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Exact Calculation of the NMR Spectrum of a Twelve Spin 1/2 System: Application to the Structure of the Aromatic Core of a Main-Chain Nematic Polymer

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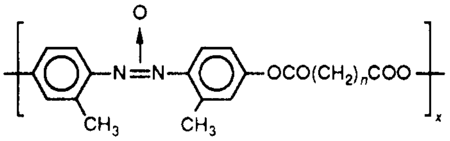
ABSTRACT: The anisotropic proton NMR spectrum of the 2,2′-dimethylazoxybenzene moiety, a twelve spin $^1/_2$ system, is calculated exactly and compared to the experimental spectra of (i) 4,4′-diacetoxy-2,2′-dimethylazoxybenzene deuterated on the methyl groups (Ac9Acd6) and dissolved in the nematic phase of perdeuterated *p*-azoxyanisole (PAAd14) and (ii) two spacer deuterated main-chain thermotropic nematic polymers, [poly[oxy(3-methyl-1,4-phenylene)azoxy(2-methyl-1,4-phenylene)oxy(α,ω-dioxy-α,ω-alkanediyl)] (ME9Sn, with n = 7 and 10 (AZA9d14 and DDA9d20))] in their bulk nematic phase. Modeling in terms of the single conformation model allows satisfactory fits of the experimental spectra. The structure and orientational features of this mesogenic moiety in Ac9Ac and in the polymers are found to be very similar. Similarities and differences with the parent moiety azoxybenzene (the aromatic core of PAA) are pointed out. The similarities lie mainly in very similar distortions of the backbone, constituted by the azoxy group and the two para axes of the rings, and in the orientation of the principal axis. The differences lie in the absence of π-flips of the rings (such flips exist in PAA and are uncorrelated) and in larger values of the dihedral angles between the three rigid moieties. The simulations permit the determination of the proportionality constant between the main splitting of the spectra and the uniaxial order parameter. Some weak information on the anisotropic components of the chemical shift tensors of the phenyl and methyl protons and on the biaxiality of the order is also obtained.

1. Introduction

As a continuation of our work[1,2] on molecular aspects in nematic main-chain polymers of the form $(RF)_x$, where R is a mesogenic unit and F a flexible spacer $(CH_2)_n$, we have undertaken the detailed study of the proton NMR spectrum of the mesogenic unit of polymers ME9Sn[3,4] with chemical formula



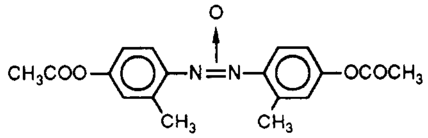
A recent review of the properties of these polymers, with numerous references, is made in ref 5.

The mesogenic unit is the azoxybenzene moiety where two methyl groups are substituted on the phenyl rings as indicated. This study is aimed at obtaining information on the structure and conformation of this unit as well as its orientational order. For this purpose, exact simulation of the proton NMR spectrum is one of the most powerful methods provided the experimental spectrum is sufficiently well resolved (that is, it exhibits sufficient significant features) and the number of spins is not too large. In the case of ME9Sn polymers, these two conditions are not fulfilled because (i) the number of spins per repeat unit is very large ($12 + 2n$) and (*ii*) there are broadening effects due to slow motions (slow elastic modes[6]) and polydispersity (heterogeneity of macroscopic samples due to segregation by chain lengths[7]).

The first complication can be practically eliminated by deuteration of the spacers, thus reducing the number of protons to only 12. Each polymer can now be considered as the juxtaposition of x mesogens without magnetic interaction, because two consecutive mesogens are far apart from each other. Moreover, the linkage carboxylic group is magnetically inactive and relatively bulky, so that the broadening effect on the proton spectrum due to dipole interaction with the spacer deuterons is also very weak. The broadening effects due to the polymeric nature remain however, which blurr details of the spectra.

The broadening effect due to viscosity can be reduced by using short polymers. However, end-chain effects become more important and increase the degree of heterogeneity: the width of the nematic plus isotropic (N+I) biphase indeed increases for ME9Sn polymers when the average molecular mass decreases.[5,8]

The molecule 4,4′-diacetoxy-2,2′-dimethylazoxybenzene, hereafter labeled Ac9Ac, with chemical formula



may be considered as a model for the mesogenic unit of ME9Sn polymers.

Mixtures of Ac9Ac with perdeuterated *p*-azoxyanisole (PAAd14) have been studied in detail, and the results are described in ref 9. Bulk Ac9Ac is not nematic. The molecule has a poor mesogenic character, the virtual clearing point being about 220 K,[9] compared to 409 K for

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PAA. The consequence of this situation is the existence of a broad N+I biphasic range in the PAAd14/Ac9Ac phase diagram and of very long times to obtain homogeneous samples in NMR tubes, in which stirring is not possible.[7] The equilibrium properties of several Ac9Ac/PAAd14 mixtures are described in ref 9, and the kinetics of homogenization of these mixtures as well as of mixtures of ME9S*n* polymers with PAAd14 is described in ref 7.

