AN INTERNAL ORDER APPROACH TO THE INVESTIGATION OF INTRAMOLECULAR ROTATIONS IN LIQUID CRYSTALS BY NMR: 3-PHENYL-THIOPHENE IN PCH AND PHASE IV

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The internal order parameter formalism is used to analyze the proton NMR spectrum of 3-phenyl-thiophene in two nematic phases: PCH and phase IV. Using a maximum-entropy approach we have obtained from the experimental dipolar couplings purely orientational order parameters for the two rings as well as an approximate rotamer distribution. The distribution in PCH peaks at 27° with a much smaller hump at 90° while the distribution in phase IV again peaks at 27° but is much broader, suggesting a noticeable solvent effect.

1. Introduction

The determination of structural parameters for rigid and non-rigid molecules in the fluid phase has been an important field of study for a number of years [1–4]. Nuclear magnetic resonance of molecules dissolved in liquid crystals (LXNMR) has long proved a useful technique for structural determinations on rigid solutes [1,2]. However, all the techniques applied to flexible molecules – including LXNMR – have met various difficulties, some of a theoretical nature concerning the description of ordering in these systems, and some connected with the extraction of the relevant information from the experimental data [3,5]. The description of orientational ordering in molecules with internal degrees of freedom has been considered by various authors [6–11]. In most of these different approaches a non-rigid molecule is considered as a collection of conformers, each treated as a rigid molecule. For example in refs. [6,9,10] an ordering matrix is assigned to every conformer and one is also calculated by averaging over the conformers. Here we employ an alternative approach, presented in ref. [11], where a rotameric molecule is considered to be made up of rigid fragments, with a certain distribution of interfragment angles. The orientation of one particular fragment is given with respect to the laboratory and the orientaton of the others is specified with respect to the previous one. Within this picture a rigid molecule is just a special case of a flexible one with complete internal order. The goal of this study is to show how to apply this internal order approach to obtain conformational information in the fluid phase. The treatment will be very briefly summarized and applied to a re-analysis of the proton dipolar couplings of 3-phenyl-thiophene (PTP). This molecule was studied elsewhere [12] with a more conventional approach and we shall emphasize the additional information that can be obtained with the new method. In particular, we obtain the best approximate rotamer distribution compatible with the experimental data.

2. Internal order parameter formalism

The orientation of a classical rigid particle is specified by three orientational parameters ω, e.g. three Euler angles α, β, γ [13]. The characterization of the state of a non-rigid molecule requires extra variables [14]. We are interested in molecules with internal rotors [5] and we consider them as a collection of rigid subunits rotating one with respect to the other. A relatively general treatment was given in ref. [11]; here we shall concentrate on a molecule with just one internal rotor, i.e. 3-phenyl-thiophene (see fig. 1). We assume that a coordinate frame M_i can be placed on each of the two fragments and we shall conventionally call one of the two fragments the "rigid" one. We define its orientation with respect to the laboratory frame while the orientation of the other ("mobile") fragment will be given with reference to the first one. Although the choice of the two frames is in principle completely arbitrary, it is reasonable to choose the reference fragment as the best characterized one for the experiment at hand. For our specific example we choose the phenyl fragment as the "rigid" fragment and the thiophene as the "mobile" one.

We write the probability of finding the molecule in a certain orientational–conformational state as the probability of finding the first fragment at orientation ω with respect to the laboratory director frame and the second fragment at an angle ϕ from the first, i.e. $f(\omega, \phi)$. This one-particle distribution is then expanded in a composite Wigner–Fourier basis set. We have

$$f(\omega,\phi)=\sum_{L,m,n,q}\left(\frac{2L+1}{16\pi^3}\right)f^L_{mnq}D^{L*}_{mn}(\omega)\times\exp(-iq\phi), \qquad (1)$$

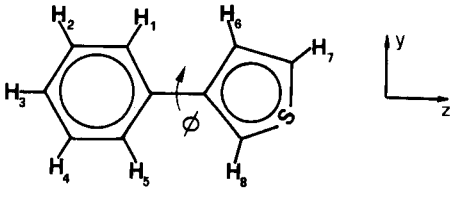

Fig. 1. Structure and atomic labeling of 3-phenyl-thiophene together with the phenyl axis system. The thiophene ring system is rotated over an angle ϕ from the phenyl ring.

