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Deuterium NMR Study of Molecular Order and Dynamics in 60CB

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To test models for molecular reorientation in liquid crystals, the biphenyl core of a perdeuterated nematic liquid crystal, 4-cyano-4′-hexyloxy-d_{13}-biphenyl-d_8 (60CB-d_{21}) was studied using deuterium NMR spectroscopy. Two overlapped doublets, one from each deuterated phenyl ring, were seen in the deuterium spectrum of 60CB-d_{21}. An order parameter tensor of the molecular core was used to account for these doublet splittings. The asymmetry parameter η of the electric field gradient was found to be different for the deuterons on the two rings.

The spin-lattice relaxation times T_{1Z} and T_{1Q} were measured at 15.3 MHz for these rings, using a deconvolution routine that found the areas of two peaks in partially relaxed spectra. Four spectral densities of motion were derived as a function of temperature in the nematic phase. The small step rotational diffusion model or the "third rate anisotropic viscosity" model may be used to account for the measured spectral densities.

Keywords: nematic liquid crystals, NMR relaxation, molecular order, dynamics

I. INTRODUCTION

Nuclear spin relaxation is a powerful technique in studying the dynamics of molecular systems in their condensed phases. Thermotropic liquid crystals[1] are of interest because molecular ordering and its effects on molecular dynamics in their mesophases may be studied. Each mesogenic molecule may be idealized by a rigid core with flexible pendant hydrocarbon chains. Deuterium NMR[2–6] relaxation study has been used to study anisotropic reorientation, internal rotations and director fluctuations[7] in liquid crystals. The deuterium spectrum of a deuteriated liquid crystal normally shows well-resolved doublets, whose quadrupolar splittings reflect the effect of averaging various C—^{2}H bonds with respect to the director by anisotropic motions. By using multi-pulse sequences,[2,8] partially relaxed deuterium spectra allow determination of spectral densities of motion $J_1(\omega_0)$ and $J_2(2\omega_0)$ for various atomic sites in liquid crystals. The site, temperature and frequency dependences of $J_1^{(i)}(\omega)$ and $J_2^{(i)}(2\omega)$ provide information on the dynamical processes of mesogens.

We have chosen to study the biphenyl core of a perdeuterated nematic liquid crystal 4-cyano-4′-hexyloxy-d_{13}-biphenyl-d_8 (60CB-d_{21}). Only the biphenyl ring deu-

terons will be considered in the present study. Two doublets, one from each ring, are observed to be overlapping (Figure 1). One of these (label ring 0), with the larger splitting, is also overlapped by the methyl deuteron signal. The assignment of peak 0 and 1 in Figure 1 is tentative but is not unreasonable in view of the previous deuteron data[9] and a slightly sharper line for peak 0. Since the spin-lattice relaxation times of the aromatic deuterons are much shorter than those of the methyl deuterons, the methyl deuteron signal can be suppressed by saturation using suitable repetition time in data acquisition (see Figure 1). This technique works well except perhaps at temperatures near T_c (see below). Orientational order of 60CB has been reported using deuterium[9] and carbon-13[10] NMR spectroscopy. In particular, the value of $S_{xx} - S_{yy}$ was found to be small. We report in this study the order parameter S_{zz} and the deuterium spectral densities of motion for the phenyl rings in the nematics phase of 60CB.

II. EXPERIMENTAL

The perdeuterated liquid crystal 60CB-d_{21} (T_c = 75°C) purchased from Merck Sharp and Dohme Canada Ltd. was used without further purification. The temperature of the oven containing the sample was maintained by an external bath circulator. The sample temperature was monitored by a copper-constantan ther-

