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THE ANISOTROPY OF MAGNETIC SUSCEPTIBILITY OF PARA-AZOXY-ANISOLE AND OF RELATED NEMATIC POLYMER MODEL COMPOUNDS

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Abstract The anisotropy of magnetic susceptibility of para-azoxy-anisole and of two related model compounds of main-chain nematic polymers (mono-methyl substituted on the phenyl rings) has been deduced from SQUID magnetometer measurements, and analyzed in terms of the theory of Horn and Faber [2]. For PAA, the results support our most recent analysis of NMR data [5] in which it was found that the anisotropy parameter η_s of the molecular orientational order varies between $\sim$ 0.1 and 0.3 throughout the nematic phase. For the two model compounds, η_s is probably much smaller, suggesting that their mesogenic units are more cylindrical in shape than PAA.

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INTRODUCTION

The macroscopic orientational order of uniaxial nematic phases [1] is usually characterized by second order tensorial properties such as the optical anisotropy Σ or the anisotropy of diamagnetic susceptibility $\Delta\chi^{(m)}$. At the molecular level, the orientational order is described by the so-called ordering matrix $\overset{\approx}{S}$. This matrix is diagonal in the principal frame $Ox_0y_0z_0$ and has two independent eigenvalues $S_{z_0z_0}$ and $\delta = S_{x_0x_0} - S_{y_0y_0}$ ($\overset{\approx}{S}$ is traceless). $S_{z_0z_0}$ is the usual nematic order parameter which describes the average orientation of the "long molecular axis" Oz_0 with respect to the macroscopic director (uniaxial term) and δ describes the difference in ordering of the two other principal axes Ox_0 and Oy_0 (biaxial term). The ratio $\eta_s = \delta / S_{z_0z_0}$ is the anisotropy parameter of the molecular orientational order.

Horn and Faber [2] have shown that, for rigid molecules, $\Delta\chi^{(m)}$ is likely to be related to microscopic quantities by an equation of the form :

$$\Delta\chi^{(m)} = S_{z_0z_0}(\Delta\chi_1 + \eta_s \Delta\chi_2) \tag{1}$$

with

$$\Delta\chi_1 = \chi_{z_0z_0} - \frac{1}{2}\left(\chi_{x_0x_0} + \chi_{y_0y_0}\right) \tag{2}$$

and

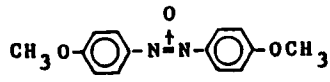
$$\Delta\chi_2 = \frac{1}{2}\left(\chi_{x_0x_0} - \chi_{y_0y_0}\right) \tag{3}$$

In these expressions, $\chi_{x_0x_0}$, $\chi_{y_0y_0}$, $\chi_{z_0z_0}$ are the components of the molecular susceptibility tensor $\overset{\approx}{\chi}$ along the principal axes of $\overset{\approx}{S}$. $\Delta\chi_1$ and $\Delta\chi_2$ characterize the uniaxiality and biaxiality of tensor $\overset{\approx}{\chi}$ in the principal frame of $\overset{\approx}{S}$, respectively.

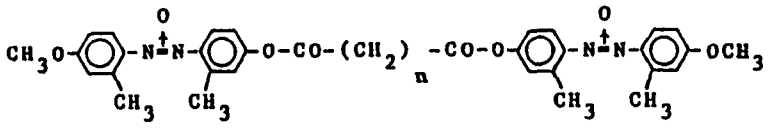
Similar equations can be written for Σ, in which $\overset{\leftrightarrow}{\chi}$ is replaced by the molecular polarisability tensor $\overset{\leftrightarrow}{\alpha}$. Bunning et al [3] have found that for a number of nematics, $\Delta\chi^{(m)}$ and Σ do not behave in quite the same way as a function of temperature, and conclude that η_s is non-zero in these systems. Indeed, although η_s is expected to be relatively small, $\Delta\chi_2$ is generally comparable or larger than $\Delta\chi_1$ so that the second term in Eq(1) may contribute significantly to $\Delta\chi^{(m)}$. On the contrary, $\Delta\alpha_2$ is usually (much) smaller than $\Delta\alpha_1$; the second term in Eq(1) is negligeable and, in practice, Σ reflects the temperature dependence of $S_{z_0 z_0}$ only. Quantitative agreement with the theory was achieved for pentyl-cyano-biphenyl (5CB) using NMR results of Emsley et al [4] and molecular susceptibility data of biphenyl compounds [3]. Test of this theory on other compounds is of high interest since, if well established, this means that information about molecular biaxiality may be extracted from macroscopic measurements.