where $D^L_{mn}(\omega)$ is a Wigner rotation matrix [13] and in general $q=0, \pm1, \pm2, \ldots$. The angle ϕ, with $0\leqslant\phi\leqslant2\pi$, is the dihedral rotation angle around the interfragment vector between the two fragments. The orthogonality relation of the chosen basis immediately yields the expansion coefficients as

$$f^L_{mnq}=\langle D^L_{mn}(\omega)\exp(iq\phi)\rangle, \qquad (2)$$

where the angular brackets denote an orientational–conformational average over the distribution $f(\omega, \phi)$. As usual [15] the singlet distribution expansion coefficients are related to the order parameters for the system. A uniaxial phase rotational invariance around the director gives $f^L_{mnq}=f^L_{0nq}\delta_{m0}$. We have, as discussed in ref. [11], three types of order parameters:

Purely orientational

$$f^L_{0n0}=\langle D^L_{0n}(M_1-L)\rangle. \qquad (3)$$

We have used the notation $B-A$ to indicate the rotation from A to B, e.g. here $M_1-L\equiv\omega$. This type of expansion coefficient is essentially an ordinary orientational order parameter for the molecular frame. It gives the average orientation of the reference fragment of the molecule with respect to the director frame, whatever the conformation.

Purely internal

$$f^0_{00q}=\langle\exp(iq\phi)\rangle, \quad q=0, \pm1, \pm2, \ldots. \qquad (4)$$

These parameters describe the ordering of the second part of the molecule with respect to the first irrespective of the overall orientation. They are quite important since they can be considered expansion coefficients of the rotameric distribution $f(\phi)$ in the fluid obtained by integrating eq. (1) over ω. They can be different from zero even in the isotropic phase if there is some preferential orientation of the second fragment around the internal axis.

Mixed internal–external order parameters. These parameters arise when both L and q are different from zero in eq. (2). They describe coupling between internal and external degrees of freedom. As we shall see, a particular subset allows the recovery of purely orientational order parameters for the second subunit.

3. Data analysis

Our aim here is to obtain as much information as possible on $f(\omega, \phi)$ from an analysis of the available dipolar couplings. To do this, we first relate these to the various types of order parameters introduced. If we choose our laboratory system with the Z axis along the director, the experimental component of the nuclear dipolar coupling $\langle [T_{ij}]^{2,0}_{\mathrm{LAB}} \rangle \equiv \sqrt{\frac{3}{2}} D_{ij}$ between two nuclei i and j can be written as

$$\langle [T_{ij}]^{2,0}_{\mathrm{LAB}} \rangle = \sum_n \langle D^{2*}_{0n}(M_1 - L) [T_{ij}]^{2,n}_{M_1} \rangle \,. \tag{5}$$

For a molecule with one internal rotor we have three possibilities:

(i) The two nuclei i and j belong to the fragment on which the molecular frame has been placed. In this case $[T_{ij}]^{2,n}_{M_1}$ are constant whatever the conformation and we have

$$\langle [T_{ij}]^{2,0}_{\mathrm{LAB}} \rangle = \sum_n (-1)^n f^2_{0\,-n0} [T_{ij}]^{2,n}_{M_1} \,,$$

$$i, j \in M_1 \,. \tag{6}$$

These couplings can be employed to obtain the ordering matrix of the rigid part. The situation here is formally the same as that of a truly rigid molecule. In PTP we have six couplings for the phenyl ring, D_{12}, D_{13}, D_{14}, D_{15}, D_{23} and D_{24}, which can be used to obtain the parameters $f^2_{00,0}$ and $f^2_{02,0}$, needed to specify the orientational order of the phenyl fragment, assumed planar.