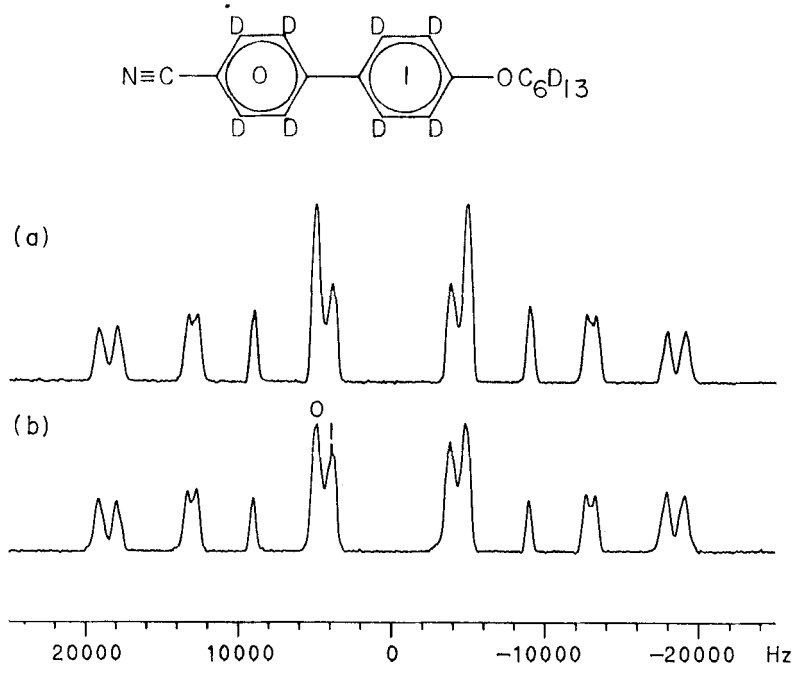

FIGURE 1 Typical deuterium NMR spectrum of 60CB-d_{21}. Peaks with label 0 and 1 are signals from ring 0 and ring 1, respectively. (a) was obtained with a repetition time of 1 s, while (b) with a repetition time of 90 ms. Also shown is a sketch of 60CB.

mocouple with the thermal gradient across the sample estimated to be better than 0.3°C. The deuterium NMR spectra were obtained at 15.3 MHz using a home-built superheterodyne coherent pulse spectrometer[11] and a Varian 15 in. high-resolution electromagnet. A General Electric 1280 computer was used for pulse control, signal averaging, Fourier transformation and data processing.

The deuterium Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times of the biphenyl rings were simultaneously measured using the Jeener-Broekaert pulse sequence[2,6] with appropriate phase-cycling of r.f. and receiver phases.[12] The pulse sequence was modified using an additional monitoring 45° pulse to minimize any long-term instability of the spectrometer. This pulse was phase-cycled to have the net effect of subtracting an M_∞ signal from the Jeener-Broekaert signal. The experimental details and procedures for data reductions to give T_{1Z} and T_{1Q} have been documented.[12] To minimize the signal due to the methyl deuterons overlapping with the signal of ring 0, the repetition time was set at 90 ms. The data for ring 0 deuterons near T_c might be influenced by an incomplete recovery of their magnetization due to the repetition rate. However we estimated that their T_1 values might be shortened by about 5–10%. On the other hand, the methyl signal might not be completely saturated at the low temperature end leading to slightly longer T_1 values for ring 0 deuterons. Thus the data for ring 0 at low temperatures should be checked using a ring-deuterated 60CB sample. Signal collection was started 8μs after each monitoring 45° pulse and averaged over 1200 scans. A deconvolution routine, with each line assumed to be 100% Gaussian, was employed[12] to find the areas of the two peaks under the doublets. The deconvolution into two lines was found to be acceptable, keeping in mind the dipole-dipole interactions between deuterons within each ring had been ignored. The experimental errors for the spectral densities might be seen (Figure 3) in the scattering of data measured at the same temperature. We estimated an error of about ± 5% and ± 10% for $J_1(\omega)$ and $J_2(2\omega)$, respectively. Data were found to agree within experimental errors by varying repetition rate between 60 and 150 ms.

III. THEORY

In this section we outline two models that describe reorientation of a symmetric-top in an anisotropic potential of mean torque. They differ mainly in the choice of principal frame for diagonalizing the rotational diffusion tensor of a molecule. In the small-step rotational diffusion model proposed by Nordio *et al.*,[13] the rotational diffusion equation is solved with the rotational diffusion tensor of a molecule being diagonalized in a molecule-fixed frame. In the "anisotropic viscosity" model proposed by Freed *et al.*,[14] this tensor is diagonalized in a laboratory (director) frame to reflect anisotropic viscosity in liquid crystals. The latter model has been extended[15] to include rotation of molecule about its long molecular (Z_M) axis in addition to diffusive motion of the Z_M axis around and towards the director. This is referred to as the "third rate anisotropic viscosity" model.[5,16]