Para-azoxy-anisole (PAA) is one of the most studied nematics. Bunning et al [3] have shown that, despite the large experimental uncertainty, the ratio $\Delta\chi^{(m)}/\Sigma$ also appears to be temperature dependent for this compound. On the other hand, in a recent paper [5], Galland et al have analyzed a large number of NMR data of PAA in terms of a simple model including both molecular non-rigidity and biaxiality. A detailed picture of the internal motions was obtained and values of order parameters were deduced in the whole nematic range.

In this paper, we present high sensitivity (SQUID) magnetic susceptibility data on PAA (M = 258) :



and on two related model compounds of main-chain nematic polymers (siamese twin) :



in which the phenyl rings of the aromatic cores are mono-methyl substituted as indicated. The two compounds studied 9DDA9 (n=10, M=738) and 9AZA9 (n=7, M=696) differ by the parity (and number) of methylene units in the flexible spacer. Detailed information on these compounds can be found in ref. [6].

For PAA, analysis of the data in terms of Eq(1) gives results which are consistent with the fact that η_s varies between $\sim$ 0.1 to $\sim$ 0.3 throughout the whole nematic phase [5]. For the two model compounds, using values of $S_{z_0 z_0}$ estimated by proton NMR, we find that η_s is probably much smaller than for PAA.

EXPERIMENTAL

The magnetic susceptibility measurements were performed using a SHE Corporation SQUID magnetometer working at 4 Tesla. The samples $\sim$ 50mg were contained in plastic containers. Thermal contact of the samples with the regulating temperature device was achieved using helium gaz. The presence of helium depressed the clearing point T_{NI} of the three samples studied by several degrees . Comparison with results obtained by other techniques is achieved by plotting the data as a function of reduced temperature $T^* = T/T_{NI}$. The experiments were performed by cooling from the isotropic phase by steps of 1 to 3 degrees. The contribution of the sample holder was

measured in a prior experiment performed in the same experimental conditions, and substracted from the raw data. The mass of the sample was measured before and after the experiment. Small variations of $\sim$ 1% were found, associated with the fact that the sample holders are not hermetically closed in these experiments. Fig.1 shows $\chi^{(m)}$ versus T^* for the three samples studied. It is observed that in the isotropic phase, $\chi^{(m)} = \chi^{(m)}_{iso}$ is constant and negative. In the nematic phase, $\chi^{(m)}$ increases with decreasing temperature. For sample 9DDA9, the nematic–solid transition is also observed around $T^* = 0.915$. The relatively sharp decrease of $\chi^{(m)}$ confirms the result inferred by NMR that solidification in such system is accompanied by loss of the macroscopic orientation of the nematic phase [7,8].

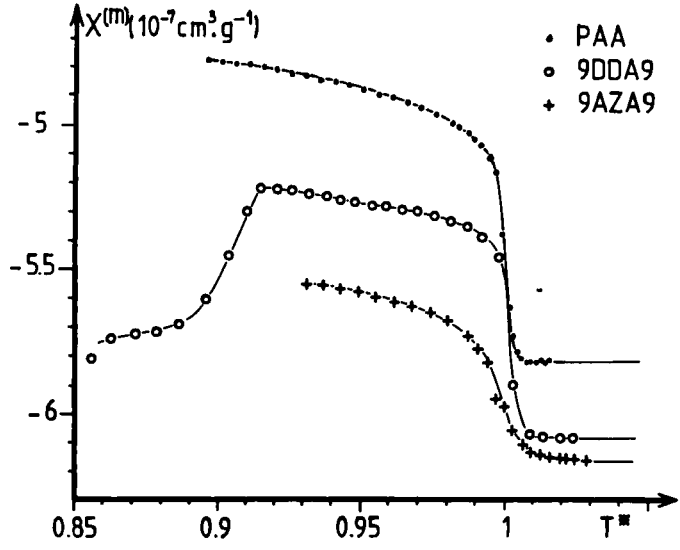


FIGURE 1. Specific magnetic susceptibility of PAA and of model compounds 9DDA9 and 9AZA9 versus reduced temperature. The clearing temperature T_{NI} is determined by comparison with the NMR data.