(ii) The two nuclei both belong to the second ("mobile") part of the molecule. The molecular frame couplings $[T_{ij}]^{2,n}_{M_1}$ exhibit in this case a dependence on the internal rotation angle ϕ which could be removed by a change of frame. Indeed, when $i, j \in M_2$ eq. (5) becomes

$$\begin{aligned} &\langle [T_{ij}]^{2,0}_{\mathrm{LAB}} \rangle \\ &= \sum_{m,n} \langle D^{2*}_{0m}(M_1 - L)\, D^{2*}_{mn}(M_2 - M_1) \rangle [T_{ij}]^{2,n}_{M_2} \\ &= \sum_n \langle D^{2*}_{0n}(M_2 - L) \rangle [T_{ij}]^{2,n}_{M_2} \end{aligned} \tag{7}$$

by transforming to a frame M_2 fixed on the second fragment and coupling the two Wigner rotation matrices with the closure relation. For a molecule where the internal rotation axis coincides with the molecular frame z axis, we have

$$D^{L*}_{mn}(M_2 - M_1) = \delta_{mn} \exp(in\phi) \tag{8}$$

and eq. (7) becomes

$$\langle [T_{ij}]^{2,0}_{\mathrm{LAB}} \rangle = \sum_n (-1)^n f_{0\,-nn} [T_{ij}]^{2,n}_{M_2} \,,$$

$$i, j \in M_2 \,. \tag{9}$$

These couplings therefore give information about the alignment of the second fragment. It is interesting to see that if enough information is available on the ordering of the first fragment and the internal distribution, the order parameters of the second ring $f_{0\,-nn}$ can be obtained even when the number of couplings within the second ring is by itself insufficient. We shall take advantage of this in PTP where the ordering matrix of the thiophene ring could not be obtained from a standard analysis [12].

(iii) Each of the two nuclei belongs to a different sub-unit. These are the couplings that allow us to obtain information on intramolecular rotation. We have [11]

$$\langle [T_{ij}]^{2,0}_{\mathrm{LAB}} \rangle = \sum_n \langle D^{2*}_{0n}(M_1 - L) [T_{ij}]^{2,n}_{M_1}(\phi) \rangle \,,$$

$$i \in M_1, j \in M_2 \,, \tag{10}$$

where the dipolar coupling between the two nuclei, being a function of the internuclear distance (see, e.g. ref. [4]), is now a function of the internal rotation angle ϕ. By Fourier expansion of the tensor component $[T_{ij}]^{2,n}_{M_1}(\phi)$ we can write

$$[T_{ij}]^{2,n}_{M_1}(\phi) = \sum_q [T_{ij;q}]^{2,n}_{M_1} \exp(iq\phi) \,. \tag{11}$$

The couplings $[T_{ij}]^{2,n}_{M_1}(\phi)$ and therefore the Fourier components $[T_{ij;q}]^{2,n}_{M_1}$ can of course be computed for every pair of nuclei when the geometry of the fragments is known. In fig. 2 we show as an example the Fourier components for the coupling $[T_{16;q}]^{2,n}_{M_1}$ calculated from the skeleton geometry given in ref. [12] for PTP in phase IV. We report Fourier components from $q = -10$ to 10. Substitution of eq. (11) in eq. (10) thus gives

$$\begin{aligned} &\langle [T_{ij}]^{2,0}_{\mathrm{LAB}} \rangle \\ &= \sum_n \sum_q \langle D^{2*}_{0n}(M_1 - L) \exp(iq\phi) \rangle [T_{ij;q}]^{2,n}_{M_1} \\ &= \sum_n \sum_q (-1)^n f^2_{0\,-nq} [T_{ij;q}]^{2,n}_{M_1} \,, \end{aligned} \tag{12}$$

