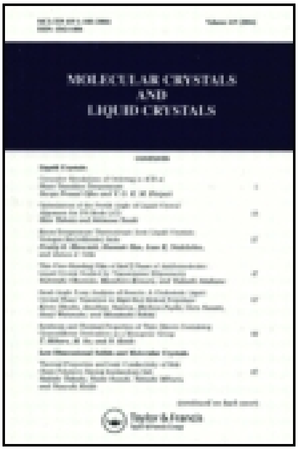

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The Exact Calculation of the NMR Spectrum of an Eight Spin 1/2 System Applied to Nematic Para-Azoxy-Anisole

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THE EXACT CALCULATION OF THE NMR SPECTRUM OF AN EIGHT SPIN 1/2 SYSTEM APPLIED TO NEMATIC PARA-AZOXY-ANISOLE

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Abstract The first exact calculation of the NMR spectrum of an eight spin 1/2 system with dipolar interactions is presented. The method is used to simulate the proton NMR spectrum of methyl-deuterated para-azoxy-anisole (PAAd6) in the nematic phase. Comparison with experiment shows that reasonable fits are obtained only if rotations of the two phenyl rings around their para-axes are noncorrelated. This study reveals the limitations of the one order parameter model of Dianoux et al[5] to interpret the data. The need for a second order parameter is suggested. Comparison with approximate methods applied previously to the same problem is also made.

INTRODUCTION

Although deuterium magnetic resonance (DMR) has become a very popular tool to study molecular properties of liquid crystals, proton magnetic resonance (PMR) is still unique to obtain specific information, in particular on the nature of relative motions within the molecules. The reason is that, unlike DMR, PMR is governed

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also by long-range dipolar interactions, and interaction between proton spins of different rigid fragments may contribute significantly to the PMR lineshapes. The main inconvenience of PMR compared to DMR is that exact calculation of PMR spectra becomes rapidly more complex as the number of interacting spins increases. This inconvenience is nowadays overcome by the use of numerical computational techniques.

Nematic para-azoxy-anisole (PAA) is one of the most studied systems, in particular by NMR. All PMR spectra of normal and partially deuterated PAA are well known, but no rigorous treatment of the PMR problem has been done so far. Only approximate methods have been applied[1-4], in order to reduce the mathematical complexity. Although these methods can give some information about internal motions (essentially the same information as obtained by DMR), the results are at most semi-quantitative because the approximations blur partially or completely the (weak) effect under study.

In the present paper, we are interested in the nature of the relative rotations of the two rings of the aromatic core of PAA. For this purpose, the PMR spectrum of PAA deuterated on the two methyl groups (PAAd6) is the most interesting. The reason is that it contains "only" eight ring protons, the influence of the methyl deuterons being the splitting of the PMR lines in a way which can be evaluated using DMR data. Exact calculation of an eight spin $\frac{1}{2}$ spectrum requires the knowledge of the 28 dipolar interactions between the 8 spins. In PAA, the actual values of these quantities depend on structural, conformational and dynamical parameters and it is of great importance to have the maximum of independent molecular information in order to reduce the number of residual adjustable parameters.

In a previous paper[5], a large number of DMR data on fully and partially deuterated PAA were analyzed in terms of a simple model, and molecular information was deduced from the analysis. This information shall be extensively used in the present study. However since this information is necessarily somehow dependent on the model adopted, this study will also provide an additional test for this model.

THE PMR SPECTRUM OF 8 SPINS ½ WITH DIPOLAR INTERACTIONS

In high field PMR, the relevant pertubation of the Zeeman hamiltonian is the following dipolar hamiltonian H_d[6]

$$H_d = \frac{3\,h\,\gamma^2}{4\,\pi^2} \sum_{i<j} B_{ij}\,(I_{iz}I_{jz} - \frac{1}{3}\,\vec{I_i}\vec{I_j}) \qquad (1)$$

$$\text{with } B_{ij} = \left\langle \frac{P_2(\cos\Theta'_{ij})}{r_{ij}^3} \right\rangle \qquad (2)$$

