\Delta\nu_{\text{cal}}$ are the theoretical splittings calculated using the fitted values

of the parameters in Eq. (1A) to (3B). The index i runs over the six splittings and the twelve temperatures. This value of δ_{fit} should be compared to the experimental uncertainty $|\delta_{\text{exp}}|$. In Table I of Ref. 14, it is claimed that $\delta_{\text{exp}} = \pm 20$ Hz. However, looking at the numbers in this Table, it seems that this value is underestimated and indeed the error bars in Figures 4 and 5 of the same reference indicate that $|\delta_{\text{exp}}|$ is 2 to 3 times larger. Thus, an average $|\delta_{\text{exp}}| \sim 40$–$60$ Hz seems to be more reasonable. The fit yields $\delta^1_{\text{fit}} \approx 35$ Hz, $\delta^2_{\text{fit}} \approx 110$ Hz and $\delta^3_{\text{fit}} \approx 51$ Hz for assignments 1, 2 and 3 respectively. Consequently, at this level, only assignment 2 can be rejected. Concerning the values of the parameters themselves, it turns out that the fit is mainly sensitive to the temperature variation of S, T_A and T_B, but little to the absolute value of these quantities. Changing slightly the values of the angles u and ε shift the absolute values of S and T still keeping the same value of δ_{fit}, within less than 1 Hz.

To remove the uncertainty on S, we have used the values of the dipole-dipole splittings $|\Delta\nu_{\text{dip}}|$. The calculation is as follows: since $\mathbf{r}_{\text{DD}}$ in a ring is practically parallel to Oz, it is easy to show that we have

$$|\Delta\nu_{\text{dip}}| = \frac{h\gamma_{\text{D}}^2}{2\pi^2 r_{\text{DD}}^3} P_2(\cos\varepsilon_A) S \tag{4a}$$

The result strongly depends on the value of r_{DD}. With $r_{DD} = 2.487$ Å, $h\gamma_D^2/2\pi^2 = 5663$ Hz × Å^3 and $\varepsilon_A = 11.54°$ (cf. Section 4), Eq. (4a) becomes

$$|\Delta\nu_{\text{dip}}| = 346 \times S \tag{4b}$$

This equation has been used to scale the absolute values of S.

The temperature dependence of T_A and T_B is well determined by the model—in particular, both are found to increase with temperature—but, as for S, there is some uncertainty on the absolute values. If $\langle\cos 2\varphi'\rangle$ is known, T_A and T_B yield ϕ_A and ϕ_B. This allows us to estimate the dihedral angle α between the two anizole fragments through the relation (cf. Figure 2)

$$\alpha \approx 180 - |\phi_A| - |\phi_B|$$

where we use the symbol $\approx$ because the two internal rotation axes $\text{Oz}_{A,B}$ may not be strictly parallel. This angle α is probably never smaller than 22.6°, the value in the solid phase.[15] Using $\langle\cos 2\varphi'\rangle = 0.7$,[1] we have removed the above mentioned uncertainty assuming that at low temperature, α is larger but relatively near 22.6°, and that $\varepsilon_A \approx \varepsilon_B$. With these additional (weak) constraints the fit of the model is practically univocal. In the next section we give the results for assignment 1, keeping in mind that the results for assignment 3 are very similar. The preference for assignment 1 comes mainly from the fact that the fit is significantly better: $\delta^1_{\text{fit}} \approx 35$ Hz compared to $\delta^3_{\text{fit}} \approx 51$ Hz.

4 RESULTS AND DISCUSSION

Values of the angles u and ε which give a satisfactory fit for assignment 1 are:

$$u_{r_1}^A = 58.40^\circ \quad u_{r_2}^A = 56.68^\circ \quad u_m^A = 52.01^\circ \quad \varepsilon_A = 11.54^\circ$$

$$u_{r_1}^B = 57.39^\circ \quad u_{r_2}^B = 57.39^\circ \quad u_m^B = 52.75^\circ \quad \varepsilon_B = 11.54^\circ$$

The corresponding values of the temperature dependent parameters S, T_A and T_B are shown in Figures 4 and 5. The quality of the fit is shown in Table II where we give the calculated and experimental splittings. It corresponds to $\delta_{\text{fit}} = 34.7$ Hz. A more suggestive indication of this quality is given by the temperature dependence of ratios of splittings. As examples, we show in Figures 6a, b the results for $\Delta\nu_3/\Delta\nu_1$ and $\Delta\nu_5/\Delta\nu_4$ which exhibit different temperature dependences. It is seen that the model predicts the correct variation within experimental accuracy.

