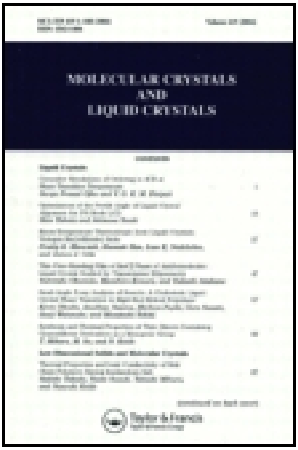

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Molecular Aspects in Main-Chain Nematic Polymers

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Molecular Aspects in Main-Chain Nematic Polymers

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Results concerning the nature of molecular orientational order and conformation of the flexible spacer $(CH_2)_n$ (n = 10 and 7) in a class of main-chain nematic polymers and corresponding dimer model compounds, are presented. The order is found to be biaxial, and the biaxiality increases with increasing both temperature and molecular mass. The conformations of even and odd spacers are found to be different and somewhat complementary. The two halves of even spacers are all trans with a significant defect localized on the central C—C bond. On the contrary, the central part of odd spacers is all trans and connected to the rest of the spacer by two C—C bonds with defects of the gauche type. These results have been obtained by analysis of NMR and magnetic susceptibility data in terms of a model in which the repeating units are assumed to exchange between two orientationally equivalent conformations, mirror images of one another. For dimer with n = 10, the results concerning the conformation of the spacer are contrasted with similar results of the literature, obtained from analysis of the same NMR data in terms of a model based on the Rotational Isomeric State (RIS) approximation. It is shown that the two models are conceptually different, and some of their consequences are discussed.

1. INTRODUCTION

In this paper, we want to review results obtained during these last years in our laboratories concerning the molecular conformation and orientational order in a class of main-chain polymers of the form $(RF)_x$, where R is a mesogenic unit and F a flexible spacer. These results have been obtained via the analysis of proton NMR, deuterium NMR and magnetic susceptibility data in terms of a simple model in which the repeating units are assumed to exist in essentially two equivalent conformations, mirror images of one another. Due to the limited space available, only the basic ideas and the most important results will be presented. A comparison will also be made with results of a similar study based on the Rotational Isomeric State (RIS) model, and we will try to explain why, in our opinion, our approach

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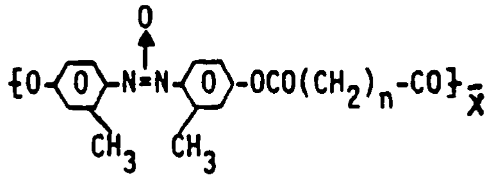
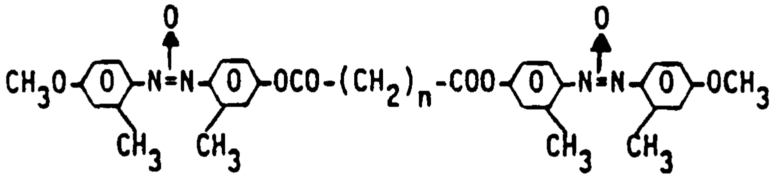
is closer to the physical reality. For details, the reader is directed to the corresponding references, some of them being published, and some other being in preparation.

2. EXPERIMENTAL

The general formula of the $(RF)_x$ polymers and corresponding RFR dimer model compounds studied are given below:





Polymers with $n = 7$ (odd) and $n = 10$ (even), labeled AZA9 and DDA9 polymers respectively, have been studied over a wide range of molecular lengths $\bar{x}$ ($4.4 \lesssim \bar{x} \lesssim 18.$) and temperature. Some polymers were deuterated on the spacers and called AZA9d14 (dimer 9AZA9d14) and DDA9d20 (dimer 9DDA9d20). The synthesis and characterisation of these polymers and dimers are extensively described in the literature.[1-7] Briefly, these compounds exhibit a nematic phase at reasonable temperatures, and the clearing temperature T_{IN} increases with molecular length $\bar{x}$ and levels off for $\bar{x} \geq 10$. A strong odd-even effect in the transition enthalpies and entropies ΔH_{IN} and ΔS_{IN} is observed.[1] This effect is accompanied by a corresponding odd-even effect in the orientational order, the nematic phase of odd polymers being significantly less ordered than that of even polymers.[4] The NMR experiments were performed with Brücker spectrometers (CXP90 for proton and WM250 for deuterium) and the magnetic susceptibility (MS) experiments with a S.H.E. SQUID magnetometer. Generally, the same samples were used, and the same experimental conditions were chosen (in particular the thermal histories), in the three kinds of experiments. This procedure allows accurate comparison between the temperature dependences of the various physical quantities measured, which is essential in the analysis. These physical quantities are (i) the width δ_o of the proton NMR (PMR) spectra, (ii) the anisotropy of magnetic susceptibility χ_a and (iii) the deuterium NMR (DMR) splittings $\Delta\nu_i$ associated with the various methylene deuterons of the deuterated spacers. Most of these data are presented in [8], and will not be reproduced here. Exception will be made for typical DMR spectra of AZA9d14 and