In these expressions, the indices i and j run over the 8 spins, $\vec{r_{ij}}$ is the vector joining spins i and j and Θ'_{ij} is the angle between $\vec{r_{ij}}$ and the static magnetic field $\vec{H_0}$ directed along the Oz axis of the laboratory frame. The brackets in (2) stand for averages over (fast) motions of the nuclei possessing the spins. For protons, $3h\,\gamma^2/4\,\pi^2 = 360.3$ KHz.Å^3. For 8 spins ½, the dimension of the spin Hilbert space is $2^8 = 256$. Calculation of the PMR spectrum requires :

(i) diagonalisation of a 256 x 256 matrix whose elements are functions of the 28 B_{ij}

(ii) search of the frequencies of all $|\Delta M| = 1$ allowed transitions : there are 5720 such transitions symmetrically distributed around the unperturbed Larmor frequency ν_o

(iii) calculation of their intensities.

It is out of the scope of this paper to give the details of the algorithm used for the computation, but it may be obtained on request from one of the authors (J.B.F). It must be said that the computer must have sufficient memory space available to store a considerable amount of data, including 22 matrices, the largest one being 70 x 70. The final result of this computation are the 5720 frequency differences $\nu_k - \nu_o$ and the corresponding intensities I_k. The theoretical spectrum G (ν) is composed by the superposition of infinitely sharp lines at frequency ν_k and may be expressed as

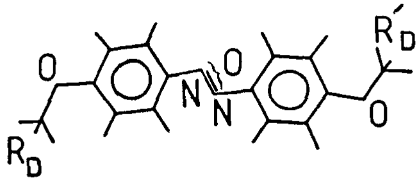
$$G(\nu) = \sum_k I_k \, \delta \, (\nu - \nu_k) \qquad (3)$$

In practice, the lines are not infinitely sharp (field inhomogeneity, inhomogeneous broadening due to neighboring unlike spins ...) and each δ function must be replaced by some lineshape function which depends on the particular system under study. It will be discussed in the next section for our PMR experiments on nematic PAAd6.

THE PMR SPECTRUM OF PAAd6 -

a/- experimental spectrum

The PMR spectrum of PAAd6 is shown in Fig.1 for two extreme temperatures in the nematic phase. They have been recorded using a CXP 90 Brüker spectrometer working at 90 MHz. Great care was taken in the experimental conditions since they may affect the lineshapes. A small sample (< 50mg) was used in order to reduce temperature and field inhomogeneities over the sample volume (samples were degassed and sealed under vacuum). The RF pulse width was reduced to ∿ 1μsec, corresponding to an



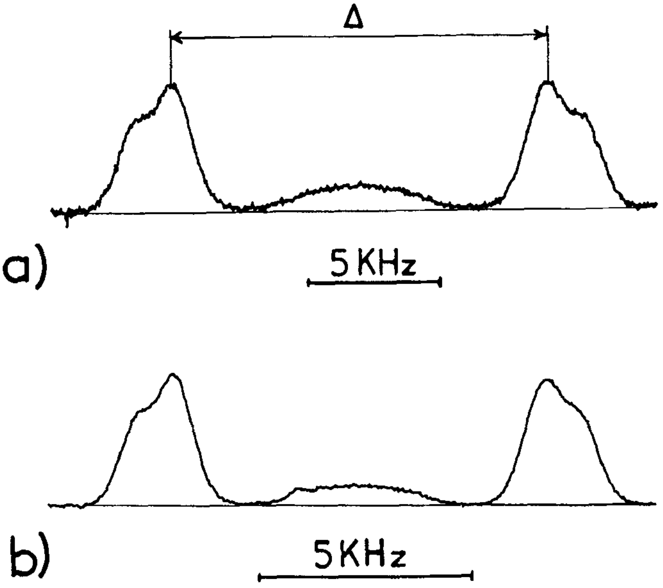


FIGURE 1. 90 MHz PMR spectra of PAAd6 at two extreme temperatures in the nematic phase : (a) : $T - T_C = 38°C$ (b) : $T - T_C = 1°C$. The broad component in the center of the spectrum comes from molecules which are also partially deuterated on the phenyl rings near the azoxy group (cf. ref. |5|). The overall instrumental resolution is ∿400 Hz full width at half maximum.

