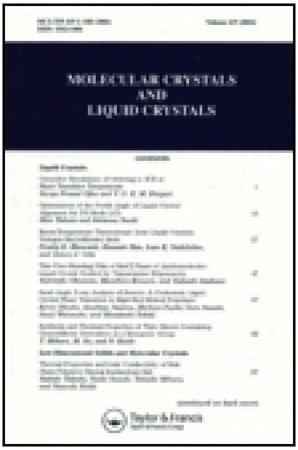

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Can Global Target Analysis of the Splitting and Spin Relaxation from a Ring-Deuterated Mesogen Produce Dynamical Information?

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We report on the measurements of quadrupolar splitting and spectral densities of motion for the phenylthio ring deuterons as a function of temperature in 4-pentylphenylthio-4'-octyloxybenzoate ($\bar{8}S5-d_4$). A global analysis of all these observables at 9 different temperatures in the nematic and smectic A phases is shown to give useful information on the core dynamics of $\bar{8}S5$. Inclusion of the smectic C phase in the global analysis is possible, but gives a poorer overall fitting quality factor.

Keywords: deuteron spin relaxation; smectogen; rotational diffusion

INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy is one of many experimental techniques which may be used to study molecular motions in condensed matter phases. Deuterium NMR relaxation measurements are particularly useful and effective, and have been employed by many research groups[1] to determine spectral densities of motion in liquid crystals. Although a recent report[2] has shown DMR spectra of a liquid crystal for deuterons in the natural abundance using proton decoupling, it is clear that at this low sensitivity one may not possibly carry out any meaningful relaxation study. Therefore isotopic substitution of protons by deuterons for such a study is necessary. Indeed, all published DMR relaxation studies of liquid crystals rely on deuterated materials. To prepare deuterated liquid crystals is often tedious and expensive. The advantage is that DMR spectra of liquid crystals show well-resolved quadrupolar doublets from different atom sites in a molecule. This results from different motional averaging effects at various sites. For instance, the relaxation of deuterons residing on the molecular core is governed by the reorientation of the molecule and/or director fluctuations[1] in liquid crystals. For deuterons residing on flexible end chains of the molecule, in addition to the above motions internal bond rotations[3,4] within the chain can also relax the deuteron spins. Since it is tedious to deuterate the entire mesogen, partially deuterated liquid crystals are often the choice. Thus, many workers[5] have often resorted to easily synthesized ring-deuterated materials. The present study is to examine whether under some reasonable assumptions, a DMR study of a ring-deuterated liquid crystal contains sufficient experimental observables to render a meaningful assessment of the molecular dynamics.

EXPERIMENTAL

A home-built superheterodyne coherent pulse spectrometer was operated for deuterons at 15.1 and 46.05 MHz. A typical $\pi/2$ pulse length was 4 μs. We have measured the quadrupolar splitting (Fig. 1) for the phenylthiol ring deuterons of 4-pentylphenylthio-4′-octyloxybenzoate ($\bar{8}$S5 $- d_4$) in the nematic (N), smectic A (SmA) and C (SmC) phases of $\bar{8}$S5. A broadband Jeener-Broekaert pulse sequence was used to measure simultaneously the Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times. Signal collection was started 10 μs after each monitoring $\pi/4$ pulse, and averaged up to 4096 scans. The spectral densities $J_1(\omega)$ and $J_2(2\omega)$, determined

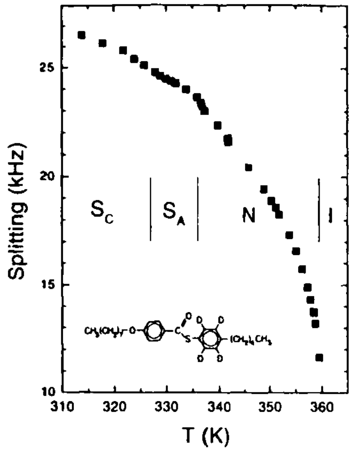

FIGURE 1 Plot of the quadrupolar splitting versus the temperature in $\overline{8}S5 - d_4$ and its molecular structure.