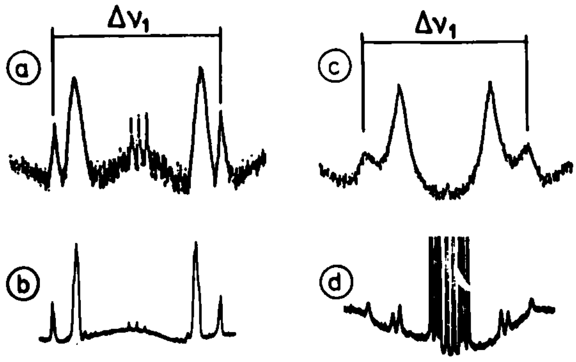


FIGURE 1 Typical deuterium NMR spectra of samples labelled on the spacers: a) polymer DDA9d20, $\bar{x} \sim 5.6$, $T = 107°\text{C}$; b) dimer 9DDA9d20, $T \approx 94°\text{C}$; c) polymer AZA9d14, $\bar{x} \sim 10.1$, $T = 128°\text{C}$; d) dimer 9AZA9d14 in solution (~ 10% w/w) in para-azoxyanisole (PAA). The central part of spectrum d) is the spectrum of a small amount of perdeuterated PAA (PAAd14). Spectral widths range typically between 60 and 100 kHz.

DDA92d20 polymers and those of the corresponding deuterated dimer compounds, which are shown in Figure 1.

3. MODEL

The philosophy underlying the model used to analyze the data has recently been developed in two papers devoted to molecular aspects in nematic para-azoxyanisole.[9,10] In short, this model pictures the molecules as objects (or a succession of objects constituted by the repeating units in the case of our polymers) whose orientational order with respect to the mean director can be characterized by a single ordering matrix. A single ordering matrix does not mean that the objects are rigid. It means that the possible internal motions exchange the objects between conformations whose orientational orders are characterized by the same matrix. Such is the case for motions that leave the conformation unchanged, typically π flips of phenyl rings and methyl group rotations. But more importantly, this is also the case for exchange of the conformation with the mirror image conformation, with respect to a plane containing the Oz principal axis. Such exchange can occur by (quasi) simultaneous rotations around the single covalent bonds, and will be called dynamical racemization. More specifically, if a conformation is characterized by a set of angles $\{\phi_i\}$ around successive single bonds, the mirror image conformation is characterized by the set $\{-\phi_i\}$. This racemization corresponds to large amplitude internal motions without any change of the orientation, at least as far as this orientation is characterized by a second rank order tensor. It insures that the two deuterons of a methylene group are magnetically equivalent, as is always observed with molecules containing no opticaly asymmetric chemical moiety, and allows substantial magnetic decoupling between neighbouring molecules, these two aspects being important for NMR.

Within the framework of this model, the parameters that must ideally be deduced from the comparison with experimental data are the two order parameters $S_{zz} = -S_{xx} - S_{yy}$ and $\delta = S_{xx} - S_{yy}$, three geometrical quantities characterizing the orientation of the principal frame of the ordering matrix, and a number of dihedral angles between adjacent moieties. For convenience, the data are split into two sets: (i) the data concerning essentially the mesogenic unit, namely δ_o, χ_a and the DMR splitting $\Delta\nu_1 = \Delta\nu_n$ associated with the first methylene groups of the spacer, which are used to estimate the order parameters and characterize the conformation at the level of the ester group and (ii) the other DMR splitting $\Delta\nu_i$ ($i = 2$ to $n - 1$) associated with the other methylene groups, which are used to characterize the conformation of the spacer. We successively review the corresponding results.