irradiation spectral width of $\sim$1MHz compared to overall extension of $\sim$20KHz of the experimental spectra. It is observed that, within experimental accuracy, the spectra are symmetrical with respect to the central frequency, showing that the spread of chemical shifts of the various phenyl protons ($\sim$1.3 ppm as measured in the isotropic phase) can be neglected. They are composed of a main doublet whose components exhibit some structure varying slightly with temperature, namely the external shoulders tend to smear out as temperature increases. This effect is reproducible, despite its relative weakness.

b/- Theoretical spectrum

As stated above, $G(\nu)$ can be exactly calculated once all B_{ij} are known. The geometrical problem is sketched in Fig.2a,b, which shows the central core of PAAd6 with the eight spins labelled 1 to 8 as indicated. A molecular frame is attached to the azoxy fragment, with Oz parallel to the NC bonds (assumed to be parallel) and Ox in the plane of this group. The long molecular axis Oz_0 is defined, in this frame, by polar and azimuthal angles ε and Γ . The polar and azimuthal angles of Oz_0 in the A and B ring frames of the most probable conformation are ε_A, Φ_A and ε_B, Φ_B, these frames having Oz along the para-axis and Ox in the ring plane. To calculate the B_{ij}, knowledge of the exact geometry and dynamics are required. For this purpose, we use the results of ref.|5| :

(i) for the geometry, we have $\varepsilon_A = 15.10°$ and $\varepsilon_B = 15.70°$, and $|\Phi_A| \sim |\Phi_B| \sim 70°$. The distances between orthoprotons are not the same for the two rings, namely :

$$r_A = r_{12} = r_{34} = 2.493 \text{ Å}; \text{ and } r_B = r_{56} = r_{58} = 2.530 \text{ Å} \qquad (4)$$

For the present calculation we write, with evident notations :

$$r_{A,B} = 2.5115\ (1 \mp a) \qquad (5)$$

with $a = 7.37 \times 10^{-3}$

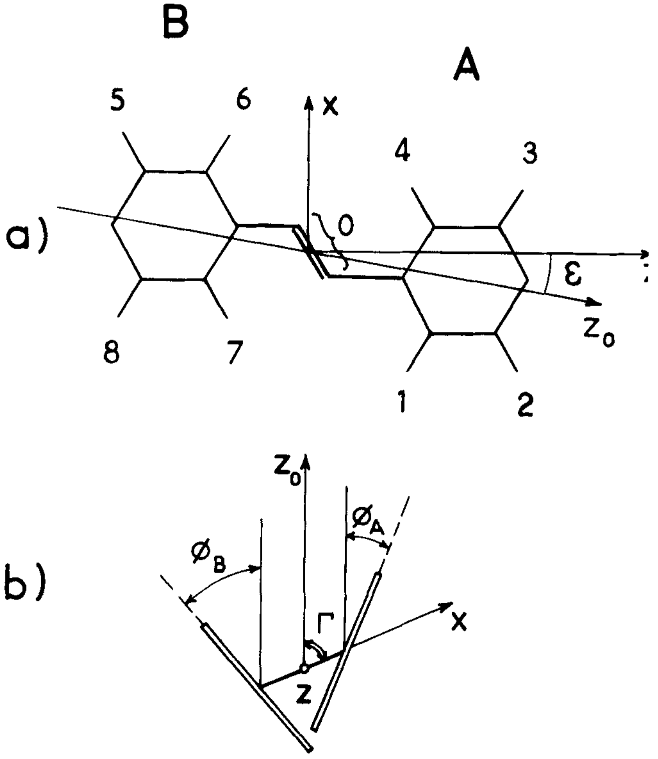


FIGURE 2. Sketch of the central aromatic core of the PAA molecule

a) side view in a planar conformation

b) top view along the para-axes of the phenyl rings, assumed to be parallel.

For other intra ring distances, we take

$$r_{14} = r_{23} = r_{67} = r_{58} = 2.5115 \times \sqrt{3}\,(1+m) \qquad (6)$$

where m is a (small) adjustable parameter allowing for (slight) distorsion of the rings perpendicular to the para-axes ; the other intra-ring distances are deduced from simple geometrical considerations.