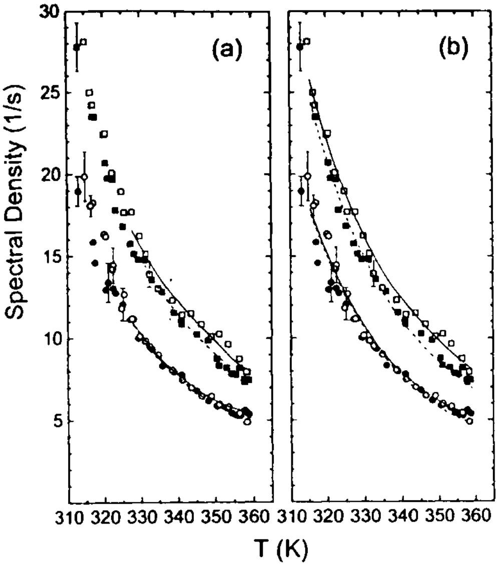

FIGURE 2 Plots of spectral densities $J_1(\omega)$ (squares) and $J_2(2\omega)$ (circles) versus temperature. Open and closed symbols denote data at 15.1 and 46 MHz, respectively. Solid (15.1 MHz) and dashed lines (46 MHz) denote fits using the Nordio model with (a) N and SmA data, and (b) N, SmA and SmC data.

from these relaxation times, are plotted versus the temperature in Fig. 2. The quadrupolar splitting was measured from the DMR spectrum obtained by FFT the free-induction decay signal after a $\pi/2$ pulse. Data collection and reduction has been detailed elsewhere[6].

ANALYSIS AND DISCUSSION

It is well-known that director fluctuations have little effect on the spin relaxation of ring deuterons in the MHz region. Because the deuterated sites reside in the molecular core, the complication from conformation changes[1] in the chains need not be addressed. A small-step rotational diffusion model is used[7,8] to describe the molecular reorientation, from which the rotational diffusion constants $D_{\|}$ and $D_{\perp}$ are derived. The $D_{\|}$ and $D_{\perp}$ describe rotations of the molecule about its long and short axes, respectively. In addition to the overall motion, internal ring rotation about the para axis of the phenylthio ring (with a diffusion constant D_R) also exists. As long as the para axis does not coincide with the principal z axis of the diffusion tensor, it is possible to separate D_R from $D_{\|}$. Thus we have targeted three dynamical parameters ($D_{\|}$, $D_{\perp}$ and D_R) to explain the relaxation data. Because there is a lack of different deuterated sites in our molecule, a global target approach[9] is chosen to analyze both the quadrupolar splitting and the spectral densities at 9 temperatures, covering the N and SmA phases.

The observed quadrupolar splitting is not sufficient to determine the order parameter tensor of a rigid molecule. Since the $\overline{8}$S5 molecule has many configurations due to its two end chains, the order parameter tensor for the 'average' conformer cannot be determined without a chain-deuterated sample. The best one can do here is to obtain the local order parameter S'_{zz} for the para axis of the ring albeit with some approximations, or to use the ring splitting plus the relaxation data to locate the long z_M axis of the 'average' molecule and its corresponding S_{zz}. In the local frame on the ring, the ring deuteron has a quadrupolar splitting given by[10]

$$\begin{aligned} \triangle\nu &= -\frac{3}{4}q_{CD}\{S'_{zz}[(3l_{zb}^2 - 1) + \eta(l_{za}^2 - l_{zc}^2)] \\ &\quad +(S'_{xx} - S'_{yy})[l_{xb}^2 - l_{yb}^2 + \frac{\eta}{3}(l_{xa}^2 - l_{xc}^2 - l_{ya}^2 + l_{yc}^2)]\} \end{aligned} \tag{1}$$

where $q_{CD} = 185$ kHz is the quadrupolar coupling constant, the direction cosines l_{za} etc. relate the principal axes (xyz) of $\mathbf{S}'$ to the principal axes (abc) of the quadrupole interaction tensor with its b axis along the C-D bond, and the a and c axes chosen to give a positive asymmetry parameter η (a value of 0.04 is assumed).