4. ORIENTATIONAL ORDER AND STRUCTURE OF THE LINKAGE GROUP

These results will only be briefly summarized here since they have been presented in a previous conference (Freiburg 1988) and have just been published.[8] The aim was essentially to investigate the nature of the order (uniaxial or biaxial) as a function of temperature, a molecular mass and parity of the spacer. The basic idea was this: since a single ordering matrix $\underset{\approx}{S}$ can be associated with the repeating unit, the average value of the component q along the director of any traceless molecular tensor $\underset{\approx}{Q}$ attached to this unit is given by:

$$\bar{q} = \frac{2}{3} S_{zz} (A_Q + B_Q \eta_s)$$

where

$$A_Q = Q_{zz} - \frac{1}{2}(Q_{xx} + Q_{yy})$$

and

$$B_Q = \frac{1}{2}(Q_{xx} - Q_{yy})$$

are the uniaxial and biaxial components of $\underset{\approx}{Q}$ in the principal frame of $\underset{\approx}{S}$, and $\eta_s = (S_{xx} - S_{yy})/S_{zz}$ is the anisotropy parameter of the molecular orientational order. Since A_Q and B_Q are constant, or weakly temperature dependent if one introduces small amplitude vibrations and librations, and since the ratios B_Q/A_Q are (very) different for the tensors associated with δ_o, χ_a and $\Delta\nu_1$, a careful comparison between the temperature dependences of ratios of these quantities allows to check if $\eta_s \neq 0$, and eventually determine its value and/or values of A_Q and B_Q. The results of this study are the following[8]: (i) for polymers $n = 7$ and 10, the molecular ordering is biaxial, and the biaxiality parameter η_s increases with increasing temperature, (ii) the biaxiality is very weak for the dimer model compounds and increases with increasing molecular mass of the polymers, (iii) this

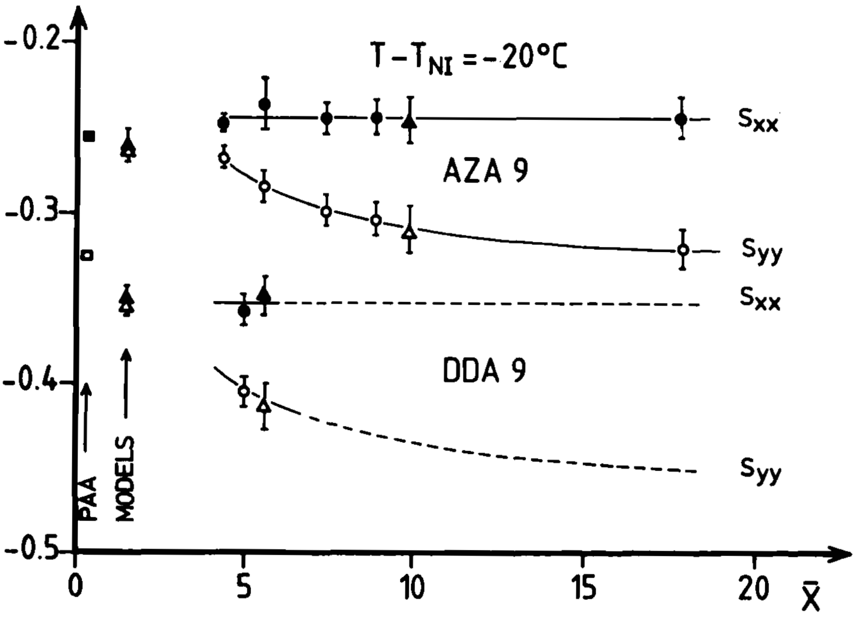


FIGURE 2 Chain length dependence of S_{xx} and S_{yy} for DDA9 and AZA9 polymers at $T - T_{NI} = -20°C$ (reproducted from [8]. Data for the dimers and PAA are also shown. The two order parameters $S_{zz} = - S_{xx} - S_{yy}$ and $\delta = S_{xx} - S_{yy}$ are easily deduced from these curves. Note that absolute values may be off by ~ 10% (cf. [8] for details).

increase of biaxiality, associated with a well established increase of the main order parameter S_{zz} (at fixed reduced temperature) allows to conclude that this increase of order occurs mainly via a decrease of S_{yy} and S_{xx} remaining constant; in other words, the order increases via a progressive reduction of the orientational disorder in the yOz plane, the disorder in perpendicular xOz plane (the easy plane) being not affected, (iv) and odd-even effect with the parity of the spacer, in phase with that of S_{zz}, is found for $S_{xx} - S_{yy}$, (v) the "plane" of the mesogenic core makes a large angle with the plane of the ester group. Results (iii) and (iv) are illustrated in Figure 2, extracted from [8].