The proton NMR (PMR) absorption spectra of the two model compounds were obtained using a CXP90 Brüker spectrometer working at 90 MHz. The same samples as in the SQUID experiment were used. The results are essentially the same as those previously obtained [6]. Both samples exhibit a nematic plus isotropic (N + I) biphase. The nematic fraction f_N in the N + I biphase was deduced from intensity measurements and the clearing temperature T_{NI} was defined as the temperature for which $f_N = 0.5$. The main order parameter $S_{z_0z_0}$ was estimated from the value of the main splitting $2\delta_N$ of the PMR spectra by the relation [6,7,8]

$$2\delta_N \approx K.\ S_{z_0z_0} \tag{4}$$

with $K \approx 24.06$ KHz.

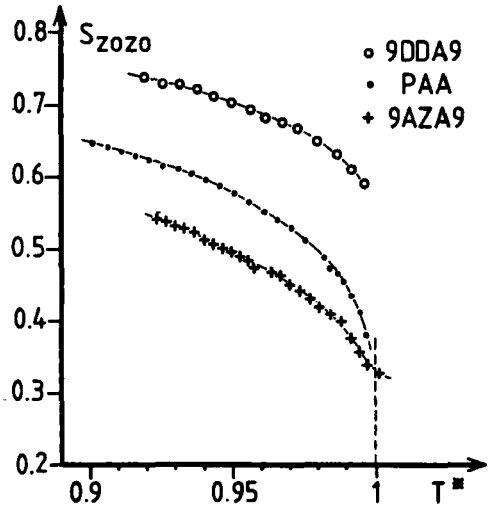


FIGURE 2. Main order parameter $S_{z_0z_0}$ of PAA and of model compounds 9DDA9 and 9AZA9 versus reduced temperature. The clearing temperature T_{NI} is defined by $f_N = 0.5$ when a N + I biphase is present.

Although proportionality between splittings and main order parameter is rigourous only if the motion is purely uniaxial, the detailed study of the PMR spectrum of methyl deuterated PAA [5] suggests that Eq(4) is probably a very good approximation even in the presence of biaxiality. It is difficult to estimate the uncertainty on the proportionality constant itself, but the same study suggests that this value may be slightly overestimated by a few per cent, that is the values of $S_{z_0z_0}$ slightly underestimated by the same amount. A detailed study of the PMR lineshapes of these compounds is however necessary to confirm this result, so that for the present purpose, we keep the above value. Fig.2 shows $S_{z_0z_0}$ versus reduced temperature for the three samples studied. For PAA, the values are taken from ref. [5].

RESULTS

The anisotropy of diamagnetic susceptibility $\Delta\chi^{(m)}$ for an aligned nematic sample is defined as

$$\Delta\chi^{(m)} = \chi_{/\!/}^{(m)} - \chi_{\perp}^{(m)} \tag{5}$$

in which $\chi_{/\!/}^{(m)}$ and $\chi_{\perp}^{(m)}$ are the components of the macroscopic susceptibility tensor $\tilde{\chi}^{(m)}$ parallel and perpendicular to the director. For the three samples studied, $\Delta\chi^{(m)}$ is expected to be positive so that the director aligns along the static magnetic field of the SQUID (or NMR) instrument. In this case, the value of $\chi^{(m)}$ measured in the nematic phase should be identified with $\chi_{/\!/}^{(m)}$. On the other hand, in the isotropic phase, we have :

$$\chi_{iso}^{(m)} = \frac{1}{3}\left(\chi_{/\!/}^{(m)} + 2\,\chi_{\perp}^{(m)}\right) \tag{6}$$

Combining Eqs.(5) and (6), we obtain :

$$\Delta\chi^{(m)} = \frac{3}{2}\left(\chi_{//}^{(m)} - \chi_{iso}^{(m)}\right) \qquad (7)$$