Although the use of a small molecule in a low molecular mass nematic allows one to get rid of the broadening effect due to polydispersity and viscosity, two problems remain: (i) the existence of the two terminal methyl groups in the Ac9Ac molecule and (ii) the difficulty of obtaining Ac9Ac/PAAd14 mixtures with sufficiently uniform composition over the sample volume, ~0.1 cm^3. The first difficulty has been solved by synthesizing Ac9Acd6, deuterated on the terminal methyl groups, but the second difficulty can only be solved by patience. In fact, the most homogeneous nematic state is obtained when the sample is in the N+I biphase. The external part of the spectrum, which corresponds to the nematic component, is well resolved, but, clearly, the central part is completely hidden by the sharp signal of the isotropic component.

Figure 1 illustrates the effects described. Figure 1a is the proton spectrum of spacer-deuterated ME9S10 polymer with $x \sim 5.6$ (hereafter called DDA9d20 polymer), and Figure 1b is that of spacer-deuterated ME9S7 polymer with $x \sim 10$ (hereafter called AZA9d14 polymer), both in their nematic phase. These two polymers are the same as those used in ref 2. Figure 1c is the spectrum of Ac9Acd6 in solution (15% w/w) in PAAd14 at ≈90 °C in the pure nematic phase of the mixture, and Figure 1d is the spectrum of the same sample at a higher temperature, ≈116 °C, in the N+I biphase. It is observed that all these spectra are similar, although some small differences are apparent, in particular in the central part of the spectra. They are not symmetrical with respect to the center, showing that the various spins (essentially the phenyl and methyl protons) do not have the same chemical shifts. Spectrum 1d appears to be the best resolved spectrum, although the central part is completely hidden by the sharp isotropic component. Comparison between all spectra suggests that the central sharp peak on the spectrum of the polymers (Figure 1a,b) is probably due to residual isotropic droplets within the nematic samples, reminiscent of the N+I biphase which exists at higher temperature. This observation substantiates the effect of heterogeneity of composition on the proton line shapes. This effect is better seen on the deuterium line shapes of the polymers (cf. the spectra published in refs 1 and 2), and this aspect will be discussed in detail elsewhere. The present purpose is to obtain information on the structure and orientational order of the mesogenic unit in Ac9Acd6 and in the ME9S*n* polymers from exact simulation of the corresponding twelve spin $^1/_2$ system.

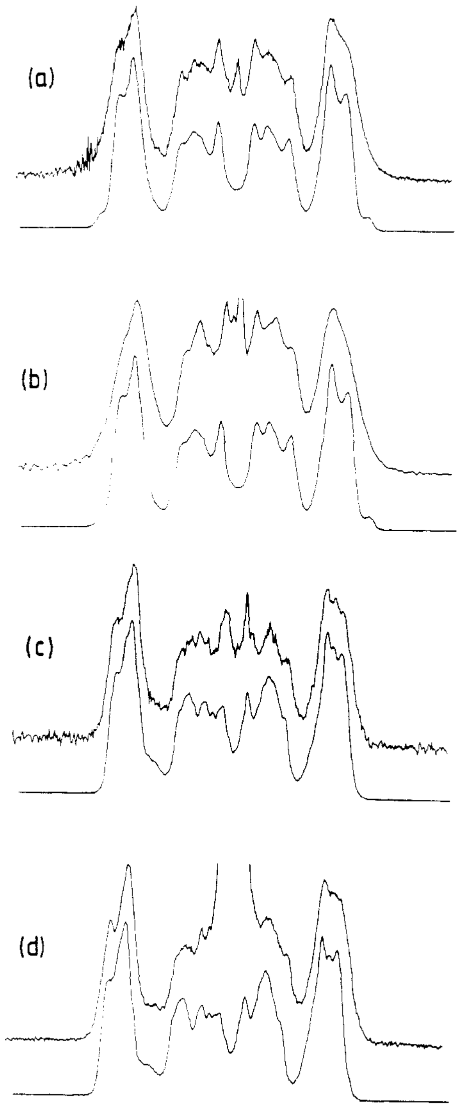

Figure 1. Experimental (upper) and simulated (lower) proton NMR spectra of DDA9d20 polymer (a) and AZA9d14 polymer (b) in their bulk nematic phase and of Ac9Acd6 dissolved in PAAd14 at ≈90 °C in the pure nematic phase (c) and at ≈116 °C in the nematic plus isotropic biphase (d). The uniaxial order parameter S_0 deduced from eq 1 and the relative chemical shift $\Delta\sigma$ (in ppm) used in the simulations are respectively 0.77 and 3.8 (a), 0.485 and 3.4 (b), 0.50 and 3.4 (c), and 0.33 and 3.6 (d). Note that the dipolar interactions used for spectra b and d are the same as those used for spectra a and c given in the Appendix, respectively, properly scaled by S_0.