5. CONFORMATION OF SPACERS

5.1 General

The work concerning this aspect is not yet completed: only partial but important results concerning the dimer model compounds have been obtained so far. In this study, the dimers are indeed a good starting point for two reasons (i) the lines of the DMR spectra are narrow and allow measurements of accurate DMR splitting $\Delta\nu_i$ (Figure 1b, d) and (ii) the biaxiality of the ordering being small,[8] it can be neglected in the calculations. The spectra of the polymers on the contrary are much broader (Figure 1a, c). This broadening comes from two factors: (i) polydispersity which produces significant broadening of the individual lines of each doublet, due to a distribution of order parameters inside domains of (slightly) different compositions[7,11] and (ii) static broadening which originates from the fact that a finite amount of elastic modes are slow on the NMR time scale.[12] A preliminary attempt to deconvolute the spectra from these two effects indicate that the basic spectra are very similar to those of the corresponding dimer, suggesting a similar conformation of the spacer in polymer and dimer. Before any calculation can be attempted, the problem of the assignment of the various slittings to specific methylene groups must be discussed. The only well accepted result is that for both dimers, the largest splitting corresponds to the first methylene groups $\Delta\nu_1$ (adjacent to the ester group). The other assignments are unknown. For $n = 10$ (Figure 1a), the four remaining splittings $\Delta\nu_2$, $\Delta\nu_3$, $\Delta\nu_4$, $\Delta\nu_5$ correspond in fact to 24 possible different assignments. However, these four values being very close to one another, a good starting point is to assume that these four splittings are equal. For $n = 7$ (Figure 1c), the assignment of $\Delta\nu_4$ is unambiguous for intensity reasons, so that only two possible assignments are left, namely $\Delta\nu_2$ is either larger or smaller that $\Delta\nu_3$. We have considered these two possible assignments in our analysis.

5.2. Theoretical Basis

Since the ordering is assumed to be uniaxial, the DMR splitting $\Delta\nu_i$ associated with deuterium D_i is given by

$$\Delta\nu_i = \frac{3}{2}\frac{e^2qQ}{h} S_{zz} \langle P_2 (\cos \theta_i)\rangle$$

where θ_i is the angle between the CD_i bond and Oz and $\langle\ \rangle$ symbolizes the average over the internal motions. For a given conformation of the spacer $\{\phi_i\}$, it is easy to express $P_2(\cos \theta_i)$ as a function of the $\{\phi_i\}$ and to average over $\pm\ \phi_i$ to account for the fast racemization, which is the only internal motion that we consider in the model. Small amplitude librations are neglected in the present simplified analysis. Since $n - 1$ angles ϕ_i (ϕ_2 to ϕ_n) are sufficient to characterize the conformation (cf. Figure 3), and that there are $n - 1$ ratios of splittings $\Delta\nu_i/\Delta\nu_1$, the problem can in principle be solved if the additional parameters of the problem are known. There are in fact two such parameters, namely the two angles which define the orientation of the Oz principal axis of $\underset{\approx}{S}$ in the frame of the spacer. These two quantities have been also treated as unknown parameters so that the problem reduces in the determination of $n + 1$ parameters with $n - 1$ data. In the calculation, all the structural angles, namely CCC, CCD and DCD have been chosen according to the literature, namely 113, 109 and 107.70° respectively, and the convention for the origin of the ϕ_i is such that the all-trans conformation corresponds to $\delta_i = 0$. ($i = 2$ to n). The definitions are summarized in Figures 3a and 3b for molecules with $n = 10$ and $n = 7$ respectively.