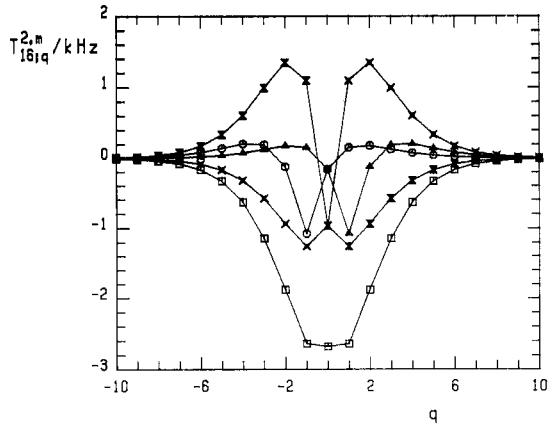

Fig. 2 The Fourier components $[T_{16;q}]^{2,n}_{M_1}$ from $q=-10$ to 10. We report the non-vanishing parts, i.e. $\mathrm{Re}[T_{16;q}]^{2,0}_{M_1}$ (squares), $\mathrm{Re}[T_{16;q}]^{2,2}_{M_1}$ (circles), $\mathrm{Re}[T_{16;q}]^{2,-2}_{M_1}$ (triangles), $\mathrm{Im}\,[T_{16;q}]^{2,1}_{M_1}$ (crosses) and $\mathrm{Im}\,[T_{16;q}]^{2,-1}_{M_1}$ (hourglasses). The line connecting the points is just a guide to the eye.

where $n=0, \pm1, \pm2$, $q=0, \pm1, \pm2, \pm\ldots$. We see that this type of coupling contains information on internal order parameters. Dipolar couplings between different pairs of nuclei i and j can be expressed in terms of the same set of order parameters $f^2_{0n,q}$. The Fourier series in q is, strictly, an infinite one and the number of parameters is not limited by an orthogonality selection rule as in the rigid solute case. The convergence of the Fourier expansion of $[T_{ij}]^{2,n}_{M_1}(\phi)$ will somewhat limit the number of relevant terms but, as we can see from fig. 2, the convergence is not necessarily fast. If enough couplings can be collected a fitting procedure similar to that employed in the rigid molecule limit [1,2] can be used to extract a set of order parameters. In general this will not be possible, but in a sense the slow convergence can be an advantage, since it means that the quantities we measure contain contributions from higher harmonics. This in turn would allow in principle a better determination of the internal rotational distribution. The problem of course is that we only have a finite and often small number of experimental couplings to employ in this determination. We shall thus resort to using a maximum entropy technique [16], which is a powerful tool in the approximate solution of underdetermined inverse problems of this type [17–19]. As we have seen, the most general form the dipole coupling can take is that of an average of a suitable set of second-rank Wigner–Fourier functions (see eq. (12)). Indeed the most general form for the dipolar coupling between i and j when the molecule is at orientation ω and conformation angle ϕ is

$$[T_{ij}]^{2,0}_{\mathrm{LAB}}(\omega,\phi) = \sum_n \sum_q [T_{ij;q}]^{2,n}_{M_1} D^{2*}_{0n}(\omega)\exp(\mathrm{i}q\phi)\,, \tag{13}$$

where we can formally set

$$[T_{ij;q}]^{2,n}_{M_1} = \delta_{q,0}[T_{ij}]^{2,n}_{M_1} \quad \text{if } i,j \in M_1\,,$$

$$[T_{ij;q}]^{2,n}_{M_1} = \delta_{q,n}[T_{ij}]^{2,n}_{M_2} \quad \text{if } i,j \in M_2\,.$$

Note that this expression holds for rigid molecules as well. The LXNMR experiment determines averages of a set of these angular functions over $f(\omega,\phi)$. Thus the best (least biased) approximation to the true distribution in the uniaxial mesophase obtainable from a LXNMR experiment will be of the form

$$f(\omega,\phi) = \exp\left(\sum_{n,q} a_{n;q} D^{2*}_{0n}(\omega)\exp(\mathrm{i}q\phi)\right), \tag{14}$$

where the coefficients $a_{n;q}$ are determined by minimizing the squared difference between the experimental couplings and those obtained by integrating eq. (13) over $f(\omega,\phi)$. More precisely we calculate averages

$$\langle [T_{ij}]^{2,0}_{\mathrm{LAB}} \rangle = \int \mathrm{d}\omega\,\mathrm{d}\phi\,[T_{ij}]^{2,0}_{\mathrm{LAB}}(\omega,\phi) \times \exp\left(\sum_{n,q} a_{n;q} D^{2*}_{0n}(\omega)\exp(\mathrm{i}q\phi)\right), \tag{15}$$