The distances between spins of different rings depend on the geometry of the azoxy moiety and on the dihedral angles. Using data from the solid phase[7], namely C-N = 1.496 Å, N=N = 1.218 Å, an average value of the angle NNC of 113.25° (average between 111.8 and 114.7°), CH = 1.08 Å, all inter-ring distances can be calculated if dihedral angles are known.

(ii) for the dynamics, the model of ref.|5| assumes that the (rotational) motions are split into external and internal motions. The external motions correspond to uniform rotation around Oz_0 and fluctuations of this axis about the director. This implies that all splittings are proportional to the single order parameter S. In particular, the B_{ij} can be written

$$B_{ij} = S\,T_{ij} \qquad (7)$$

with $$T_{ij} = \left\langle\!\left\langle \frac{P_2(\cos\Theta_{ij})}{r_{ij}^3} \right\rangle\!\right\rangle \qquad (8)$$

where Θ_{ij} is the angle between $\vec{r}_{ij}$ and $\vec{Oz}_0$, and the double brackets stand for average over internal motions only. Assuming that S is given by the analysis of optical measurements of ref.|8| it was deduced in ref.|5| that the main splitting Δ as defined in Fig.1 is related to S by

$$\Delta/\mathrm{KHz} = 19.93 \times S \qquad (9)$$

It follows from (7) that all experimental spectra can be plotted in a normalized frequency scale(ν /S), with S given by (9), allowing for easier comparison with the theoretical spectra, which can then be simulated by taking S = 1 and $B_{ij} = T_{ij}$.

The internal motions are essentially rotations of the rings and associated methoxy groups around the para-axes. These rotations can be described by assuming that they occur in a mean potential of C_{2v} symmetry of the form

$$W(\psi_A, \psi_B) = U\left[\sin^2(\psi_A - \Phi_A) + \sin^2(\psi_B - \Phi_B)\right] \qquad (10)$$

where U is a constant parameter.

This form implies that the rings perform π flips plus (large amplitude) librations around the most stable positions Φ_A and Φ_B, and that these motions are equivalent for the two rings. The mean amplitudes of these librations are characterized by the ring order parameters $\langle\cos 2\psi\rangle = \langle\cos 2\psi_A\rangle \sim \langle\cos 2\psi_B\rangle$ which were found to vary between $\sim$ 0.94 at low temperature in the nematic phase to $\sim$ 0.31 near the clearing point.[5] The value of $\langle\cos 2\psi\rangle$ may be used to determine the value of U via the relation

$$\langle\cos 2\psi_A\rangle = \frac{1}{Z}\int \cos 2\psi_A \exp\left[-W(\psi_A,\psi_B)/kT\right] d\psi_A d\psi_B \qquad (11)$$

where Z is a normalization constant.

The nature of the relative motions of the two rings depend on the interdependence of the current angles ψ_A and ψ_B. Two extreme cases can be considered :

(a) the rotations of the two rings are uncoupled : in this case, ψ_A and ψ_B must be considered as independent variables,

(b) the rotations are completely coupled, presumably in opposite

senses : in this case, we have $\psi_A = - \psi_B$.
Whether or not ψ_A and ψ_B are coupled variables is irrelevant for calculating the T_{ij} involving spins belonging to the same ring. This is no more the case for T_{ij} which connect the two rings. The result is in fact significantly different and this affects the PMR spectrum.

The parameters which could not be determined by the analysis of ref.|5| are :

(i) the azimuthal angle Γ of the long axis Oz_0 in the azoxy frame,

(ii) the relative signs of Φ_A and Φ_B, i.e. whether the dihedral angle between the two rings is 0 (rings are parallel) or $\Phi_A - \Phi_B \simeq 40°$,

(iii) the degree of coupling of the rotations of the two rings.