Suppose that a molecular (x_M, y_M, z_M) frame in which the z_M axis makes an angle θ with the ring para axis and the y_M axis lies on the ring plane, is assumed to diagonalize both the order parameter tensor and the rotational diffusion tensor. By taking into account fast ring rotations, one can easily find the following expression for the ring splitting:

$$\triangle\nu = -\frac{3}{8}q_{CD}\left[S_{zz}f(\theta) - \frac{1}{2}(S_{xx} - S_{yy})g(\theta)\right] \tag{2}$$

where $f(\theta) = 3\sin^2\theta + \eta\cos^2\theta + (\eta - 1)/2$ and $g(\theta) = 1 + 2\cos^2\theta + \eta(5 + 2\sin^2\theta)/3$. In Eq.(2), a nominal value of 60° for the angle $(\beta_{R,Q})$ between the CD bond and the para axis, and the average of quadrupolar splittings from the two non-equivalent CD bonds in the (x_M, y_M, z_M) frame have been used. The above equation is insufficient to determine the nematic order parameter $< P_2 >$ $(\equiv S_{zz})$ without prior knowledge of $S_{xx} - S_{yy}$ and the angle θ, as well as their temperature dependences. For a given θ and molecular biaxial parameter $(\xi = a_{22}/a_{20})$ of the orientation potential

$U(\Omega)$, $\langle P_2\rangle$ (or a_{20}) may be calculated[8] using the ring quadrupolar splitting. The determination of θ and ξ requires additional information such as spectral densities and the assumption of both ξ and θ being independent of the temperature. The assumption appears to be acceptable in the following analysis of N and SmA data.

The ring spectral densities can be written[11] as

$$\begin{aligned} J_m\left(m\omega\right) &= \frac{3\pi^2}{2}\left(q_{CD}\right)^2 \sum_n \sum_{n'} \sum_p \left[d^2_{p0}\left(\beta_{R,Q}\right)\right]^2 d^2_{np}\left(\theta\right) d^2_{n'p}\left(\theta\right) \qquad (3) \\ &\quad \times \sum_K \frac{\left(\beta^2_{mnn'}\right)_K \left[\left(\alpha^2_{mnn'}\right)_K + \left(1-\delta_{p0}\right) D_R\right]}{m^2\omega^2 + \left[\left(\alpha^2_{mnn'}\right)_K + \left(1-\delta_{p0}\right) D_R\right]^2} \end{aligned}$$

where $\left(\alpha^2_{mnn'}\right)_K / D_\perp$, the decay constants, are the eigenvalues and $\left(\beta^2_{mnn'}\right)_K$, the relative weights of the exponentials, are the corresponding eigenvectors from diagonalizing the rotational diffusion matrix Γ. The ring rotation about its para axis is taken to be in the strong collision limit. Eq.(3) is applicable to the uniaxial N and SmA phases. An optimization routine (AMOEBA)[12] was used to minimize the sum-squared error F

TABLE I: Order and potential parameters using $\xi = 0.1$. a_{20} in $U\left(\Omega\right)/kT = a_{20}P_2\left(\cos\beta\right) + a_{22}\sqrt{\frac{3}{2}}\sin^2\beta\cos 2\gamma$

$T\,(K)$	$\langle P_2\rangle$	$(S_{xx} - S_{yy})$	a_{20}
359.5	0.318	0.0100	-1.428
355.5	0.471	0.0103	-2.170
351.5	0.546	0.0097	-2.601
347.5	0.605	0.0089	-3.005
343.5	0.653	0.0080	-3.396
339.5	0.696	0.0071	-3.825
335.5	0.750	0.0058	-4.534
331.5	0.777	0.0051	-5.000
327.5	0.797	0.0047	-5.424
323.5	0.823	0.0040	-6.134
319.5	0.849	0.0033	-7.077
315.5	0.866	0.0029	-7.895

$$F = \sum_k \sum_\omega \sum_m \left[J_m^{calc}(m\omega) - J_m^{\exp}(m\omega)\right]_k^2 \tag{4}$$

where the sum over k is for 9 temperatures, the sum over ω for two Larmor frequencies and $m = 1$ or 2. The fitting quality factor Q is defined by the percent mean-squared deviation