where

$$a_{n;q} = \sum_{\langle ij \rangle} \lambda_{ij}[T_{ij;q}]^{2,n}_{M_1} \tag{16}$$

and the λ_{ij} are Lagrange multipliers to be determined by non-linear least-squares minimization of the difference between the measured and the trial couplings. The sum runs over the subset of couplings $\langle ij \rangle$ that we include to try and fit the whole set. The coefficient $a_{0;0}$ is obtained from the normalization condition $\langle 1 \rangle = 1$. The procedure was tested first on a molecule containing protons and observable dipolar couplings only on the rigid fragment. Thus we reanalyzed data for nitrobenzene in PCH employing the geometry in ref. [20] and we were able to re-

cover the same values published in ref. [21] for the order parameters.

4. Results and discussion

For PTP in PCH and in phase IV we have respectively 18 and 17 utilizable experimental couplings (D_{78} is very small and comparable to its error in phase IV) [12] which we have fitted with a total of seven parameters each: λ_{12}, λ_{15}, λ_{16}, λ_{17}, λ_{26}, λ_{36} and λ_{67}. A few tests show that inclusion of further parameters does not significantly improve the fit. Notice that the six couplings on the phenyl and the three of the thiophene can be determined by the order parameters $f^2_{00,0}, f^2_{02,0}, f^2_{0-1,1}, f^2_{0-2,2}$. As mentioned before the geometry for the two rings has been taken from ref. [12]. The root-mean-square error of the two fits is 2.1 Hz for PCH and 1.6 Hz for phase IV. The matrix of coefficients $a_{n,q}$ obtained for the two solvents defines the orientational conformational distribution. In table 1 we give these coefficients for $|q|$ up to 12. Here we give two examples of interesting observables. First we show in table 2 the order parameters we have obtained for the two rigid rings.

Table 2
Order parameters for the phenyl (M_1) and the thiophene (M_2) rings

Order parameters	PCH	Phase IV
$\mathrm{Re}\langle D^2_{00}(M_1-L)\rangle$	0.4281 ± 0.0002	0.2756 ± 0.0002
$\mathrm{Re}\langle D^2_{02}(M_1-L)\rangle$	-0.0859 ± 0.0002	-0.0252 ± 0.0001
$\mathrm{Im}\langle D^2_{01}(M_2-L)\rangle$	0.0007 ± 0.0001	-0.0216 ± 0.0001
$\mathrm{Re}\langle D^2_{02}(M_2-L)\rangle$	-0.0835 ± 0.0002	-0.0186 ± 0.0002

Table 1
The first coefficients $a_{n;q}$ defining the maximum entropy distribution (eq. (14)) as obtained for phenyl thiophene in PCH and in phase IV. The estimated error is in the fourth figure (not shown)