We have considered four extreme cases for the dihedral angles by combining $\Gamma = 0$ or $90°$, and $\Phi_A = \Phi_B = 70°$ or $\Phi_A = -\Phi_B = 70°$ (cf. Fig.3), and calculated the corresponding PMR spectra when rotations are assumed to be either completely coupled or independant ; that is, in all, 8 possible situations.

c/- Width function

The width function mentionned in section 2 must be estimated before any comparison with experiment can be made. In nematic PAAd6, the main source of intrinsic broadening of the PMR lines comes from dipolar interaction with methyl deuterons. This interaction is strong for outer protons 2, 3, 5, 8 and weaker for inner protons 1, 4, 6, 7. For one single proton, interaction with three equivalent deuterons splits the Zeeman line into a septet of equidistant lines with relative intensities 1 : 3 : 6 : 7 : 6 : 3 : 1. This distance was measured by DMR in ref.|5| and estimated to $\delta_{out} \simeq 665$ Hz for outer protons. From the same data, we estimate $\delta_{in} \simeq 140$ Hz for inner protons. For a two proton spin system such as one outer and one inner proton, it can be

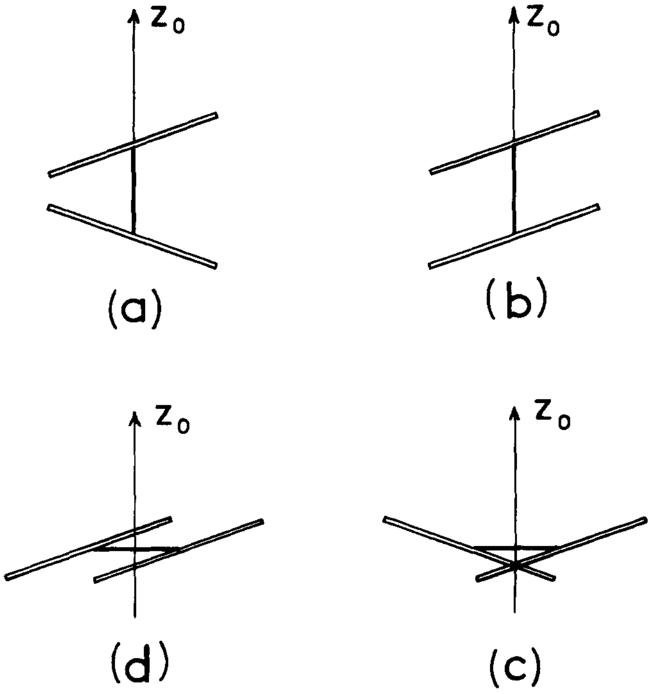


FIGURE 3. Top views of four extreme possible conformations of the PAA molecule which are consistent with the results of ref. [5].

a) $\Gamma = 0$, $\Phi_A = -\Phi_B = 70°$ b) $\Gamma = 0$, $\Phi_A = \Phi_B = 70°$
c) $\Gamma = 90°$, $\Phi_A = -\Phi_B = 70°$ d) $\Gamma = 90°$, $\Phi_A = \Phi_B = 70°$.

shown that each line of the PMR spectrum is split into the above mentionned septet with a distance between lines of $\delta_{av} = (\delta_{out} + \delta_{in})/2$. For a larger number of protons spins, this result is no more rigorous. For our eight spin system, we estimated that the actual value of δ_{av} is about 15% smaller than the arithmetic average. We have taken $\delta = 330$ Hz. The remaining origin of broadening comes from combination of spread of chemical shifts $\sim$ 120 Hz and magnetic field inhomogeneity. In our experiment, we estimated this total residual broadening to $\sim$ 400 Hz. For the calculation, we assumed a gaussian shape $R(\nu)$ with full width at half height $2\Delta \sim$ 400 Hz, the same for all spectral lines,

$$R(\nu) = \frac{1}{\Delta}\left(\frac{\mathrm{Ln}2}{\pi}\right)^{\frac{1}{2}} \exp\left[-\frac{\nu^2\,\mathrm{Ln}2}{\Delta^2}\right] \qquad (12)$$