$$Q = 100F/\sum_k \sum_\omega \sum_m [J_m^{\exp}(m\omega)]_k^2 \tag{5}$$

In a global target analysis of the splittings and spectral densities at 9 different temperatures in the N and SmA phases, we found that the best Q (0.04%) requires $\xi = 0.1$ and $\theta = 3°$. The derived $\langle P_2 \rangle$, $S_{xx} - S_{yy}$ and a_{20} are given in Table I. $\langle P_2 \rangle$ varies between 0.318 at the clearing point and ~0.8 at the high end of SmC phase. To check the θ value, other choices of θ were found to produce unreasonably high or low $\langle P_2 \rangle$ values. The small ξ or $S_{xx} - S_{yy}$ value is expected (i.e. the 'average' molecule is essentially uniaxial). The derived orientation potential is used to solve the rotational diffusion equation $\left(D_{xx} = D_{yy} = D_\perp, D_{zz} = D_\parallel\right)$ in a manner described in ref. [8]. Our analysis uses the Nordio model with the modification of a small non-zero a_{22}. As the experimental spectral densities vary continuously across the different phases (see Fig. 2), model parameters are expected to vary smoothly across the N–SmA transition. Thus, the following Arrhenius equations are assumed:

$$D_\perp = D_\perp^\circ \exp\left(-E_a^{D_\perp}/RT\right) \tag{6}$$

$$D_\parallel = D_\parallel^\circ \exp\left(-E_a^{D_\parallel}/RT\right) \tag{7}$$

$$D_R = D_R^\circ \exp\left(-E_a^{D_R}/RT\right) \tag{8}$$

where $D_\perp^\circ$, $D_\parallel^\circ$ and D_R°, the pre-exponentials, as well as their corresponding activation energies $E_a^{D_\perp}$, $E_a^{D_\parallel}$ and $E_a^{D_R}$ are the global parameters. For convenience, Eqs.(6)-(8) were rewritten in terms of $D'_{\perp}$, $D'_{\|}$ and D'_R at T_{max}=359.5 K, the highest temperature used in the global analysis. A total of 36 spectral densities was used to obtain six global parameters ($D'_{\perp}$, $D'_{\|}$, D'_R and three activation energies) with $\xi = 0.1$ and $\theta = 3°$. The calculated spectral densities in the N and SmA phases are shown as solid and dashed curves in Fig. 2(a). As the Q value of 0.04% is small, the fits to these data are very good. The derived $D_{\perp}$, $D_{\|}$ and D_R are plotted in Fig. 3(a). Their activation energies are 29.9, 47.8 and 22 kJ/mol, respectively. It is common in relaxation studies[1] to find $E_a^{D_{\perp}}$ being slightly less than $E_a^{D_{\|}}$. At each temperature, $D_R > D_{\|} > D_{\perp}$ as expected for a rod-like molecule like $\bar{8}$S5. Since the $\langle P_2 \rangle$ value is known to be sensitive to the $\beta_{R,Q}$ value, to see how this affects the above calculations we have tried $\beta_{R,Q} = 59.5°$ while retaining $\xi = 0.1$ and $\theta = 3°$. This choice only affects $f(\theta)$ and $g(\theta)$ in Eq.(2). We found that the $\langle P_2 \rangle$ values are raised substantially (e.g., $\langle P_2 \rangle = 0.91$ and $a_{20} = -9.365$ at 327.5 K). Now the $\langle P_2 \rangle$ value at the low end of the SmA phase appears too high for the particular choice of θ. However, the Q value is marginally lower. The model parameters are shown as solid lines in Fig. 3(a). In particular, the activation energies of $D_{\|}$ (47.9 kJ/mol) and D_R (23.9 kJ/mol) are essentially unchanged, while that of $D_{\perp}$ (55.3 kJ/mol) is larger than that of $D_{\|}$. This indicates that the uncertainty in $D_{\perp}$ is usually large and its value is also sensitive to the $\beta_{R,Q}$ value.