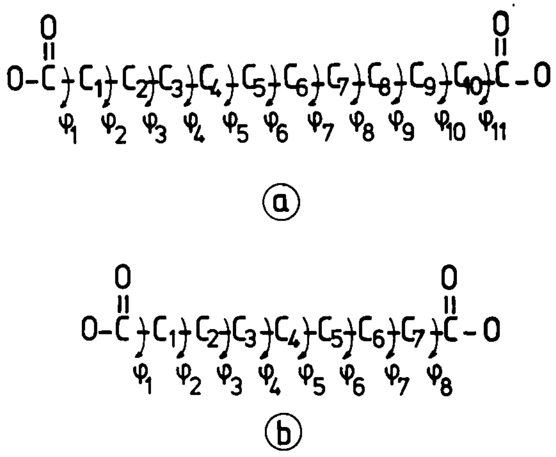


FIGURE 3 Schematic drawings of spacers, showing the labelling of the various carbon atoms C_i of bonds C_{i-1} C_i, and of torsional angles ϕ_i: a) DDA9: $n = 10$; b) AZA9: $n = 7$.

5.3. Results and Discussion

For $n = 10$, several solutions are found for practically each of the 24 possible assignments of the splittings. For $n = 7$, two solutions are found for each of the two possible assignments. Despite this undeterminacy, a remarkable fact emerges: for both $n = 10$ and 7, all solutions correspond to practically identical values for the angles ϕ_3 to ϕ_{n-1}, the differences between the various solutions lying in different values of ϕ_2 ($= \phi_n$), and in the orientation of Oz. In other words, the model predicts rather well defined conformations for the central part of the spacers.

For $n = 10$, typical values are:

$\phi_3 = \phi_9 \approx 0$, $\phi_4 = \phi_8 \approx 0$, $\phi_5 = \phi_9 \approx 0$, with ϕ_6 ranging between $\sim 40°$ and $80°$, and $|\phi_2| = |\phi_{10}|$ never larger than $\sim 30°$.

For $n = 7$, a typical set of solutions is:
With assignment $\Delta\nu_2 > \Delta\nu_3$

a) $\phi_3 = \phi_6 = 78.34°$, $\phi_4 = \phi_5 = 0.00°$, with $\phi_2 = \phi_7 = 16.40°$

b) $\phi_3 = \phi_6 = 78.34°$, $\phi_4 = \phi_5 = 0.00°$, with $\phi_2 = \phi_7 = 62.45°$

With assignment $\Delta\nu_2 < \Delta\nu_4$

a) $\phi_3 = \phi_6 = 83.50°$, $\phi_4 = \phi_5 = -4.45°$, with $\phi_2 = \phi_7 = 20.25°$

b) $\phi_3 = \phi_6 = 83.50°$, $\phi_4 = \phi_5 = -4.45°$, with $\phi_2 = \phi_7 = 57.32°$

Note that the two assignments lead to practically the same two possible conformations of the $n = 7$ spacer.

Close inspection of these results show that the conformations of even and odd spacers are somewhat complementary. Roughly speaking, the two halves of the even spacer are all trans, and are connected by a central C—C bond with a significant defect, whereas for odd spacers, the central part is all trans and followed by two C—C bonds with defects of the gauche type ($|\phi_3| = |\phi_6| > 60°$). The two last C—C bonds insure the linkage with the ester group presumably via (weak) defects of the trans type.

Concerning the conformation of the whole repeating unit, the problem is more complex, partly due to the non-unicity of the solution. A conclusion can be made only if independent information is introduced in the analysis. Such information is contained in the actual shape of the proton NMR spectra. Detailed analysis of such spectra is underway, and the results of this study as well as a more complete account of the present results will be published elsewhere.

6. COMPARISON WITH OTHER MODELS AND CONCLUSION

In this section, we compare the above results with results found in the literature concerning the analysis of similar NMR data on similar compounds. Several papers have been published on this subject[13–17] and fortunately, one of them[17] treats the case of the same $n = 10$ dimer (9DDA9d20). A detailed comparison will thus be made with the results of this particular paper. Generally, the above papers do not consider the problem of a possible biaxiality of the ordering, but essentially focus on the conformation of the flexible spacer. Comparison will thus be made on this particular aspect only.