Using the data of fig.1 it is possible to evaluate $\Delta\chi^{(m)}$. The results agree with previous measurements [9]. Combination of these values with the data of fig.2 gives $\Delta\chi^{(m)}/S_{z_0z_0}$. Fig.3 shows this quantity versus reduced temperature in the pure nematic phase for the three samples studied. It is observed that (i) for PAA $\Delta\chi^{(m)}/S_{z_0z_0}$ increases by about $\sim$ 10% throughout the nematic phase and (ii) for the two model compounds $\Delta\chi^{(m)}/S_{z_0z_0}$ is practically constant. In terms of Eq(1)

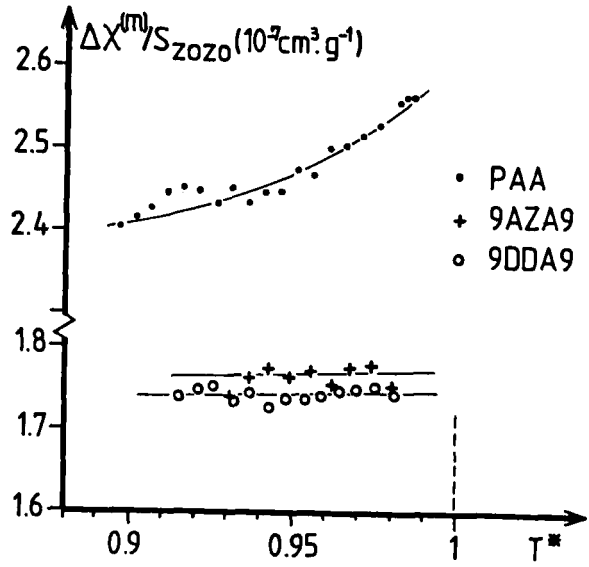


FIGURE 3. Ratio of specific anisotropy of magnetic susceptibility $\Delta\chi^{(m)}$ to main order parameter $S_{z_0z_0}$ versus reduced temperature, in the pure nematic phases of PAA and of model compounds 9DDA9 and 9AZA9, (deduced from fig.1 and 2).

this means that (i) η_s is non-zero for PAA, and increases with increasing temperature, and (ii) for the two model compounds, η_s and/or $\Delta\chi_2$ is much smaller than for PAA. A quantitative analysis of these results is presented in the next section.

ANALYSIS

It is in principle possible to check quantitatively Eq(1) at least in the case of PAA since the anisotropy parameter η_s has been estimated independently by NMR [5]. In fact, the situation is not so simple because the PAA molecule is not rigid, but composed of five rigid moieties which can rotate one with respect to another around single covalent bonds. These moieties are one

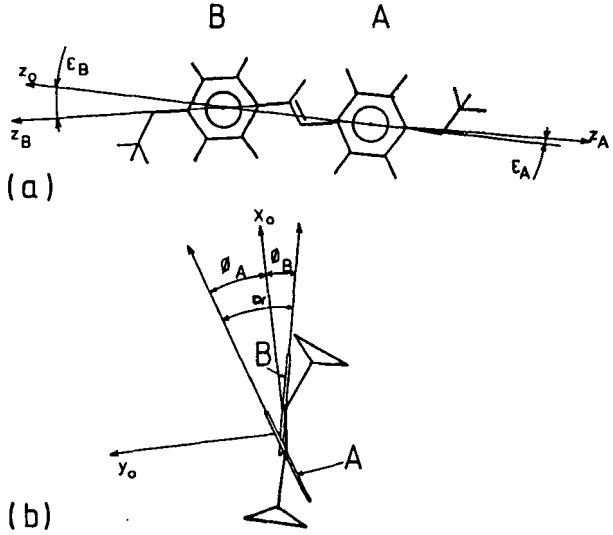


FIGURE 4. Sketch of the PAA molecule showing the main structural axes and angles : (a) lateral view in a planar conformation (b) top view along the para-axes of the phenyl rings assumed to be parallel.