2. Determination of Molecular Structure from Simulation of NMR Spectra

Simulation of the (single quantum or multiquantum) proton NMR spectrum of a molecule containing N protons in a fluid anisotropic medium requires knowledge of the $N(N-1)/2$ dipolar interactions and of the N chemical shifts with respect to an arbitrary reference. Indirect J–J couplings are also of interest, but they are usually small and they will be neglected here. The dipolar interactions are directly functions of the structure of the molecule and of the (anisotropic) motions of the spins. The chemical shifts are also functions of the latter. Ideally, the problem should be split into two parts. The first part would be to measure the dipolar interactions from the NMR experiments, and the second part would be to interpret these data in terms of molecular structure, conformation, and motions. The first part of this task becomes very difficult as soon as the number of spins becomes large (say larger than eight spins) and requires sophisticated multipulse methods and/or selective or random partial deuteration. This approach has been applied recently to *n*-hexane (a 14-proton system) in solution in a nematic solvent.[10] Even here, however, the complete unequivocal assignment of the interactions is impossible directly, and one has to rely on the use of models. This shows that, in practice, the two parts of the problem cannot be solved independently when the number of spins is large, as is the case here.

The other, more pragmatic, way to approach the problem is to assume a structure for the molecule, choose a model for the motions and order, calculate the dipole interactions, simulate the spectrum, and compare with the experimental spectrum. This trial and error method turns out to be

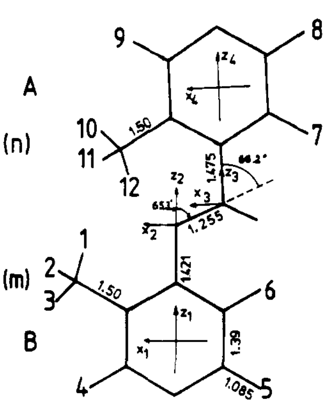

Figure 2. Sketch of the 2,2′-dimethylazoxybenzene moiety showing (i) the main bond angles, bond distances, and molecular frames used in the study and (ii) the labeling of the 12 proton spins.

very successful when sufficient reliable information is priorly known, in particular structural information. This method is used by several groups.[11,12] It is important, however, that the calculations are performed exactly.[12b,13] For the particular case of nematic PAA, the exact simulation of the proton spectrum of PAA deuterated on the methyl groups—an eight-proton system—using results obtained from deuterium NMR data has unambiguously demonstrated that the structure of the core is very close to that in the solid phase, that the two phenyl rings perform uncorrelated π-flips, and that the orientational order is biaxial.[13-15]

The present problem may be considered as a generalization of the PAAd6 problem in the sense that the core is the same, the only difference being the substitution of protons in positions 2,2′ on the rings by two methyl groups.

3. Modeling the 2,2′-Dimethylazoxybenzene Aromatic Core

This moiety is constituted by the succession of three rigid moieties, namely the methyl-substituted phenyl ring B, the CNNOC azoxy group, and the methyl-substituted phenyl ring A, linked by two single covalent bonds (Figure 2). In PAA, the alignments of the two rings are different[15] so that one might expect that the situation is the same here. A first indication of this asymmetry is given by the deuterium spectrum of Ac9Acd6 in PAAd14, which shows that the alignment of the two terminal methyl groups is not the same. This nonequivalence will become obvious when attempting to simulate the proton spectra.

An important aspect is that of the internal motions. Clearly, methyl group rotation, or rather jumps among three equivalent positions, are highly probable. The question of the ring flips about their para axis, which exists in PAA (more generally, in all molecules with normal or symmetrically substituted phenyl rings: to our knowledge, there is no known counterexample in fluid phases), is different here due to breaking of the C_{2v} symmetry of the rings by the presence of the methyl groups in the 2 position (and in the 2′ position). In several papers,[13-17] we have argued that, due to the similarity of the local molecular packing in solid and liquid phases of the same substance (solidlike picture of a liquid[17]), the only large-amplitude internal motions (i.e., motions which produce significant averaging of the magnetic interactions) allowed are symmetry operations. We shall thus assume here that the π-flips of the methyl-substituted phenyl rings are forbidden and that the only internal motions within the aromatic core are the methyl group rotations and exchange with the mirror image conformation. The conformations obtained after these symmetry operations are identical (or very similar), and the orientational orders of these conformations are described by the same order tensor. This allows the problem of the magnetic interactions in such nonrigid molecules to be treated in a completely rigid molecular geometry, inside which the spins are allowed to exchange via the symmetry operations. Since all the conformations are known if one of them is known, this model is called the single-conformation model (the name single-order tensor model would however be more appropriate). These ideas are discussed in detail in ref 17, but also in refs 14–16.