TABLE II

Values of $\Delta\nu_{\text{exp}}$ and $\Delta\nu_{\text{cal}}$ for the single order parameter model with assignment 1, using c_r = 185 kHz, c_m = 172 kHz. The value of δ_{fit} defined in Section 3 is 34.7 Hz. The values of $\Delta\nu_{\text{exp}}$ are taken from Table 1 of Ref. 14.

$\Delta\nu_{1\,\text{exp}}$	$\Delta\nu_{1\,\text{cal}}$	$\Delta\nu_{5\,\text{exp}}$	$\Delta\nu_{5\,\text{cal}}$	$\Delta\nu_{3\,\text{exp}}$	$\Delta\nu_{3\,\text{cal}}$
18132.0	18091.9	10728.0	10778.3	3076.0	3107.6
17532.0	17498.1	10377.0	10416.6	2999.0	3015.1
16860.0	16866.7	9980.0	9969.9	3002.0	2990.7
16134.0	16111.5	9380.0	9403.0	3002.0	3000.4
16134.0	16079.4	9329.0	9388.7	2978.0	2989.1
16136.0	16194.6	9630.0	9568.9	2877.0	2876.0
15284.0	15332.6	9029.0	8966.6	2877.0	2833.7
14732.0	14795.1	8727.0	8645.4	2801.0	2742.5
13935.0	13978.6	8180.0	8125.0	2678.0	2642.8
12459.0	12450.1	7032.0	7053.8	2526.0	2571.5
11181.0	11189.2	6227.0	6214.0	2477.0	2460.5
10208.0	10136.3	5429.0	5524.6	2277.0	2353.7
$\Delta\nu_{2\,\text{exp}}$	$\Delta\nu_{2\,\text{cal}}$	$\Delta\nu_{4\,\text{exp}}$	$\Delta\nu_{4\,\text{cal}}$	$\Delta\nu_{6\,\text{exp}}$	$\Delta\nu_{6\,\text{cal}}$
13728.0	13728.6	13728.0	13728.6	2078.0	2082.7
13229.0	13230.9	13229.0	13230.9	2021.0	2034.4
12656.0	12655.8	12656.0	12655.8	2052.0	2050.8
12032.0	12035.9	12032.0	12035.9	2052.0	2080.5
11981.0	11988.2	11981.0	11988.2	2027.0	2079.0
12233.0	12222.7	12233.0	12222.7	2027.0	1952.7
11355.0	11353.4	11355.0	11353.4	2003.0	1991.7
10929.0	10927.0	10929.0	10927.0	1950.0	1935.8
10332.0	10330.4	10332.0	10330.4	1877.0	1865.6
9383.0	9379.1	9383.0	9379.1	1802.0	1774.1
8178.0	8181.1	8178.0	8181.1	1752.0	1774.3
7506.0	7508.9	7506.0	7508.9	1652.0	1673.1