central azoxy group, two non equivalent phenyl rings A and B and two associated methoxy groups (see fig.4). Each moiety i is characterized by a susceptibility tensor $\overset{\approx}{\chi}_i$ and an ordering matrix $\overset{\approx}{S}_i$ with principal frame $Ox_i y_i z_i$ and principal valus S^i_{zz} and δ^i (or $\eta^i_s = \delta^i / S^i_{zz}$). Eq(1) is easily generalized to this case writing :

$$\Delta\chi^{(m)} = \sum_i S^i_{zz} \left(\Delta\chi^i_1 + \eta^i_s \Delta\chi^i_2 \right) \qquad (8)$$

For the two rings A and B, as defined in fig.4 for the location of the azoxy oxygen atom, it is shown in ref.[5] that the corresponding $\overset{\approx}{S}_i$ are diagonal in frames where Oz_i is along the para-axis and Ox_i in the plane of the ring. This is so because the rings flip around their para-axes and because the PAA molecule exchange between levo and dextro conformations (racemisation). The values of S^i_{zz} and δ^i are given in fig.3 of ref.[5]. It is expected on general grounds that an important contribution to the anisotropy of diamagnetic susceptibility of a molecule like PAA comes from the two phenyl rings. We test here this idea by limiting the summation in Eq.(8) to the two rings A and B. The main order parameter S^A_{zz} associated with ring A and molecular order parameter $S_{z_o z_o}$ and δ are related by (idem for B) [5] :

$$S^A_{zz} \approx P_2(\cos\varepsilon_A)\, S_{z_o z_o} + \frac{1}{2}\,\delta\, \sin^2\varepsilon_A \qquad (9)$$

In this expression, $\varepsilon_A = 4.55°$ and $\varepsilon_B = 11.87°$ are the inclinations of the para axes on the long axis Oz_o [5]. Neglecting the second term in the right hand side of Eq.(9) which is always much smaller than the first one (<1%),Eq.(8) can finally be written :

$$\frac{\Delta\chi^{(m)}}{S_{z_o z_o}} \approx \Delta\chi^P_1 \left[P_2(\cos\varepsilon_A) + P_2(\cos\varepsilon_B) \right] + 2\Delta\chi^P_2\, \bar{\eta}^P_s \qquad (10)$$

where $\Delta\chi_1^P$ and $\Delta\chi_2^P$ as defined by Eqs.(2) and (3) refer to one phenyl ring, and where

$$\bar{\eta}_S^P = \frac{1}{2}\left[\eta_S^A P_2(\cos\varepsilon_A) + \eta_S^B P_2(\cos\varepsilon_B)\right] \qquad (11)$$

may be understood as an average anisotropy parameter of the orientational order of the two rings. Using the data of ref.[5], it is possible to plot $\Delta\chi^{(m)}/S_{z_0z_0}$ versus $\bar{\eta}_S^P$. Fig.5a shows such a plot and it is observed that the dependence is linear within experimental accuracy. The best fit of Eq.(10) to these data, taking $\Delta\chi_1^P$ and $\Delta\chi_2^P$ as parameters, gives the following values, expressed in 10^{-6} cm ^{3} per mole of phenyl ring : $\Delta\chi_1^P = 26 \pm 1$ and $\Delta\chi_2^P = 58 \pm 8$. The corresponding experimental values for

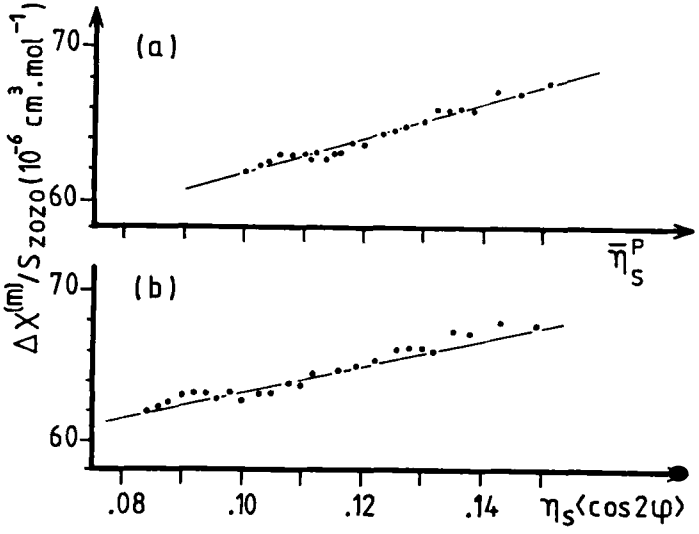


FIGURE 5. Ratio of molar anisotropy of magnetic susceptibility $\Delta\chi^{(m)}$ to main order parameter $S_{z_0z_0}$ of PAA versus $\bar{\eta}_S^P$ (a) and $\eta_S\langle\cos2\varphi\rangle$ (b). The straight lines are the best fits of Eq.(10) (a) and Eq.(15) (b) to the data.