Although SmC phase is biaxial, molecules are known to align along the magnetic field with smectic layers tilted[13]. As a consequence, Eq.(3) was assumed to be applicable in SmC phases[14]. By including 3 additional temperatures from the SmC phase, we re-analyzed a total of 48 spectral densities with the same ξ and θ as well as $\beta_{R,Q} = 60°$ to give a poorer overall Q value of 0.14%. The calculated spectral densities are compared to the experimental values in Fig. 2(b), and the derived $D_\perp$, $D_\parallel$ and D_R are plotted in Fig. 3(b). Their activation energies are 33 ± 1, 42 ± 1, and 30.2 ± 0.2 kJ/mol, respectively. The pre-exponentials $D^\circ_\perp$, $D^\circ_\parallel$ and D°_R are calculated as $4.6 \times 10^{12} s^{-1}$, $2.9 \times 10^{15} s^{-1}$, $5.0 \times 10^{14} s^{-1}$, respectively. These parameters represent reasonable "collision" frequencies for the different motional processes. In the fitting, correlations between activation energies and pre-exponentials are[15] normally high (up to 0.99), while correlations between the remaining couples of parameters are around 0.5.

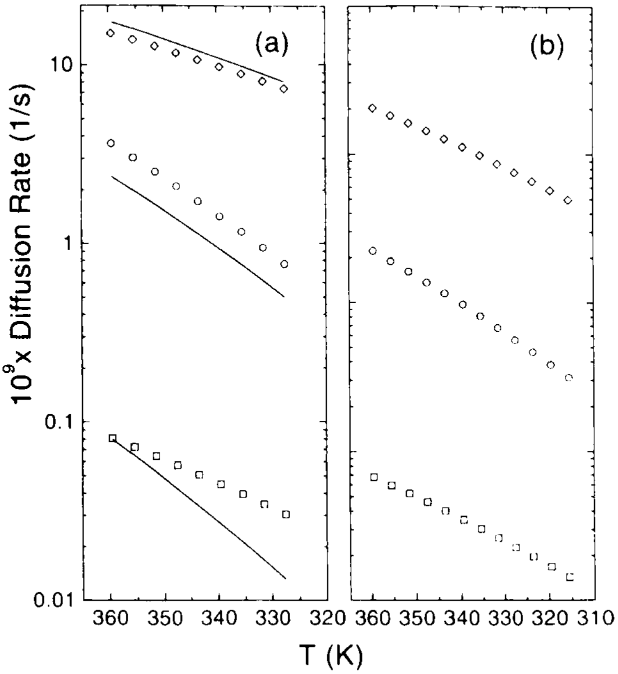

FIGURE 3 Plots of diffusion constants versus the temperature derived from (a) the N and SmA data, (b) the N, SmA and SmC data. Square, circle and diamond denote $D_\perp$, $D_\parallel$ and D_R. Solid lines in (a) denote diffusion constants using $\beta_{R,Q} = 59.5°$.

The error limit for $D_\perp^\circ$ is (3.4-6.2) $\times 10^{12} s^{-1}$, for $D_\parallel^\circ$ is (2.1-3.8) $\times 10^{15} s^{-1}$, and for D_R° is (4.8-5.3) $\times 10^{14} s^{-1}$. For a particular global parameter, the error limit was estimated by varying the one under consideration to give an approximate doubling in the Q value while keeping all other global parameters identical to those for the minimum Q. We note that the inclusion of SmC data has altered significantly the activation energies. Systematic deviations between experimental and predicted spectral densities do occur, especially at low temperatures of SmC phase. In particular, the model predicts almost no frequency dependence in $J_2(2\omega)$ in the SmC phase compared with the SmA and N phases. This seems to contrast with the experiment inspite of sizable experimental errors in J_2. The discrepancy may be understood if Eq.(3) is invalid in the SmC phase, because either the director is not aligned along the magnetic field and/or the contributions from biaxial spectral densities[14] are not negligible. Another factor could come from assuming both ξ and θ to be insensitive to different phases.

In summary, the relaxation data of the phenylthio ring deuterons and their quadrupolar splitting may provide information on the core dynamics. Despite the model parameters are somewhat sensitive to the data from selected phases, and only one type of deuterated site is available, the global target approach is useful in giving dynamical information. Finally, Eqs.(6)-(8) appear to be a good approximation for all three phases unless one would argue that a three-fold increase in Q is unacceptable.

Acknowledgments

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