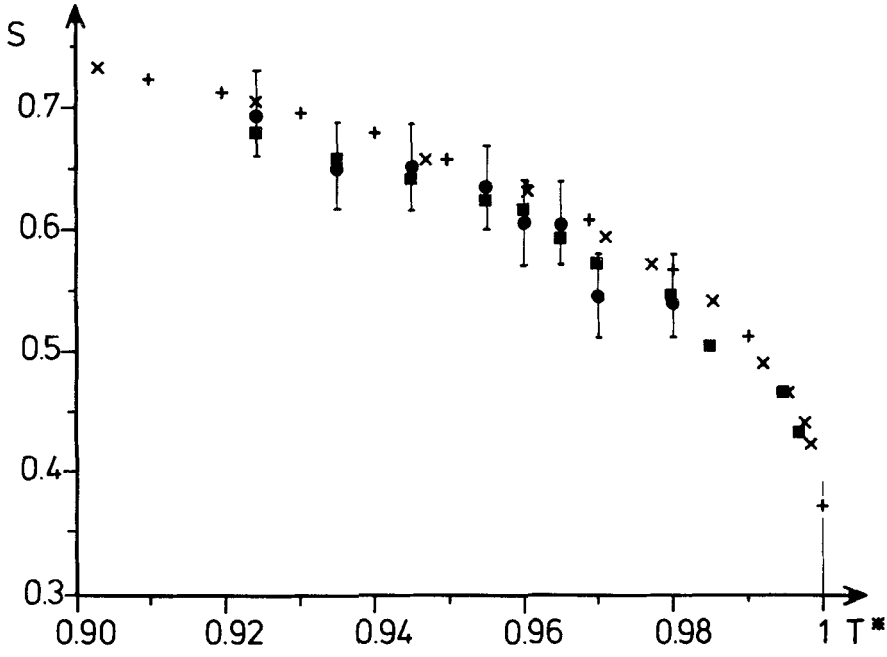

FIGURE 4 Nematic order parameter S versus reduced temperature T^* obtained from the fit of the single order parameter model, assuming assignment 1: ■ from the fit: ● from $|\Delta\nu_{dip}|$ with $r_{DD} = 2.487$ Å. The error bar correspond to an uncertainty on $\Delta\nu_{dip}$ of ± 12 Hz; + and × represent the values of S deduced from ^{13}C NMR measurements[20] and optical measurements[21] respectively. The points are reproduced from Figure (5a) of Ref. 21.

We now discuss the values of the parameters themselves.

i) The values of ε_A and ε_B are of the order of 11.5° and the u_r are smaller than 60° by less than 3.5°. These results are similar to those found in previous works[12–14] and will not be discussed further here. However, it is interesting to note that the u_r are all practically equal within $\pm 1°$.

ii) The values of u_m, which both are found to be *smaller* than the magic angle, give a rather precise information on where the effective internal rotation axes Oz are. If we consider the values of the bond angles in the solid phase, the found values of u_m mean that the effective internal rotation axes Oz are intermediate between the para-axis of the ring and the N—ϕ bond of the anizole fragments (cf. Figure 1). This is the place where we expect them reasonably to be, given the distorted structure of the PAA molecule and the nature of the motions. This has an important consequence in the analysis since it justifies that the two $\Delta\nu_m$ are negative.

iii) The values of S are found to decrease from ~ 0.7 to ~ 0.4 at the nematic

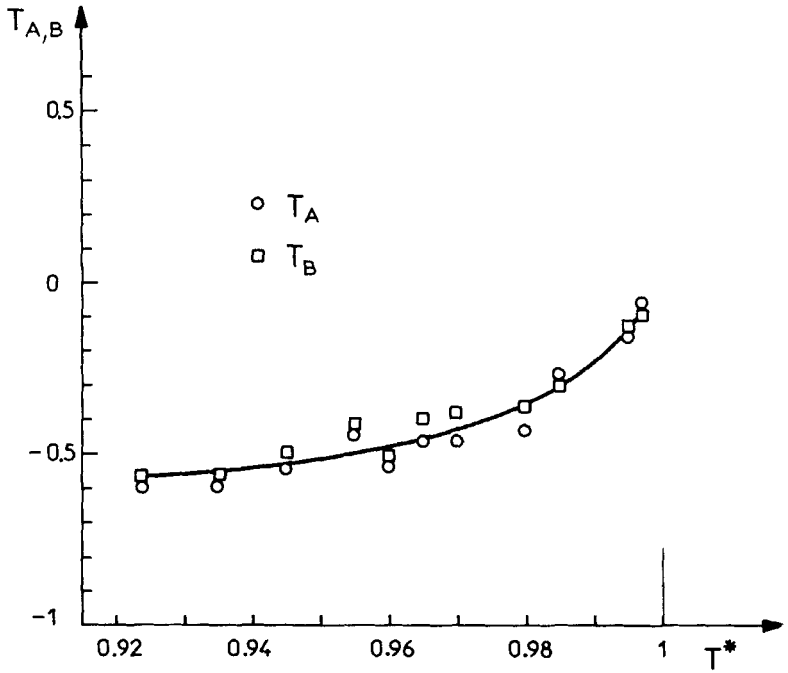

FIGURE 5 Parameters T_A and T_B versus reduced temperature T^* obtained from the fit of the single order parameter model assuming assignment 1. The line is a guide to the eye. See text for details.