benzene are 29.85 and 29.85 [10,12]. It is seen that the fitted value of $\Delta\chi_1^P$ is smaller than that of benzene by $\sim$ 13% whereas $\Delta\chi_2^P$ is significantly larger.

This trend is qualitatively consistent with what is expected for molecules composed of two rings linked by a small group. In ref.[11] are given the principal values of $\tilde{\chi}$ for a number of such molecules from which the corresponding values of $\Delta\chi_1^P$ and $\Delta\chi_2^P$ can be extracted. For example, with the linkages CH = CH, C $\equiv$ C, C $\equiv$ C - C $\equiv$ C, the values are, $\Delta\chi_1^P$ = 27.88, 22.02, 15.08 and $\Delta\chi_2^P$ = 39.87, 32.25, 32.85, respectively ; that is $\Delta\chi_1^P$ is smaller than for benzene whereas $\Delta\chi_2^P$ is larger.

A conclusion which may be drawn from this discussion is that the contribution to the azoxy and methoxy moieties to $\Delta\chi_1$ is relatively small whereas it is comparable to that of the phenyl rings to $\Delta\chi_2$.

The above analysis has considered the PAA molecule as a succession of rigid units. In ref.[5], we have developped a model in which the molecule is considered as a single (average) object with internal motions. The overall molecular rotational motion is pictured as motion of the molecular frame with respect to the director and motions of the moieties within this frame. Such model could explain self-consistently the whole set of NMR data considered and information about molecular quantities could be obtained. This information concerns (i) the principal frame $Ox_0y_0z_0$ and the eigenvalues $S_{z_0z_0}$ and δ (or η_S) of the molecular ordering matrix $\tilde{S}$ (ii) the azimuthal averages T_A and T_B given by (idem for B) :

$$T_A = \cos 2\,\phi_A \,(\cos 2\,\varphi_A) \qquad (12)$$

where ϕ_A (resp.ϕ_B) is the dihedral angle between the plane of ring A (resp.B) and the Ox_0z_0 principal plane,

and $\langle \cos 2\varphi_A \rangle$ (resp. $\langle \cos 2\varphi_B \rangle$) describes the mean amplitude of the librations of ring A (resp.B) about its para-axis (cf. fig.4b). The main principal axis Oz_0 was found to be the line joining the centers of two phenyl rings, but the exact position of the Ox_0z_0 plane, that is the values of $\varnothing_A$ and $\varnothing_B$, could not be determined. However since this plane lies between the two rings and since the mean conformation of the aromatic core is practically the same as in the solid phase [5], we have $\varnothing_A + \varnothing_B \approx \alpha \approx 22.6°$. The values of $S_{z_0z_0}$, δ and η_s are given in fig.6 of ref.[5] and the values of T_A and T_B are given in fig.5 of the same reference.

In the framework of this model, $\Delta\chi^{(m)}$ is expected to be given by Eq.(1) in which $\Delta\chi_1$ and $\Delta\chi_2$ refer to the average molecule, that is including the internal rotations. Let $\Delta\chi_1^0$ and $\Delta\chi_2^0$ be the corresponding values in the absence of the internal motions. Since in PAA all these internal rotations occur around axes which are close to the main axis Oz_0, we expect that $\Delta\chi_1$ is only slightly affected (lowered) by these motions :

$$\Delta\chi_1 \lesssim \Delta\chi_1^0 \tag{13}$$

On the other hand, $\Delta\chi_2$ is much strongly affected. Since the static relative disorder of the two rings is already taken into account in the value of $\Delta\chi_2^0$, we expect that $\Delta\chi_2$ will be lowered by a factor $\langle \cos 2\varphi \rangle$ where $\langle \cos 2\varphi \rangle$ is some average between $\langle \cos 2\varphi_A \rangle$ and $\langle \cos 2\varphi_B \rangle$.