The calculation of the various dipole–dipole interactions, whose expressions are given elsewhere,[16] have been performed as follows. A frame is attached to each fragment, as depicted in Figure 2. Frame $Ox_1y_1z_1$ (frame B) is attached to ring B, with Oz_1 along the para axis and Ox_1 in the plane of the ring and directed toward the side where is located the methyl group. A similar convention is made for ring A, with index 1 replaced by index 4 (frame A). The rings are assumed to be perfect hexagons, with CC = 1.39 Å and CH = 1.085 Å. The angles CCH are fixed at 120°. With these values, the distance between ortho protons is 2.475 Å. A frame is also attached to the methyl groups with Oz along the threefold axis and the Ozx plane containing one methyl proton (by convention, proton 3 for methyl B and proton 12 for methyl A). The orientation of the methyl frame with respect to the ring frame is described by three Euler angles. The first one is clearly zero, the second is assumed to be close to 60° for ring B and close to 120° for ring A (they are fixed at these values in a latter stage of the simulation; see below), and the third angle φ_m describes the orientation of the methyl group ($\varphi_m = 0$ when proton 3 (or 12) is in the ring plane). The CC_{met} distance was chosen very close to 1.5 Å, according to the structure of *o*- and *p*-polyurea[18] and of vicinal polyketones,[19] where this distance is found to lie between 1.495 and 1.525 Å, depending on the particular methyl group considered. The CH distance in the methyl groups was fixed at 1.0946 Å and the $CC_{met}H$ angle at 109.47° as in ethoxybenzene.[16] In polyketones[19] it is in addition observed that the orientations of the several methyl groups with respect to the ring planes do not have any particular symmetry, implying that the two angles φ_m are not zero or π. They have been taken as adjustable parameters in our problem.

The two rings are linked by the CNNOC azoxy moiety. Its structure is assumed to be planar, with bond angles and distances identical to those of PAA in the solid phase.[20] (This structure was also chosen to simulate the ^1H NMR spectrum of PAAd6.[13]) The values are given in Figure 2.

Finally, the last problem concerns the relative orientations of the two rings with respect to the azoxy group. In PAA, the striking feature is that in the solid phase[20] (and probably also in the nematic phase[14]) the two para axes of the rings are neither parallel nor coplanar, and significative distortions exist, corresponding to misorientations of the outgoing CN bonds of several degrees with respect to the corresponding para axes. We have thus introduced two frames, $Ox_2y_2z_2$ (frame β) and $Ox_3y_3z_3$ (frame α), with Oz along the CN bonds and Ox in the plane of the azoxy group and oriented as indicated in Figure 2.

The motional parameters are reduced to a minimum. There is no free parameter for the internal motions. The external motions are described by the five elements of the (single) order tensor. For simplicity, it will be assumed that the order is uniaxial (the biaxiality is probably weak, in any case much weaker than in PAA[2]) and the remaining single-order parameter S_0 is just a scaling factor. The orientation of the principal frame with respect to the B frame is described by three Euler angles, U_1, V_1, and W_1. The first angle is undetermined (uniaxiality), while the other two angles represent the polar and azimuthal angles of the principal axis OZ in the B frame. These two angles correspond to the only effective motional parameters of the problem.

The geometrical parameters are the ten unknown angles mentioned below. The orientation of the β frame with respect to B is described by Euler angles U_2, V_2, and W_2, the orientation of frame α with respect to frame β by Euler angles 0, $-65.3° + 68.2° = 2.9°$, and 0 (the geometry of the azoxy group is assumed to be that of PAA), and, finally, the orientation of frame A with respect to frame α by Euler angles U_3, V_3, and W_3. We recall the two angles for the methyl groups, namely the orientations of the threefold axis in the ring planes, close to 60 (120)°, and the angles φ_m.

In total, there are 12 (in practice, only ten; see below) free parameters to be determined from the simulation. This seems a priori a very difficult task to determine unambiguously all these parameters from a single spectrum such as those of Figure 1. However, it will be seen that the features of these spectra are so particular that practically only a structure (very) close to those that will be proposed can account for these features in the framework of the single-conformation model.

4. Simulation Procedure

As mentioned in previous work,[13] exact simulation of proton spectra seems to be necessary to obtain very good (and thus unequivocal) results. The reason is that, in such molecules, it is not possible to split properly the total spin system into subsets with smaller numbers of spins (as required by the approximate methods[11-13]), because there are always interactions between spins of two subsets which are large. However, such a split may help in understanding the origin of some spectral features, as shown below.

The program used to simulate the spectrum of the twelve spin $^1/_2$ system considered here is an improved version of the algorithm used previously in the case of PAAd6.[13] The improvement lies in two facts: it can be used for any number of spins (the limitation is only the memory size of the computer) and the chemical shifts of all spins may be different. The full spectrum for twelve spins was calculated using a CRAY2 computer, while intermediate six-spin spectra were calculated with a laboratory (and less expensive) computer.