To summarize, each of the 5720 lines of the PMR spectrum must be replaced by a septet of equidistant gaussian lines of width $2\Delta \sim 400$ Hz, with separation $\delta_{av} \sim 330$ Hz and with relative intensities 1 : 3 : 6 : 7 : 6 : 3 : 1. In practice, we have only considered the 5720/2 = 2860 lines corresponding to the high field part of the spectrum, each line being replaced by the septet of gaussian lines. To plot the spectrum, it is not necessary to consider the 2 860 x 7 = 20 020 lines ; it is sufficient to split the total frequency range into N intervals k' whose width is smaller than 2Δ. We have chosen N = 200. For an overall half width of the spectrum of 20 KHz, this corresponds to a frequency interval of 100 Hz. The theoretical spectrum is finally expressed as,

$$G(\nu) = K \sum_{k'} I_{k'}\, R(\nu - \nu_{k'}) \qquad (13)$$

where $I_{k'}$ is the sum of all intensities of those among the 20 020 lines which belong to interval centered at $\nu_{k'}$.

The constant coefficient K is chosen in such a way that theoretical and experimental spectra have the same area.

RESULTS -

The comparison has been systematically made with the low temperature spectrum where $\langle \cos 2\psi \rangle \gtrsim 0.85$ (ref.|5|).

Fig.4a-d, shows the results for the situation $\Gamma = 0$, $\Phi_A = -\Phi_B = 70°$ (Fig.3a). Fig.4a shows that assumption that the rotations of the

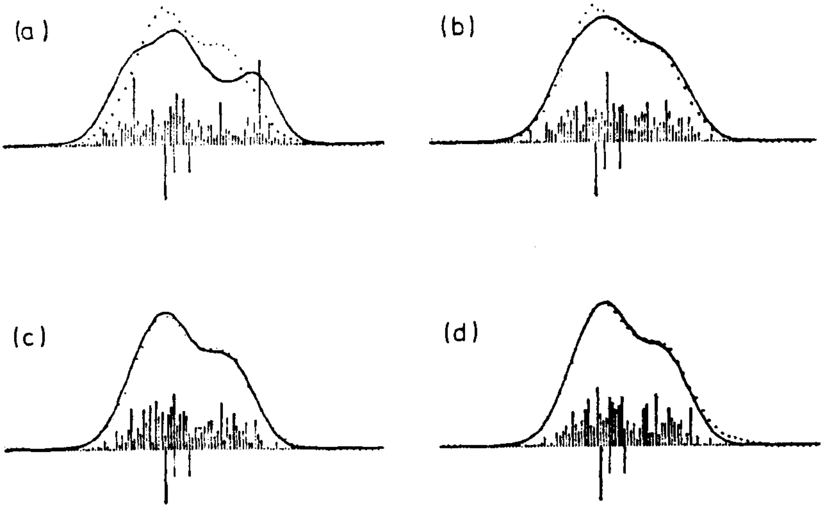


FIGURE 4. High field component of the PMR spectra of PAAd6. Dotted lines are experimental. Solid lines are calculated spectra using the exact method presented in this paper for the conformation of fig. 3a : (a) : coupled ring rotations, m = 0 , low temperature ; (b) : same as (a), but uncoupled ring rotations ; (c) : same as (b), but m = + 6.5% ; (d) : same as (c), but high temperature. The histograms represent the lines of Eq. (13). The positions of the maximum of the experimental spectrum, of the dipolar splitting between ortho-protons of ring B and of ring A are also indicated below the frequency axis (left to right).

two rings are completely correlated lead to a theoretical spectrum which is significantly different from experiment. Complete decorrelation (Fig.4b) greatly improves the situation, but the theoretical spectrum is still too broad. Close examination of the results reveals that this extra broadening comes from the fact that the T_{ij} such as T_{14}, T_{23} ... are too large. This can be overcome by assuming that the rings are slightly elongated perpendicular to the para-axis. Fig.4c shows that an extremely good fit is obtained for a value of m as defined by Eq(6), of $+ 6.5 \times 10^{-2}$. The same spectrum is calculated with $\langle \cos 2\Psi \rangle = 0.31$ and compared with the high temperature spectrum in Fig.4d. Again the agreement is very good. We have repeated this analysis for the three other possible conformations pictured in Fig.3b,c,d. In all cases, complete correlation must be excluded. For complete decorrelated rotations of the rings, cases $\Gamma = 0$, $\Phi_A = \Phi_B = 70°$ (Fig.3b) and Γ ▫ $90°$, $\Phi_A = - \Phi_B = 70°$ (Fig.3c) never give satisfactory results so that they can be excluded. Finally, the case $\Gamma = 90°$, $\Phi_A = \Phi_B = 70°$ (Fig.3d) gives results which are practically identical to those of the first case considered, Fig.3a, namely both the actual lineshape and temperature dependence are well reproduced assuming an elongation of the rings perpendicular to the para-axes of 6.5%.