isotropic transition, as expected. It is remarkable to observe that the temperature dependence of S is not only well consistent with the variation of $|\Delta\nu_{dip}|$, but also with the variation of S obtained by two completely different methods, namely from ^{13}C NMR measurements[20] and from refractive indices and optical anisotropy measurements.[21] The fact that our fitted values are systematically slightly smaller than the other ones is not a serious problem since as in our case, there is also some uncertainty in the determination of absolute values of S by the other methods. The optical values and ^{13}C NMR values fall on the same average curve only because the former values have been scaled using the latter ones.[21]

iv) Finally, the most important test of the model is given by the variation of ϕ_A and ϕ_B and consequently on $\alpha = \pi - |\phi_A| - |\phi_B|$. By drawing smooth curves through the points in Figure 4 and assuming $\langle \cos 2\varphi' \rangle = 0.7$,[1] we find that α varies from $\sim 37°$ to $\sim 82°$ throughout the nematic phase. This corresponds to an overall variation of $\sim 45°$. To understand such a relatively large variation of α, we make the following points:

a) α is *not* the angle between two adjacent rigid fragments but between

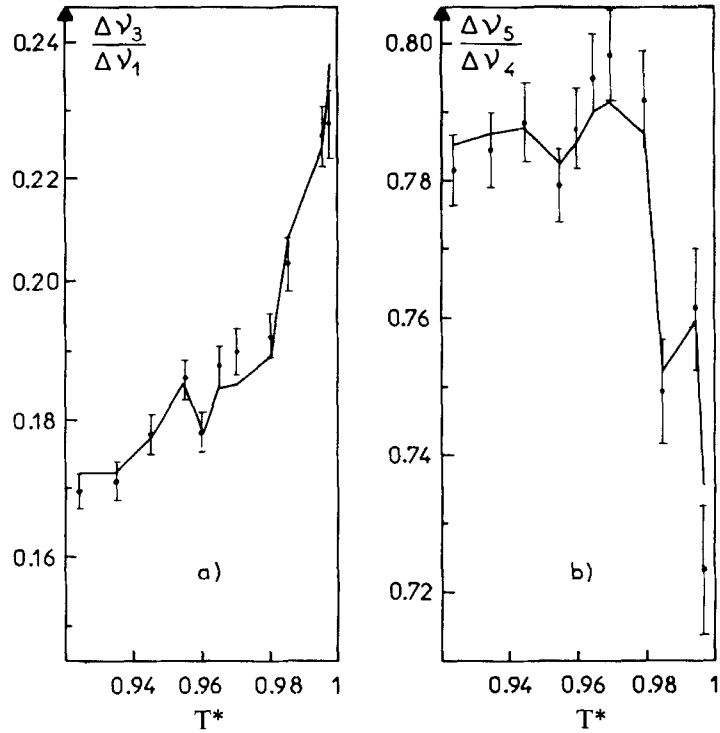

FIGURE 6 Ratios of quadrupolar splittings $\Delta\nu_3/\Delta\nu_1$ and $\Delta\nu_5/\Delta\nu_4$ as a function of reduced temperature. The error bars correspond to $\delta_{exp} = \pm 40$ Hz. The continuous lines are the values predicted by the single order parameter model assuming assignment 1.

two fragments linked by covalent bonds to the azoxy group. Since this group is very similar to an azomethine group, we expect that the potentials around the N—ϕ bonds have shallow minima.[1,4] Moreover the overall variation of α is shared between the variations of the dihedral angles between the azoxy group and the two anizole fragments.

b) The variation of α is as expected, i.e. the conformation tends to that of the isolated molecule. Steric considerations and structural similarity between the azoxy group of PAA and the azomethine group of TBBA indeed suggest that for the isolated molecule, α should be large, $\sim 90°$.[4] But, this point as well as point (a) deserves a direct confirmation from chemical theoretical calculations.

c) More instructive is the variation of ϕ_A and ϕ_B. The fact that we have $|\phi_A| \approx |\phi_B|$ means that they vary in such a way that the long axis Oz_0 is always, roughly speaking, in the bisector plane of the two anizole fragments. This is to be expected if we think of Oz_0 as a principal inertial axis of a nearly symmetric molecule (cf. Figure 2).

d) Finally, it should be noticed that $\Delta\alpha \approx 45°$ is the maximum possible variation of α since in the model, the overall relative temperature dependence of the splittings have been put in the parameters $\phi_{A,B}$ for the sake of simplicity. Any slight temperature dependence of other parameters, e.g. ε and (or) the choice of a larger value for $\langle \cos 2\varphi' \rangle$, would have reduced the overall variation of $\phi_{A,B}$ and consequently of α.