To begin the simulation, we assumed a symmetrical structure (same alignment for the two rings), with the principal axis OZ roughly along the elongation axis. Two chemical shifts were assumed, namely one for the phenyl protons and one for the methyl protons. The starting value of the relative chemical shift $\Delta\sigma$ was fixed to that measured (with a resolution of ~40 Hz) in the isotropic phase, namely $\Delta\sigma_{\text{iso}} \approx 4.9$ ppm, that is, 440 Hz for spectra taken at 90.14 MHz. The result of the simulation was very bad, whatever the dihedral angle between the rings. What could never be reproduced was the broad central part of the spectrum. It turned out that this situation occurred because the assumed structure was too symmetrical. The further step was thus to distort the molecule so that the alignments of the two rings were different. The situation improved significantly, but now the problem was to know how to describe exactly the distortion.

We thus turned to a simpler problem, namely what could be learned about the relative orientations of the two rings by ignoring the interactions between the rings, that is, by treating the problem as a two six-spin system constituted by the two methyl-substituted rings. This approach turned out to be very fruitful as it showed that the main features of the central part of the spectrum were mainly due to the intra-ring interactions. The interactions which played a major role in this analysis were the relative values of the ortho interactions D_{56} and D_{78} and that of intramethyl interactions D_{12} and $D_{10,11}$: a prerequisite for a good simulation was that these two latter interactions differ by roughly a factor of 2. After many attempts, it turned out that the least aligned ring was ring B (as in PAA[15]!) and that the corresponding methyl group was associated with the largest intramethyl interaction in absolute value. These findings gave hints on how the distortions, described by the various Euler angles mentioned above, should be chosen. These results are illustrated in Figure 3a–c, where are shown the two six-spin spectra corresponding to the two rings, calculated using values of the interactions of the final solution given below, as well as the average of these two spectra. Comparison of Figure 3c with the experimental spectra immediately reveals that the main features in the center of the spectrum are indeed due to interactions inside the six-spin systems. In particular, the doublet of sharp lines closest to the center of the spectra, well visible in the more symmetrical spectra of the polymers 1a and 1b, is essentially due to the intramethyl interaction $D_{10,11}$ of the more aligned ring A. However, comparison with Figure 1 shows that the two times six spin approximation is a bad approximation to reproduce satisfactorily the experimental spectra.

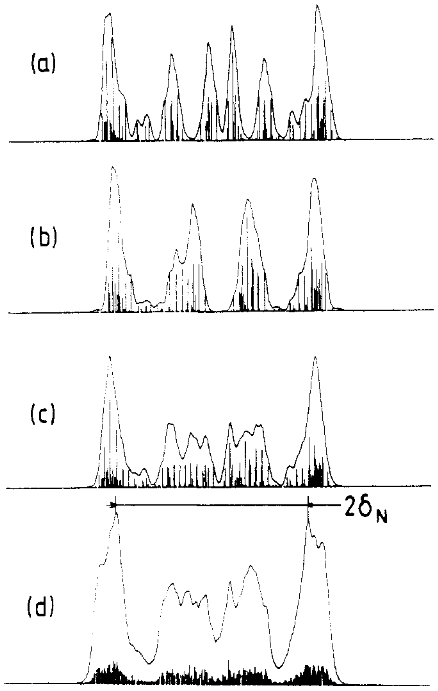

Figure 3. Simulated proton NMR spectra of the six-spin system constituted by ring A (a) and by ring B (b); average of spectra a and b (c); exact simulated spectrum of the twelve-spin system (d). The parameters are those for the best simulation of spectrum 1c.

The last part of the study thus consisted in introducing the inter-ring interactions and using the simulated (and expensive) twelve-spin spectrum to refine the simulations. The procedure was as follows: the values of the ten most important interactions were guessed to give the best simulations. These values were then introduced in a fitting program to find the values of the geometrical (and motional) parameters which allow these interactions to be reproduced. This geometry was then used to calculate all other interactions, and the spectrum was simulated again with these final values. The chemical shift was introduced as an asymmetry parameter of the spectrum, defined as the ratio of the (unknown) value of the shift to the main interaction D_{78}. This parameter cannot be considered on the same level as the other ones since it is determined by the position of the central part of the spectrum with respect to the large external doublet. This parameter is easily converted into the value of a chemical shift $\Delta\sigma$ (in ppm) by taking into account the actual width of the particular experimental spectrum considered.

This fitting procedure was a rather lengthy trial and error work. However, since the starting point was sufficiently close to the final solutions, convergence could be reached. The result is shown in Figures 3d and 1c,d for Ac9Acd6 and in Figure 1a for polymer DDA9d20, which correspond to two extreme situations. In Figure 1b is shown the theoretical spectrum corresponding to the geometry of polymer DDA9d20, but with a slightly larger chemical shift. The spectrum of polymer AZA9d14 clearly appears to be intermediate, although closer to that of DDA9d20. Thus two structures can be proposed, one for Ac9Ac and one for the polymers. It is not very useful to describe the various attempts that have been made to reach these solutions, but it may be worth mentioning the following:

(i) The two Euler angles describing the orientation of each methyl group within its ring frame played a complementary role—namely combinations of the two parameters gave identical results. Since the average value of the inclination crossed the value 60° (or 120°), we somewhat arbitrarily fixed these inclinations to these values and determined the orientation angles φ_m for the two groups as those yielding the best simulation. In this way, the number of parameters is reduced to ten as mentioned above.