At this stage, it can thus be concluded that exact calculation of PMR spectrum of PAAd6 combined with the results of ref.|5| shows that :

(i) rotations of the two rings around their para-axes are highly uncorrelated,

(ii) two among the four extreme conformations considered are possible. Among these two, only the conformation corresponding to $\Gamma = 0$ and $\Phi_A = - \Phi_B = 70°$ (Fig.3a) satisfies the condition that Oz_O is near the main inertial axis of the molecule since it lies in one bissector plane of the two rings, and practically inside the plane of the azoxy group.

Although the model of ref.|5| can very well explain the PMR lineshape and its temperature dependence, it suffers a severe drawback, namely the necessity of an elongation of the rings perpendicular to the para-axes of 6.5%. This seems to be a rather large deformation which is not justified by the structure in the solid phase[7], and somewhat in contradiction with the results of Ref.|5|, namely with the fact that the inclination of the CD bonds on the para-axes are all found to be smaller than 60°, in which case we would have expected a contraction of the rings rather than an elongation. Thus, at the present degree of accuracy in the analysis, these results correspond to a weak but definite limitation in the model of ref.|5| to explain the whole set of DMR and PMR data on PAA.

The only possibility to overcome this difficulty is to improve the model by introducing additional parameters. Since the most probable conformation found here departs from cylindricity, the most natural assumption to release is the uniform rotation around Oz_0. In other words, a second nematic order parameter must be introduced. Preliminary attempts to reinterpret the whole set of NMR data show that the main difficulty mentionned can be overcome, namely satisfactory fits can be obtained assuming no deformations of the rings. The most probable conformation is slightly different, but the conclusion concerning the independence of the ring rotations is not changed.

COMPARISON WITH RESULTS OBTAINED BY APPROXIMATE METHODS

The previous studies[1-4] of the PMR spectrum of PAAd6 have essentially used truncated dipolar hamiltonians Eq(1). In this section these approximations are tested in order to show to what extent they affect essential features of the results.

The pionnering work of Ghosh[1], besides the fact that there is an error in the analysis, neglects all inter-ring interactions such as T_{17}, T_{64}... The result of the calculation for the situation corresponding to Fig.3a, assuming that all T_{ij} connecting two rings are zero, is shown in Fig.5a. It can be seen that both the shape and the width are not reproduced showing that this approximation is rather poor in the case of PAAd6.

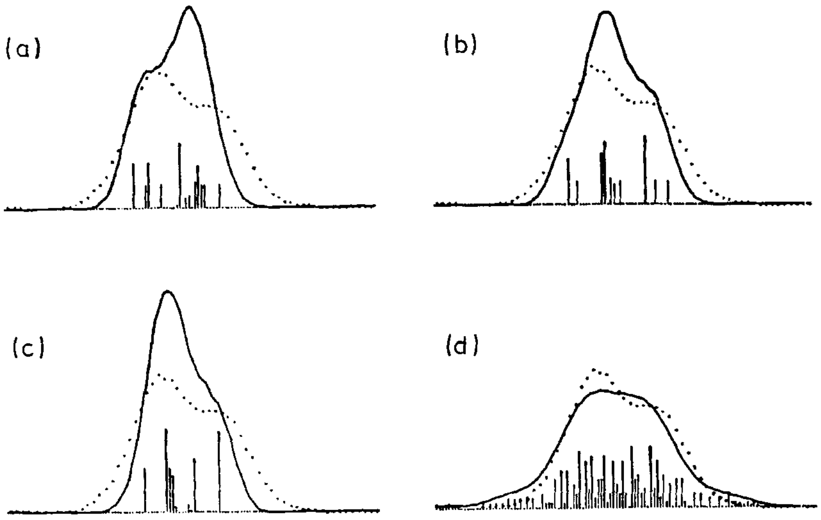


FIGURE 5. High field component of the low temperature PMR spectrum of PAAd6. Dotted lines are experimental. Solid lines are calculated using approximate methods for the conformation of fig.3a ; (a) : method of ref. |1| ; (b) : of ref. |4| ; (c) : of ref. |2| ; (d) : of ref. |3|. Other features are the same as for Fig. 4.