q	PCH					Phase IV				
	$a_{0;q}$	$a_{-1;q}$	$a_{1;q}$	$a_{-2;q}$	$a_{2;q}$	$a_{0;q}$	$a_{-1;q}$	$a_{1;q}$	$a_{-2;q}$	$a_{2;q}$
0	1.476	0.000	0.000	−1.385	−1.385	0.848	0.000	0.000	−0.189	−0.189
1	0.000	0.316	0.179	0.000	0.000	0.000	0.058	0.101	0.000	0.000
−1	0.000	0.179	0.316	0.000	0.000	0.000	0.101	0.058	0.000	0.000
2	1.817	0.000	0.000	−0.998	−1.106	0.671	0.000	0.000	−0.213	−0.111
−2	1.817	0.000	0.000	−1.106	−0.998	0.671	0.000	0.000	−0.111	−0.213
3	0.000	−0.902	−0.624	0.000	0.000	0.000	−0.220	−0.228	0.000	0.000
−3	0.000	−0.624	−0.902	0.000	0.000	0.000	−0.228	−0.220	0.000	0.000
4	−0.850	0.000	0.000	−0.218	0.142	−0.322	0.000	0.000	−0.044	0.050
−4	−0.850	0.000	0.000	0.142	−0.218	−0.322	0.000	0.000	0.050	−0.044
5	0.000	0.513	−0.327	0.000	0.000	0.000	0.195	−0.116	0.000	0.000
−5	0.000	−0.327	0.513	0.000	0.000	0.000	−0.116	0.195	0.000	0.000
6	−0.332	0.000	0.000	0.140	0.047	−0.119	0.000	0.000	0.053	0.016
−6	−0.332	0.000	0.000	0.047	0.140	−0.119	0.000	0.000	0.016	0.053
7	0.000	0.180	−0.088	0.000	0.000	0.000	0.065	−0.031	0.000	0.000
−7	0.000	−0.088	0.180	0.000	0.000	0.000	−0.031	0.065	0.000	0.000
8	−0.082	0.000	0.000	0.050	0.012	−0.029	0.000	0.000	0.018	0.004
−8	−0.082	0.000	0.000	0.012	0.050	−0.029	0.000	0.000	0.004	0.018
9	0.000	0.044	−0.020	0.000	0.000	0.000	0.015	−0.007	0.000	0.000
−9	0.000	−0.020	0.044	0.000	0.000	0.000	−0.007	0.015	0.000	0.000
10	−0.018	0.000	0.000	0.012	0.003	−0.006	0.000	0.000	0.004	0.001
−10	−0.018	0.000	0.000	0.003	0.012	−0.006	0.000	0.000	0.001	0.004
11	0.000	0.009	−0.004	0.000	0.000	0.000	0.003	−0.001	0.000	0.000
−11	0.000	−0.004	0.009	0.000	0.000	0.000	−0.001	0.003	0.000	0.000
12	−0.004	0.000	0.000	0.003	0.001	−0.001	0.000	0.000	0.001	0.000
−12	−0.004	0.000	0.000	0.001	0.003	−0.001	0.000	0.000	0.000	0.001

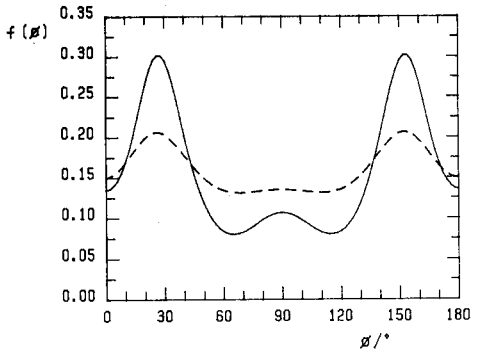

Fig. 3. The probability distribution of finding the thiophene ring at an angle ϕ from the phenyl in PCH (continuous line) and in phase IV (dashed line).

It is comforting to see that the phenyl ring order parameters are in good agreement with those obtained in ref. [12], in which the thiophene ring order parameters could not be obtained. We have also calculated the purely internal distribution $f(\phi)$ for thiophene relative to the phenyl ring by integrating $f(\omega, \phi)$ over all possible orientations ω of the molecule:

$$f(\phi) = \frac{\int d\omega\, f(\omega, \phi)}{\int d\phi\, d\omega\, f(\omega, \phi)}. \qquad (17)$$

In fig. 3 we show $f(\phi)$ for PTP in PCH and in phase IV.

It is apparent that the distribution in PCH is peaked at about 27° with a much smaller hump around 90°. Since, according to maximum entropy [16], this is the most random distribution compatible with our data, we have definite evidence that the preferred rotamer of the molecule in this phase is tilted. This is in good agreement with the one-rotamer model employed in ref. [12], where it was found that a good fit could be obtained with an angle of 24.5°. The results for the distribution in phase IV (fig. 3) shows again a peak at 27° but much broader. This suggests a noticeable solvent effect between the two nematics. It also makes clear that for such a broad rotamer distribution the one-rotamer model is not expected to be appropriate, thus explaining the poor fit obtained for this case in ref. [12].

5. Conclusions

We have demonstrated that the internal order approach can be applied to the interpretation of LXNMR dipolar coupling data without invoking a priori models for internal or overall reorientation and their decoupling. We have used the method coupled to the maximum entropy technique to obtain the best approximate rotameric distribution of PTP in two nematics. The method is quite general and we believe that it will be useful for studying solvent and temperature effects on internal rotations.

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