$$\Delta\chi_2 \approx \Delta\chi_2^0 \langle \cos 2\varphi \rangle \tag{14}$$

Eq.(1) can thus be rewritten :

$$\frac{\Delta\chi^{(m)}}{S_{z_0z_0}} \approx \Delta\chi_1^{(0)} + \eta_s \langle \cos 2\varphi \rangle \Delta\chi_2^{(0)} \tag{15}$$

A reasonable estimate of $\langle \cos 2\varphi \rangle$ can be obtained by

the relation :

$$\langle \cos 2\varphi \rangle \sim \frac{1}{2} \frac{T_A + T_B}{\cos 2\phi} \qquad (16)$$

where $\phi \sim (\phi_A + \phi_B)/2$. With $\phi \sim 11.3°$ and the data of ref.[5], it is possible to plot $\Delta\chi^{(m)} / S_{z_0 z_0}$ versus $\eta_s \langle \cos 2\varphi \rangle$. Fig.5b shows such plot and, as in the preceding analysis, it is seen that the dependence is linear within experimental accuracy. The best fit of Eq.(15) to these data taking $\Delta\chi_1^{(0)}$ and $\Delta\chi_2^{(0)}$ as parameters gives the following values, expressed in 10^{-6} cm ^{3} per mole of PAA : $\Delta\chi_1^{(0)} = 54 \pm 2$ and $\Delta\chi_2^{(0)} = 92 \pm 20$.

These values can be estimated independently by combining the magnetic susceptibility data of Foex obtained on a monocrystal of PAA [13,14] and the cristallographic results of Krigbaum et al [15] . The structure of the room temperature crystal is monoclinic with one symmetry axis of order 2, $\vec{b}$, and one symmetry plane (P) perpendicular to this axis. There are four molecules per unit cell deduced from one another (for the orientation) by these two symmetry operations. Using the results of ref.[15], it is possible to show that the long axis Oz_0 as defined above is inclined at only 2.32° on (P). Neglecting this angle, it can be considered that the long axes of the four molecules are parallel between themselves and perpendicular to the $\vec{b}$ axis. The inclinations β_A and β_B of the two phenyl rings on the $\vec{b}$ axis (defined as the complementary of the angles between $\vec{b}$ and the normals $\vec{n}_A$ and $\vec{n}_B$ to the rings) can be calculated. We find $|\beta_A| = 61.87°$ and $|\beta_B| = 41.03°$. The angle $|\beta_A| - |\beta_B| \approx 20.8°$ is slightly different from the angle α between the two normals $\vec{n}_A$ and $\vec{n}_B$ ($\alpha \approx 22.6°$) because the two para-axes are not exactly coplanar [5].

For the four molecules of the unit cell, two molecules are characterized by angles β_A and β_B and the two other, which are symmetrical with respect to (P), by $-\beta_A$ and $-\beta_B$.

Concerning the susceptibility measurements [13,14], the tensor $\overset{\approx}{\chi}^{cr}$ of the crystal is diagonal in a frame where $\vec{b}$ is one axis and where the two orthogonal axes $\vec{a'}$ and $\vec{c'}$ are in the symmetry plane. The principal values, expressed in 10^{-6} cm^3 per mole of PAA are :

$$\chi^{cr}_{bb} = -172 \quad , \quad \chi^{cr}_{a',a'} = -164 \quad , \quad \chi^{cr}_{c',c'} = -105 \ .$$

The exact location of the $\vec{a'}$ and $\vec{c'}$ axes is not known. However, given the symmetry of the problem and the above values, it is likely that $\vec{c'}$ is along Oz_o (and thus $\vec{a'}$ is perpendicular to $\vec{b}$ and $\vec{c'}$). If this is accepted, simple tensor algebra allows to express the components, in the principal $Ox_oy_oz_o$, of the molecular susceptibility tensor $\overset{\approx}{\chi}$ in terms of crystal values and of the angle β_o between the symmetry axis $\vec{b}$ and $\overrightarrow{Ox_o}$. The result for $\Delta\chi_1^{(o)}$ and $\Delta\chi_2^{(o)}$ as defined by Eqs (2,3) is finally given by :

$$\Delta\chi_1^{(o)} = \chi^{cr}_{c',c'} - \frac{1}{2}\left(\chi^{cr}_{bb} + \chi^{cr}_{a',a'}\right) \tag{17}$$

$$\Delta\chi_2^{(o)} = \frac{1}{2}\left(\chi^{cr}_{bb} - \chi^{cr}_{a',a'}\right) / \cos 2\beta_o \tag{18}$$