In conclusion to this section, it seems that this model explains reasonably well the relative temperature dependence of DMR splittings in nematic PAA since not only the fit is satisfactory, but also the values and temperature dependences of the parameters are as expected. We now consider the other extreme model of Refs. 6, 7 in terms of two order parameters.

5 ANALYSIS IN TERMS OF TWO ORDER PARAMETERS AND THE QUESTION OF STRAIGHT LINE RATIO PLOTS

If the most probable conformation does not change with temperature, but two order parameters $S_{z_0 z_0} = S$ and $S_{x_0 x_0} - S_{y_0 y_0} = \delta$ are needed to describe completely the molecular orientational order, the DMR splitting $\Delta\nu_i$ corresponding to deuteron i writes[6]

$$\Delta\nu_i = a_i S + b_i \delta \tag{5}$$

where a_i and b_i are constants which only depend on the molecular conformation. Eq. (5) tells us that if we consider any three independent splittings $\Delta\nu_i$, $\Delta\nu_j$, $\Delta\nu_k$, a plot $|\Delta\nu_i/\Delta\nu_k|$ versus $|\Delta\nu_j/\Delta\nu_k|$ should be a straight line:[7]

$$|\Delta\nu_i/\Delta\nu_k| = f\,|\Delta\nu_j/\Delta\nu_k| + g \tag{6}$$

where f and g are conformational constants which depend on $a_{i,j,k}$, $b_{i,j,k}$ and on the relative signs of the $\Delta\nu_{i,j,k}$. Thus, the straight line condition is a necessary condition for the model to be valid. The problem is to know if this is sufficient. The answer is no and we show below that the single order parameter model developed above also predict straight line ratio plots.

Consider Eqs. (1A) to (3A) or (1B) to (3B). Assuming for simplicity that $\langle \cos 2\varphi'_r \rangle = \langle \cos 2\varphi'_m \rangle$ as in the text, we can eliminate S and $\langle \cos 2\varphi' \rangle \times \cos 2\phi$ between these three equations. The result is,

$$\frac{\Delta\nu_{r_1}}{\Delta\nu_m} = p\,\frac{\Delta\nu_{r_1}}{\Delta\nu_m} + 3\left(\frac{c_{r_2}}{c_m}\,p - \frac{c_{r_1}}{c_m}\right) \tag{7}$$

where

$$p = \frac{\sin^2 u_{r_1} - \sin^2 u_m}{\sin^2 u_{r_2} - \sin^2 u_m} \tag{8}$$

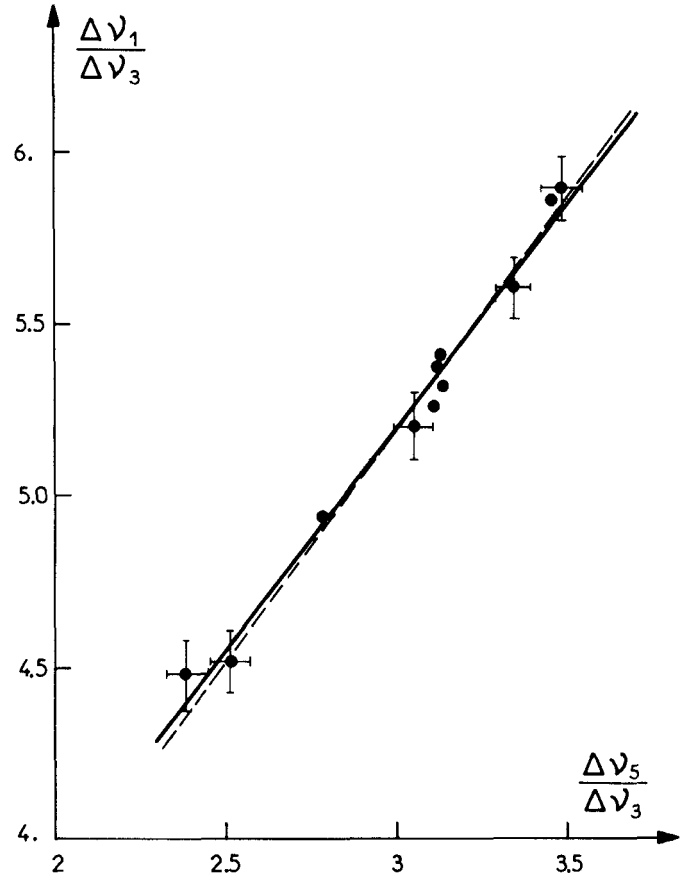

FIGURE 7 Ratio plot $\Delta\nu_1/\Delta\nu_3$ versus $\Delta\nu_5/\Delta\nu_3$. The error bars correspond to $\delta_{exp} = \pm 40$ Hz. The full line is the best-fitted two parameter straight line Eq. (6), predicted by the two order parameter model. The dashed line is the best fitted single parameter model, Eq. (7) with c_r = 185 kHz and c_m = 172 kHz, predicted by the single order parameter model with assignment 1.