Hayamizu and Yamamoto[4] have made the same approximation, but had to assume a large difference in ordering of the two rings.

This assumption was necessary in order to reproduce the experimental spectrum from the superposition of the two independent spectra produced by the four proton system in each ring (each of them having the same shape as the one shown in Fig.5a). We have taken the same geometry for the two rings, assumed $\varepsilon_A = 0$ (ring A is not inclined) and tried to reproduce the experimental spectrum using the inclination of the second ring as a parameter. In no cases, a good fit is obtained, even if a different value for ε_A is chosen. Fig.5b shows the "best" fit which corresponds to $\varepsilon_B = 16°$. For smaller or larger values of ε_B, the fit worsens very rapidly. Besides the bad quality of the fit, the difference $\varepsilon_B - \varepsilon_A = 16°$ is too large if one considers both the structure in the solid[7] and the DMR data of ref.|5|. One final criticism should be made about the simulation of the PMR spectrum of ref.|4|. The perfect fit obtained between experimental and simulated spectra, despite the fact that all inter-ring interactions are neglected, implies that some other inadequate assumption was necessarily made to compensate for such poor approximation.

At this stage, it thus appears that neglecting the inter-ring interactions corresponds to a poor approximation. This could be inferred from the present study since the degree of coupling of rotations of the two rings affects significantly the theoretical spectrum. Martins and Ayant[2] realized first the importance of inter-ring interactions in nematic PAAd6. Fig.5c shows the result of the calculation assuming that the eight spin system is replaced by the two independent four spin systems (1,2,7,8) and (3,4,6,5). It is seen that the general features of the observed spectra are now reproduced. However, the theoretical spectrum is too narrow, and the level of the external shoulder is too low.

Finally, St. Limmer et al[3] have made a different kind of approximation. In order to avoid diagonalisation of large matrices, they neglect the scalar term $\vec{I}_i\vec{I}_j$ in the dipolar hamiltonian Eq(1). Fig.5d shows the result of such approximation for the situation of Fig.3a. The main effect is that the dissymetry is almost lost. However, although the shape is not well reproduced, the overall width is almost correct because the scalar term does not contribute to the second moment of the spectrum . Another feature of this approximation is that the correlation of rotations of the two rings can be tested. Assumption that the rotations are coupled indeed yield spectra which are structureless and too broad, showing that independence of the rotations is the most likely situation.

CONCLUSION

In conclusion, we have shown that proton magnetic resonance is a very powerful tool to study molecular properties of liquid crystals, when the NMR problem is treated exactly. In some aspects, it is superior to deuterium magnetic resonance, in particular for studying degree of coupling of internal rotations. One advantage is that normal samples (non deuterated) can be used for the experiments ; the main inconvenience is that it requires large computers and a lot of computational work whenever the spin system does not have a special symmetry, as is often the case. For the particular case of nematic PAAd6, we have shown that the spectra can be very well reproduced only if certain conditions are fulfilled. It has permitted to show that rotation of the two rings around their para-axes are highly uncorrelated, that some possible conformations can be excluded, and that a second nematic order parameter is probably required to explain self-consistently the whole set of DMR and PMR results. The study has demonstrated the paramount importance of structural quantities in particular of the exact geometry of the rings. Very small uncertainties in the geometrical parameters may significantly change the conclusions concerning the dynamics and the conformation.

We are currently reexamining the whole set of NMR data on PAA in the light of the present results and of the structural results obtained in the solid phase.[7] The aim is to study to which extent a structure and conformation of the molecules as close as possible to that in the solid phase is consistent with the data, and to know in more details what is the influence of slight variations of geometrical parameters on the values of the dynamical quantities such as the order parameters and the nature of the internal motions. The results of such study will be reported elsewhere.[9]

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