(ii) The best fits to the experimental spectra are obtained with different values of the relative chemical shift. This shift decreases as the absolute width of the spectrum (proportional to S_0) increases (see below).

(iii) The fact that the fits to the experimental spectra of Ac9Acd6 (Figure 1c,d), for which there are a priori no broadening effects due to polydispersity or slow motions, are not perfect may have several causes, including (a) approximations made in the modeling, such as the choice of two different chemical shifts instead of at least eight, as suggested by the high-resolution spectra in the isotropic phase, the assumption that the azoxy moiety CNNC is a perfect plane, or even limitations of the single-conformation model itself, (b) inherent uncertainties associated with the fast Fourier transformation of an experimental free induction decay signal to obtain perfect line shapes, whatever the quality of the NMR spectrometer and the care with which the experiments are made (very broad spectral range, subtraction of an empty tube signal, etc.), and (c) imperfection of the partial deuteration, implying the contribution to the signal of nondeuterated and/or differently partially deuterated molecules. In view of all this, we can consider that the fits are satisfactory.

(iv) Finally, it is worth mentioning that introduction of biaxiality in the modeling does not improve significantly the simulations, in the sense that the effect of introducing some finite value of $(S_{XX} - S_{YY})/S_{ZZ}$ can be very easily compensated by slightly changing the geometrical parameters. This means that no significative information about the biaxiality can be extracted from these simulations only, except that it is probably weak, in agreement with the results of ref 2.

In the Appendix are given the values of the 30 dipolar interactions corresponding to the best simulated spectra of Ac9Acd6 and of DDA9d20 (shown in Figures 1c, d, and 1a, respectively).

5. Results

The optimized geometrical and motional parameters corresponding to the simulated spectra of Ac9Acd6 and of DDA9d20 polymer (in parentheses for the latter) are given below with all their numerical figures to allow the interested reader to repeat the calculations. The systematic errors are estimated to ~0.1° for polar angles and ~1° for azimuthal angles. For AZA9d14 polymer, the values are intermediate, although closer to those for DDA9d20 polymer: (i) Orientation of frame B with respect to the principal frame of the order tensor:

U_1, irrelevant due to uniaxiality

$$V_1 = 12.107° \ (11.242°)$$

$$W_1 = 82.238° \ (70.660°)$$

(ii) Orientation of frame β with respect to frame B:

$$U_2 = -54.257° \ (-63.939°)$$

$$V_2 = -10.210° \ (-11.576°)$$

$$W_2 = 15.642° \ (26.706°)$$

(iii) Orientation of frame A with respect to frame α:

$$U_3 = -33.180° \ (-32.695°)$$

$$V_3 = -2.595° \ (-2.491°)$$

$$W_3 = 7.559° \ (12.550°)$$

(iv) Orientation of methyl groups around the threefold axis, assumed to be inclined at 60° (120°) on the para axis:

$$\varphi_m{}^B = -5.060° \ (-3.587°)$$

$$\varphi_m{}^A = -26.69° \ (-1.272°)$$

From the above numbers, any geometrical quantity can be calculated. For example, the angle between the two para axes is 10.014° (11.568°). The value is 13.5° in solid PAA.[15] This angle being small, the dihedral angle between the two rings is given approximatively by $D \approx |U_2 + W_2 + U_3 + W_3| = 64.24°$ (57.38°) to be compared with 64.32° (57.82°) for the angle between the two normals to the rings (22.6° in solid PAA[15,20]). The two dihedral angles with the intermediate azoxy plane are $|U_2 + W_2| = 38.61°$ (37.23°) for ring B and $|U_3 + W_3| = 25.62°$ (20.14°) for ring A (19.7 and 3.0°, respectively, in solid PAA[20]).

It is interesting to note that these results are fully consistent with theoretical calculations on the isolated molecule made with the quantum semiempirical method PCILO:[22] the values found for these dihedral angles correspond to a point which is inside (or, for the polymer, very close to) a zone where the intramolecular energy is the lowest, namely zone I in the energy map represented in Figure 2 of ref 22.