In all these papers, the rotational isomeric state (RIS) approximation is the basic ingredient of the models. The picture is this: instead of molecules (repeating units) exchanging between two orientationally equivalent conformations as proposed in our model, in RIS type models, they exchange between a large number of (very) different conformations (conformers) defined by the relative states t ($\phi_i = 0$); g^+ ($\phi_i \approx +120°$) and g^- ($\phi_i \approx -120°$) of the successive C—C bonds of the spacer. In [17], a long axis is defined for each conformer as the line joining the centers of two consecutive mesogens, so that the orientation of each CD_i bond with respect to this axis is perfectly determined. The average of $P_2(\cos\theta_i)$ over all conformers is performed, and its value is fitted to the experimental data taking the statistical weights of the various conformers as adjustable parameters. A very good fit is thus achieved. The output of the calculation is the trans fraction f_t for each bond. Figure 4a shows f_t against bond number (defined as in Figure 3a) for $n = 10$ dimer, reproduced from Figure 4 of [17].

The question that arises at this stage of the discussion is now: how is it possible that two so different models can describe equally well the same data? The answer is because what is measured in the experiments, and consequently what is predicted by the models, are average values of functions—and very different functions can have the same average value. In the particular case of our problem, both models

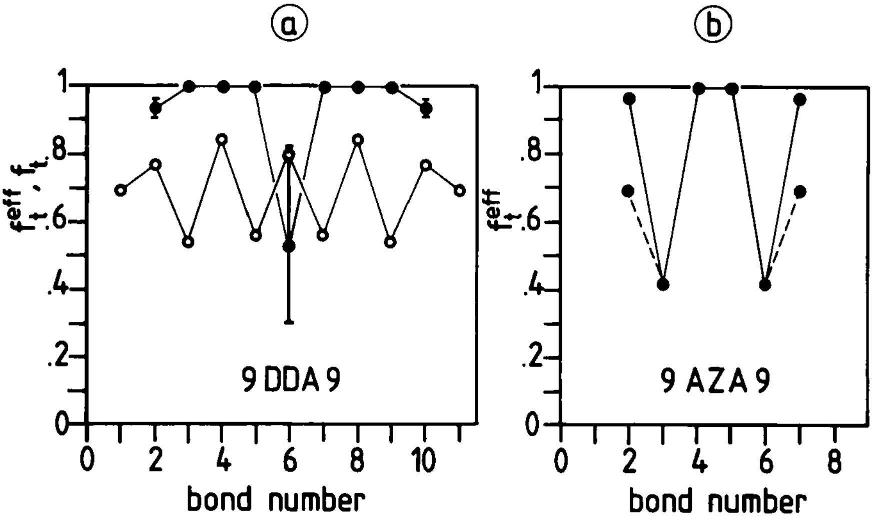


FIGURE 4 Trans fraction f_t predicted by the RIS type model of [17] (○) and effective trans fraction f_t^{eff} predicted by the present model (●) versus bond number as defined in Figure 3, for the two dimer model compounds: a) 9DDA9: $n = 10$; b) 9AZA9: $n = 7$. For $n = 10$, the error bars indicate the uncertainties existing at the present stage of the analysis, due to the non-unicity of the solution. For $n = 7$, the two possible solutions are shown. (see text for details).

predict identical values of $\langle P_2(\cos\theta_i)\rangle$. From this point of view, each of them can be considered as an equally valid operational model to describe the DMR data for $n = 10$ dimer. But the physical consequences may be very different.

To put the two descriptions on about the same basis, we have represented in Figure 4a, b the value of an *effective* trans fraction f_t^{eff} defined by:

$$\cos\phi_i = f_t^{\mathrm{eff}}\cos(0) + (1 - f_t^{\mathrm{eff}})\cos(120^\circ)$$

predicted by our model (effective because f_t has no real physical meaning in the framework of our model). It is seen that for $n = 10$, where a comparison can be made, our f_t are very different from those predicted by the RIS type model. More specifically, whereas our model predicts pure trans states ($f_t = 1$) for three consecutive bonds, the RIS type model of [17] predicts gauche states ($f_t \neq 1$) for all bonds, with an oscillation in f_t along the chain. Since such oscillation in f_t for even spacers has also been found by other authors in the analysis of similar DMR data, also using approaches based on the RIS model,[13–16] it may be concluded that this oscillation is a consequence of the RIS approximation. Another strong difference between the two models is that in our model, the defects appear to be well localized at specific sites on the spacer, whereas in RIS type models, these defects appear to be delocalized by the conformational changes.