Since all the $\Delta\nu$ are negative, Eq. (7) also holds for the moduli $|\Delta\nu|$. It is seen that, for three deuterons attached to the same fragments, our model also predicts a straight line. However, because $c_{r_2}/c_m \approx c_{r_1}/c_m \approx 1$, this line depends practically on the *single parameter p*, instead of the *two parameters* f and g in the two order parameter model. We have considered assignment 1. For fragment B, Eq. (7) is automatically verified since $\Delta\nu^B_{r_1} = \Delta\nu^B_{r_2}$. For fragment A, we have drawn in Figure 7 the ratio plot $\Delta\nu_1/\Delta\nu_3$ versus $\Delta\nu_5/\Delta\nu_3$ and it is seen that the points fall indeed on a straight line within experimental accuracy. We have also shown on the figure the best fitted two parameter straight line Eq. (6) and the best fitted single parameter straight line Eq. (7).

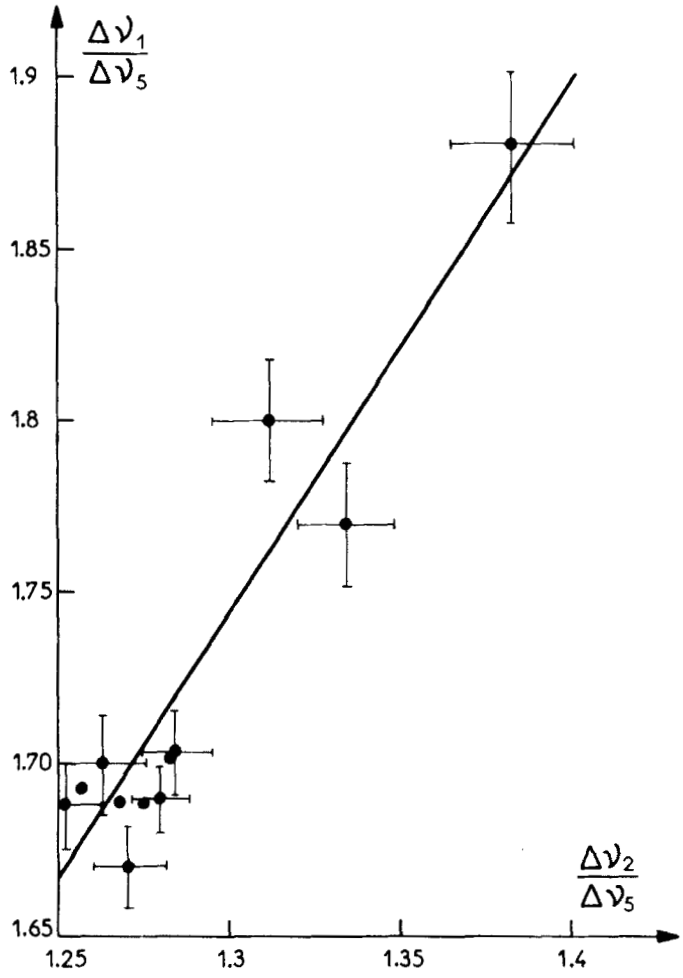

FIGURE 8 Ratio plot $\Delta\nu_1/\Delta\nu_5$ versus $\Delta\nu_2/\Delta\nu_5$. The error bars correspond to $\delta_{exp} = \pm 40$ Hz. The full line is the best fitted straight line Eq. (6), predicted by the two order parameter model.

In this latter case, the best fitted value of p is 1.3517. The value of p calculated from Eq. (8) using the best fitted values of the angles u is 1.3524.