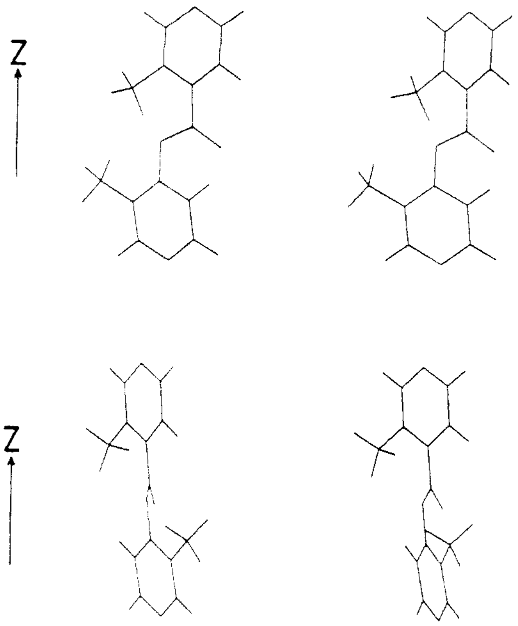

Figure 4. Stereoscopic projections of the mesogenic moiety of Ac9Acd6 dissolved in nematic PAAd14 in two perpendicular planes containing the principal axis OZ, assumed to be vertical. These two planes correspond approximately to the two bisector planes of the phenyl rings.

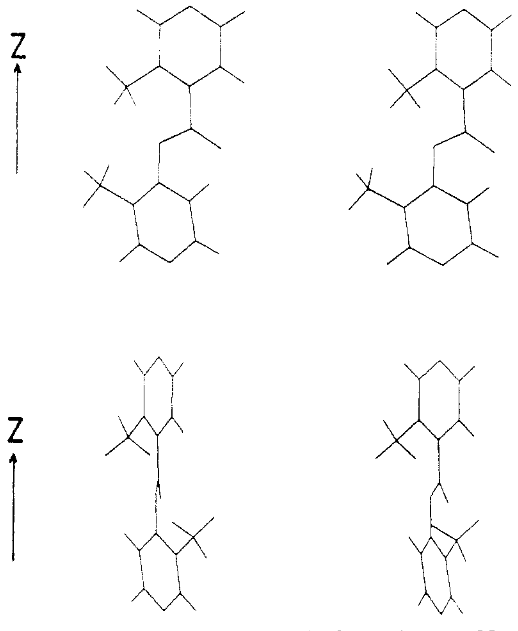

Figure 5. Same as Figure 4 for DDA9d20 polymer. Note that the moiety is globally more aligned along OZ than in Ac9Acd6.

It is observed that the differences between the structure of Ac9Ac (the monomer) in solution in PAA and the structures of the polymers in their neat nematic phase are rather subtle and lie in slight changes of the distortions, of less than 2° for polar angles and of a few degrees for azimuthal angles (except for the $\varphi_m{}^A$). Although small, these differences are sufficient to produce measurable changes in the spectra (because several angles are close to the magic angle).

Figures 4 and 5 show stereoscopic projections of the moiety in two perpendicular planes containing the principal axis O*Z*, and which roughly correspond to the two bisector planes of the phenyl rings (close to the two principal planes in a situation where the order is biaxial), for Ac9Ac and for DDA9d20. It is observed that the mesogenic moiety is more aligned along the principal axis in the polymer than in the monomer, and this result may be regarded as the contribution of the spacers (i.e., of the polymeric nature of the molecule) to the stretching of the mesogens.

The proportionality constant between the main splitting of the spectrum $2\delta_N$ as defined in Figure 3d and the main order parameter S_{ZZ} ($=S_0$ in the case of uniaxiality) is easily determined from the simulation by simply measuring the width of the simulated spectra. We obtain for the polymers

$$2\delta_N/\text{kHz} = (22.52 \mp 0.30)S_{ZZ} \qquad (1)$$

The error bar includes an uncertainty of ±0.01 Å on the distance between the ortho protons (the value of 2.475 Å is chosen in the simulations). It is worth noting that the proportionality constant of 22.74, assumed in previous works[2] and deduced from an approximate simulation of the spectrum of the nondeuterated DDA9 polymer,[21] is consistent with the present results and can thus still be used to estimate order parameters in spacer-deuterated ME9S*n* polymers (for normal polymers, the constant is larger, ≈24.06 (ref 2)). For Ac9Acd6 in PAAd14, the simulation yields a slightly smaller central value of 22.31.

Finally, the results concerning the chemical shifts $\Delta\sigma$ may be summarized as follows. For Ac9Acd6, the uncertainty on $\Delta\sigma$ deduced from the simulations is ≈±0.3, whereas for polymer DDA9d20, it is much larger, ≈1.5. It is easily shown that for uniaxial order $\Delta\sigma$ is given by (see, e.g., eqs 1–4 of ref 4)

$$\Delta\sigma = \Delta\sigma_{\text{iso}} - (\Delta\sigma_{\text{iso}} - \Delta\Sigma_{ZZ})S_0 \qquad (2)$$

where $\Delta\Sigma_{ZZ}$ is the component, along the principal axis O*Z*, of the difference between the chemical shift tensors of the phenyl and methyl protons. With $\Delta\sigma_{\text{iso}} = 4.9 \pm 0.3$ ppm, a least-squares fit of eq 2 to the three points for Ac9Acd6 yields $\Delta\Sigma_{ZZ} = 1.8 \pm 0.9$ ppm. Although we learn here that this anisotropic component is positive and smaller than $\Delta\sigma_{\text{iso}}$, this value by itself corresponds to very little information on the anisotropic part of this tensor.