The last question to be answered is: which model is the best? A pragmatic answer would be: the one which makes the better predictions. The predictions concerning the nature and localization of the torsional defects in the spacers could probably be checked by a careful analysis of relevant data obtained by other techniques, such as infra-red absorption or Raman scattering of light. In the absence of such check, at least for the particular systems considered here, we have to invoke some more heuristic arguments and consider more global predictions. A basic such argument in favour of our model comes from the fact that it keeps to the nematic phase its form of condensed matter. In this model, a nematic phase is pictured as a partially disordered solid phase, a view which is shared by most X-ray and neutron scattering experts. The local arrangement in a (pure) molecular liquid being similar to that of the corresponding solid phase, the racemization motion is the only one which appears to keep as closely as possible this local arrangement globally unchanged. All known crystallographic studies of solid phases of compounds exhibiting a nematic phase at higher temperature indeed show that the unit cell contains an even number (generally four) of molecules, whose conformations are two by two mirror images of one another. Thus, at the scale of a few molecules (or repeating units in the case of polymers), the situation must be essentially the same in the nematic and isotropic phases. The main difference between these two liquid phases does not lie in the short range order, but only in the long range orientational order. In that sense, this model predicts the correct ratio of transition entropies, at the clearing temperature, for even and odd dimers. This ratio is of the order of ~ 4, to be compared with a ratio of ~ 2 for the (long range) order parameters at the transition S_c.[6] (A S_c^2 dependence of the transition entropies is indeed predicted by the simplest molecular mean field theories). In RIS type models on the contrary, the isotropic phase is pictured as a gase phase in that sense that each molecule (or repeating unit in the case of polymers) can adopt and explore all the conformations allowed in the free state. According to this view, a nematic phase would be some kind of oriented gas phase in which a number of (highly non extended) conformations are forbidden and the remaining (more elongated) ones are pointing, in average, along some selected direction. Such a view is shared, at least implicitedly, by several NMR specialists dealing with liquid crystals, that adopt the RIS model to analyze NMR data.

This discussion leads to another difference between the two kinds of models and will allow one of the above mentioned global predictions. This difference concerns the magnitude of the entropy change ΔS_{IN} at the clearing transition. A RIS type model predicts that this change comes from two contributions: a conformational part coming from the difference in the number (and energy) of allowed conformations between isotropic and nematic phases, $\Delta_{IN}^{\text{conf}}$ and an orientational part coming from the (long range) ordering, $\Delta S_{IN}^{\text{ord}}$. For $n = 10$ dimer, the experimental value of ΔS_{IN} is $\approx 25.12\ \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$.[6] The value of $\Delta S_{IN}^{\text{conf}}$ predicted by the RIS type model of [17] is $28.32\ \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ whereas for our model, this contribution is essentially zero since the number of allowed conformations is the same (namely two) in the two phases.[18] The orientational part on the other hand, which should be about the same for both models, can be roughly estimated by comparison with para-azoxyanisole (PAA), assuming a S_c^2 dependence (PAA is a reasonable candidate due to the similarity of its structure with that of the mesogenic units of our dimers and polymers). With $S_c \sim 0.6$[6] and ~ 0.35[9] for dimer $n = 10$ and PAA respectively, and ΔS_{IN} (PAA) $\approx 8.71\ \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$,[6] we obtain $\Delta S_{IN}^{\text{ord}} \approx 25.60\ \text{J kg}^{-1} \cdot \text{K}^{-1}$, that is, practically the experimental value. Although the excellent agreement between these two values is probably rather fortuitous, it is seen that there is no need to invoke any significant conformational contribution to the transition entropy to account for the experimental data. From this point of view, at least, our model appears toi be better than the RIS type model of Reference 17.

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18. Strictly speaking, this statement is rigorous only if the conformations of the repeating units in nematic and isotropic phases have the same internal energies. This may not be the case since the conformations in both phases are probably (slightly) different. Therefore, there is a contribution to the transition entropy coming from the difference in the two internal energies. However, this contribution is expected to be relatively (very) weak compared to that coming from the long range orientational ordering. Note that such ordering includes a possible transition from coiled to extended conformation of the whole polymer chain.