What about ratio plots which combine splittings associated with fragments A and B? We have drawn two such plots in Figures 8 and 9. It is seen that the dispersion of the points is significantly greater than for the previous case, but that they can be considered roughly aligned if the uncertainty on the corresponding splittings is taken to be ~ 60 Hz. This result seems to support the two order parameter model. However, for the single order parameter

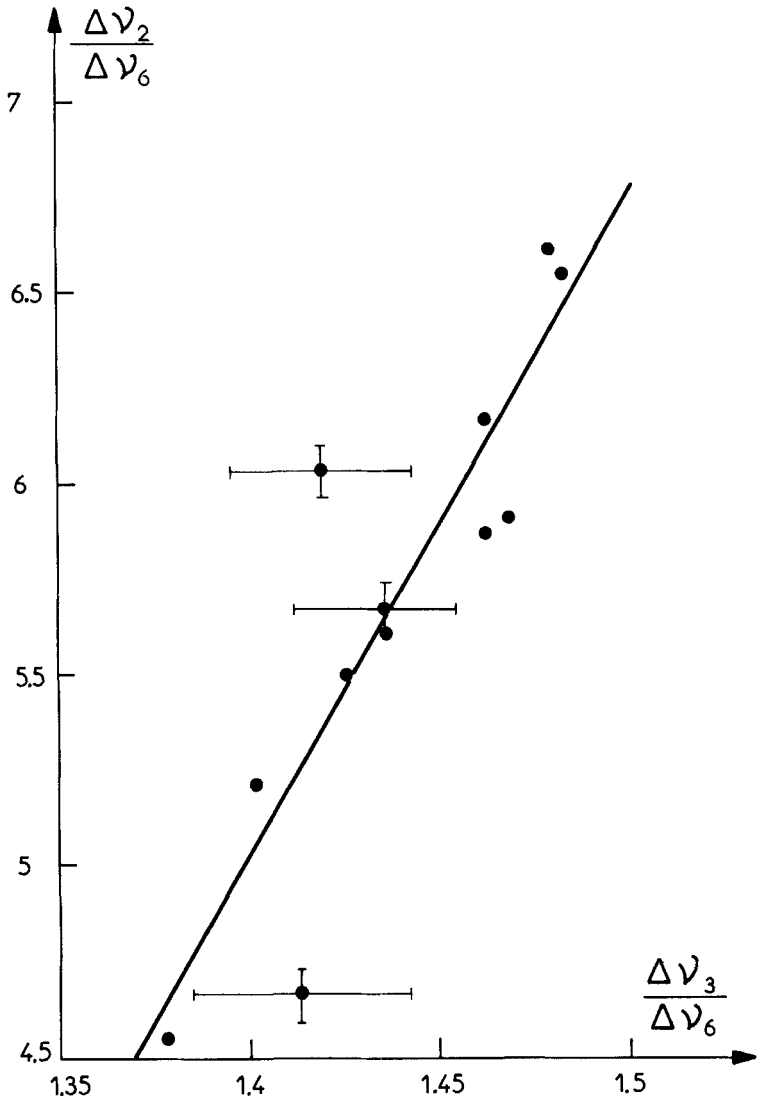

FIGURE 9 Idem as Figure 8, for the ratio plot $\Delta\nu_2/\Delta\nu_6$ versus $\Delta\nu_3/\Delta\nu_6$.

model, we have found that we always have $T_A \approx T_B$ (cf. Figure 5). It is easily seen from Eq. (1A) to (3B) that in this case, this model also predicts straight lines, but the alignment is not so good since we do not have exactly $T_A \equiv T_B$. In this case, the two extreme models, single order parameter plus conformational changes, and two order parameters but no conformational changes,

predict the same straight line ratio plots, so that this single result cannot be used to prove one or the other model.

It is interesting to discuss which physics are underlined in these straight lines. In the two order parameter model, it means either that the conformation does not change at all with temperature, i.e. a_i and b_i are constant[6,7] or that the conformational constants a_i and b_i in Eq. (6) vary in a constrained manner in such a way that f and g are constant.[8] In the single order parameter model developed in this paper for PAA, the finding of straight lines means either that the three deuterons under investigation belong to the same anizole fragment or if the three deuterons belong to different anizole fragments, that the orientation of the long axis Oz_0 with respect to these fragments vary with temperature in such a way that $T_A \approx T_B$. In the present case, this constraint means that the long molecular axis always lies, roughly speaking, in the bisector plane of the two anizole fragments, as expected for the main principal inertial axis of the molecule. It should be noted that the fact that the two extreme models discussed above lead to very similar intermediate results (the straight line plots) comes from similarity of the structure of the equations giving the splittings in both cases. But the physical meaning of the deduced parameters is different. For the single order parameter model, we have made the analysis completely. For the two order parameter model, we have only shown that the data are not inconsistent with it. This is not sufficient: it is necessary in addition to see if reasonable values of the parameters of the model give a reasonable fit. This was not the aim of this paper, but this point will be commented further in the next section.