6. Comparison with PAA

Besides the weak differences between the results for Ac9Ac (monomer) and the polymers already mentioned, the other interesting result of this study is the similarity with PAA, despite the presence of the two methyl groups. The similarities lie not only in the structure but also in the order.

For the structure, the most important similarity is the distorted character of the backbone constituted by the azoxy group and the two para axes of the rings. Apart from the absence of π-flips of the rings (which, incidently, have allowed such accurate information on the structure to be obtained due to nonaveraging of important interactions), the only significant differences lie in the larger values of the dihedral angles between the planes of the three moieties. However, as in PAA, the angle of the azoxy plane with ring B is larger than with ring A.

For the order, the similarities with PAA are even larger. Ring B is the least aligned ring. The inclination of its para axis on the principal axis O*Z* is $|\epsilon_B| = V_1 = 12.107°$ (11.242° for the polymer). The inclination of ring A is easily calculated, and its value is $|\epsilon_A| = 4.168°$ (≈0.3° for the polymer). In nematic PAA, reasonable values are $|\epsilon_B| \approx 12°$ and $|\epsilon_A| \approx 4.5°$.[14,15] This shows that the orientations of the principal axis with respect to this backbone are very similar in all molecules (practically the same for Ac9Ac and PAA).

All these similarities are probably to be associated with the high stability of the chemical structure of the azoxy group.

7. Conclusion

This study constitutes a further example which shows that simulation of (one quantum) proton NMR spectra in anisotropic media can be a powerful method to determine the structure of rather complex nonrigid molecules in a liquid phase. This has been possible because a simple theoretical framework has been chosen (the single-conformation model) and because exact simulation has been performed. To our knowledge, this is the first exact simulation with such a large number of spins (12). The structures, conformations, and orders of the aromatic core of Ac9Ac and of ME9S*n* polymers could be determined with reasonable accuracy, and analogies and differences with PAA could be put in evidence.

The most important result for the molecular physics of (polymer) liquid crystals that emerges from this study is the fact that the changes in the structure and order from monomer to polymer are rather weak. In particular, it appears that, in these nematic polymers at least, the orientational characteristics (essentially the orientation of the principal axis of the mesogen) are mainly determined by the nature of the mesogen and little by the length of the aliphatic spacer or the polymeric nature of the molecule. This result will be an important ingredient for the analysis of the deuterium NMR data of the corresponding spacer-deuterated dimers and polymers. Corresponding preliminary results have been presented in ref 1.

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Appendix

Here, we give the values (in kHz) of the 30 dipole–dipole interactions D_{ij} which correspond to Ac9Acd6 in PAAd14 and to DDA9d20 polymer. These interactions are defined by[16]

$$D_{ij} = -\frac{h\gamma_P^{\,2}}{4\pi^2}\left\langle\frac{P_2(\cos\theta_{ij})}{r_{ij}^{\,3}}\right\rangle$$

where r_{ij} is the distance between protons i and j and θ_{ij} is the angle between the vector ij and the static magnetic field. They correspond to the particular case where the orientational order is uniaxial and perfect ($S_0 = 1$). The numerical value of the constant $h\gamma_P^2/4\pi^2$ is 120.12 kHz·Å^3. The numbers correspond to Ac9Acd6. For polymers DDA9d20, they are given in parentheses. For simplicity, the (magnetically equivalent) spins of the methyl groups are labeled m for B and n for A.

intramoiety B		intramoiety A		intermoieties B–A	
i,j	D_{ij}	i,j	D_{ij}	i,j	D_{ij}
m,m	−1.8569 (−2.2802)	n,n	−0.9649 (−1.3777)	m,7	0.0451 (0.0430)
m,4	−3.1715 (−3.0499)	9,n	−3.6075 (−3.5884)	m,8	−0.0693 (−0.0682)
m,5	0.1018 (0.1250)	8,n	0.0529 (0.0755)	m,9	−0.2357 (−0.3042)
m,6	0.4388 (0.4444)	7,n	0.4180 (0.4329)	m,n	−0.3184 (−0.7475)
4,5	0.7606 (0.7529)	8,9	0.7608 (0.7623)	4,7	−0.1308 (−0.1287)
4,6	0.1036 (0.0518)	7,9	0.1591 (0.1178)	4,8	−0.0867 (−0.0869)
5,6	−7.4002 (−7.4713)	7,8	−7.8602 (−7.9225)	4,9	−0.1276 (−0.1439)
				4,n	−0.2715 (−0.3507)
				5,7	−0.4047 (−0.4084)
				5,8	−0.1697 (−0.1685)
				5,9	−0.1419 (−0.1372)
				5,n	−0.2505 (−0.2245)
				6,7	−0.8088 (−0.7869)
				6,8	−0.3550 (−0.3438)
				6,9	−0.3391 (−0.3163)
				6,n	−0.3523 (−0.2732)

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