This value of $\Delta\chi_1^{(o)} \approx 63$ is larger than the fitted value ≈ 54. However, in view of the facts that (i) the internal rotations also affect slightly the values of $\Delta\chi_1^{(o)}$ since ϵ_A and ϵ_B are non-zero and (ii) the value of 63 is obtained as the difference of two relatively larger numbers so that an experimental uncertainty of $\sim 3\%$ on the values of $\chi^{cr}_{a',a'}$, χ^{cr}_{bb} and $\chi^{cr}_{c',c'}$ is sufficient to

account for the total discrepancy, it can be considered that quantitative agreement is achieved. The result concerning $\Delta\chi_2^{(o)}$ is much more interesting since it allows an accurate determination of β_o, that is of the position of the main principal plane Ox_oz_o between the two phenyl rings. With $\chi_{bb}^{cr} - \chi_{a',a'}^{cr} = -8$, we have :

$$-4 \;/\; \cos 2\beta_o \approx 92 \qquad (19)$$

This equation means that β_o is larger, but near 45°. The solution of (19) is $|\beta_o| = 46.25°$. Even large uncertainties do not affect much the result. For a ± 100% uncertainty on the value of $\chi_{bb}^{cr} - \chi_{a',a'}^{cr}$, the values of $|\beta_o|$ range between 45.62° and 47.50°. This means that the principal plane Ox_oz_o is located between the two rings at an angle $|\varnothing_A| = |\beta_o - \beta_A| \sim 16°$ of ring A and $|\varnothing_B| = |\beta_o - \beta_B| \sim 5°$ of ring B, that is nearer ring B and very close to the plane of the azoxy group which is at ~ 3° from ring B [15]. The situation $\varnothing_A > \varnothing_B$ was suggested in ref.[5] to explain the difference in the temperature dependences found for the azimuthal parameters T_A and T_B. Note that the high accuracy obtained for β_o comes from the very weak biaxiality of the crystal compared to that of the molecule, associated with the particular arrangement of the four molecules in the unit cell.

CONCLUDING REMARKS

High sensitivity magnetic measurements combined with detailed NMR results have permitted to definitely prove that the molecular rotational motion of the PAA molecule in its neat nematic phase is not purely uniaxial. The results are in quantitative agreement with the magnitude of the degree of biaxiality found in the NMR study of ref.[5]. The present study has allowed to locate rather precisely the principal plane Ox_oz_o of the molecular ordering matrix $\tilde{\tilde{S}}$ between the two phenyl rings of the

molecule. This plane appears to be very close to that of the central azoxy group.

Concerning the two model compounds, a similar analysis cannot be made because the structure of the solid is not known and a detailed NMR study has not been performed. However, the finding that $\Delta\chi^{(m)}/S_{z_0z_0}$ is practically constant (cf fig.3) probably means that η_s is relatively much smaller than for PAA. The value of $\Delta\chi_1$ estimated from the data of fig.3 and expressed in 10^{-6} cm^3 per mole of model compound are $\Delta\chi_1^{9DDA9} \approx 128$ and $\Delta\chi_1^{9AZA9} \approx 122$. The accuracy on these values is estimated to a few per cent. The largest value found for 9DDA9 is probably meaningful and consistent with the fact that adding CH_2 groups increase $\Delta\chi_1$ [16] . Note also that these values are about twice as large as that of PAA, as expected.

The small value of η_s suggests that the mesogenic units of these model compounds are more cylindrical in shape than PAA. This quasi-cylindricity is presumably related to the presence of the methyl groups substituted on the two phenyl rings. These groups not only decrease the intrinsic biaxial character of each ring, but also probably lower the biaxiality of the molecule by increasing the mean dihedral angle between the rings.

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