6 COMMENTS ON PREVIOUS ANALYSIS OF SIMILAR DATA

In Ref. 13, DMR data concerning the ring deuterons only were produced for several temperatures and analyzed in terms of a model combining the above two models, i.e. the angle between the rings was permitted to change with temperature and the second order parameter δ was assumed to be non zero. In view of the analysis presented in this paper, it is not surprising that such a model could fit the data. However, it is interesting to note the same finding as ours, namely, that the dihedral angle between the two anizole fragments increases as the temperature increases. In Ref. 12 and 14, the analysis is approached in a rather different manner, i.e. the authors do not use the concept of molecular frame $Ox_0y_0z_0$, but only consider frames attached to molecular fragments, namely the two anizole fragments. In this kind of approach, the problem that one immediately faces with non rigid molecules is how to take into account the internal motions—characteristic time τ_i—in the calculation of the DMR splittings. These internal motions are usually

pictured as exchange between various conformations by rotation around single covalent bonds. Thus, the liquid crystal is pictured as a mixture of various molecules corresponding to the various conformations. Two extreme cases are considered, namely the internal motions are rapid, or slow, as compared to the external motions–characteristic time τ_e.

If $\tau_i \ll \tau_e$ then it can be shown that one can define an average molecule[14] that we may, at least formally, identify to the most probable molecule introduced above, and the formalism is very similar to the one used in the models described in this paper. In Ref. 14, an attempt to describe the DMR data on PAA in terms of this model has been made and it has been found that this is not possible. In terms of the two order parameter model described in Section 5, because the formal identity of the equations, this result only means that the data cannot be explained by Eq. (5) where a_i and b_i are constant. However, this does not *a priori* exclude an explanation where f and g in Eq. (6) are constant.

The other extreme case which has been considered in Ref. 14 is the one where $\tau_i \gg \tau_e$. In this case, each molecule in a given conformation should be considered as a rigid object (on the time scale τ_e) which has different order parameters. With the (relatively weak) assumption that the e.f.g. tensors acting on the deuterons are independent of the conformation, it is then possible to speak of average order parameters rather than of order parameters of an average molecule as in the previous case.[14] It is shown in Ref. 14 that this hypothesis is not in contradiction with the data. However, no conclusion can be extracted concerning the symmetry (cylindrical or not cylindrical) of the principal form of the average ordering matrices attached to the two anizole fragments. It should be noticed that all the analysis of Ref. 14 seems to exclude the possibility that the principal axes of the ordering matrices change with temperature. This is revealed by the fact that K_i in Eq. (22) of Ref. 14 is assumed to be constant. This means that the kind of model such as that developed in this paper has been discarded.

It is interesting to discuss the merits of the various approaches. Clearly, the assumption of the existence of the more or less fictitious molecular frame plus decoupling of internal and external motions seems rather strong. However, it has the merit of leading to analyses with a relatively reduced number of parameters and so far, there is no known example where this concept turned out to be inadequate. The problem of choosing between the two extreme models in PAA has not been completely solved in this paper, although it seems established that the hypothesis where the most probable molecule does not change with temperature can be excluded, and that the single order parameter model satisfactorily fits the data. Analysis which do not use the concept of molecular frame $Ox_0y_0z_0$[12,14] has the merit to be *a priori* more general. However, assumptions have to be made concerning the relative time

scales of the motions, and the situation $\tau_i \sim \tau_e$ cannot easily be handled. Moreover, the number of parameters which must be introduced in the analysis is larger than in the other approach: the analysis of Ref. 14 used six S values compared to our analysis in terms of one S and two T.

7 CONCLUSION

In conclusion, we have found with PAA a second example, other than TBBA[1], where a single order parameter model can explain quantitatively the relative temperature dependence of DMR splittings in liquid crystals, if the most probable molecule is allowed to change with temperature. Again, as for TBBA, we cannot claim that this model is definitely established, but it seems to us that the present analysis is an additional support for it. Moreover, in the particular case of PAA, we have found a simple geomètrical explanation for the existence of straight line "ratio plots".

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