Standard NMR relaxation theory[17] by nuclear quadrupole interaction for a spin

I = 1 enables the calculation of the spectral densities of motion from T_{1Z} and T_{1Q} using

$$T_{1Z}^{-1} = J_1(\omega_0) + 4J_2(2\omega_0) \tag{1}$$

$$T_{1Q}^{-1} = 3J_1(\omega_0) \tag{2}$$

where $\omega_0/2\pi$ is the Larmor precession frequency. The spectral densities $J_{m_L}(m_L\omega)$ may be calculated from

$$J_{m_L}(m_L\omega) = \frac{3\pi^2}{2}(\nu_Q)^2\left(1 + \frac{\eta^2}{3}\right)\int_0^\infty G_{m_L}(t)\cos(m_L\omega t)dt \tag{3}$$

where $\nu_Q = e^2qQ/h$ and η are the quadrupolar coupling constant and its asymmetry parameter, respectively. The superimposed rotations model[18] accounts for internal ring rotations in the biphenyl core. Using a M frame fixed on the rigid C = N subunit, one obtains[18] spectral densities for the ring deuterons:

$$J_{m_L}^{(i)}(m_L\omega) = \frac{3\pi^2}{2}(\nu_Q)^2 \sum_{m_M}\sum_{m_i} c_{m_Lm_M}[d^2_{m_i0}(\beta_{R,Q_i})]^2[d^2_{m_Mm_i}(\beta_{M,R})]^2 \times$$

$$\sum_j a^{(j)}_{m_Lm_M}[(\tau^{(j)}_{m_Lm_M})^{-1} + (1 - \delta_{m_i0})D_R^{(i)}]/[(m_L\omega)^2$$

$$+ [(\tau^{(j)}_{m_Lm_M})^{-1} + (1 - \delta_{m_i0})D_R^{(i)}]^2] \tag{4}$$

where the script i labels the ring number (i = 0, 1), m_L and m_M are projection indices for a tensor of rank two in the laboratory and molecular Z axes, respectively, $d^2_{mm'}(\beta)$ are the reduced Wigner rotation matrices which appear in the relaxation Hamiltonian, $\beta_{R,Q}$ is the angle between a C—^{2}H bond and a ring para axis, $\beta_{M,R}$ is the angle between the Z_M axis and the para axis, and $D_R^{(i)}$ is a rotational diffusion constant used to describe free internal rotation of ring i about its para axis. ν_Q is taken to be 185 kHz, and $\beta_{R,Q_i} = 60°$. $\beta_{M,R} = 0$ since Z_M axis is assumed to be parallel to the para axes (see below). Ring rotation about the para axis is considered in the strong collision limit. $a^{(j)}_{m_Lm_M}$ represent normalized relative weights of each exponential decay in the multi-exponential autocorrelation functions. The c coefficients in Equation (4) represent the initial amplitude of the autocorrelation functions and are the mean square of the Wigner rotation matrices. The form of autocorrelation times $\tau^{(j)}_{m_Lm_M}$ depends on the particular model. In the Nordio model,

$$\tau^{(j)}_{m_Lm_M} = b^{(j)}_{m_Lm_M}\tau^{(2)}_{m_M}$$

$$= b^{(j)}_{m_Lm_M}/[6D_\perp + m_M^2(D_\parallel - D_\perp)] \tag{5}$$

$\tau^{(2)}_{m_M}$ are the usual correlation times for diffusion with no ordering and are given in terms of $D_\parallel$ and $D_\perp$, rotational diffusion constants of the molecule about the Z_M

axis and of the Z_M axis, respectively. In the third rate anisotropic viscosity model,[15] a third rate constant (D_γ) was introduced to account for fast rotations of the molecule core about its long Z_M axis (γ-motion) in addition to diffusive motion of the Z_M axis around (D_α for α-motion) and towards (D_β for β-motion) the director. Hence the autocorrelation times are given by:

$$[\tau^{(j)}_{m_L m_M}]^{-1} = \{k_{m_M} + [6D_\beta + m_L^2(D_\alpha - D_\beta)]/b^{(j)}_{m_L m_M}\} \tag{6}$$

The k_{m_M} term in the above equation reflects the γ-motion. For simplicity, in the strong collision limit $k_{m_M} = (1 - \delta_{m_M 0})D_\gamma$. In developing their model, Vold and Vold make the key assumption that the γ-motion is independent of the α,β-motions. The a, b and c coefficients are all dependent on the order parameter $\bar{P}_2$, the degree of molecular orientation order, and are tabulated for a Maier-Saupe potential of mean torque in Reference (15).

IV. RESULTS AND DISCUSSION

Poon *et al.* have shown[10] by ^{13}C NMR study that the two phenyl rings of 60CB essentially have the same local order parameters, $S_{zz}(=\bar{P}_2)$ and $S_{xx} - S_{yy}$. This implies that the para axes of these rings are colinear. Counsell *et al.*[9] have studied the order parameter tensor ($\tilde{S}$) for the phenyl ring with the alkoxy chain in 60CB using deuterium NMR. Using $\nu_Q = 185$ kHz, $\eta = 0.04$ and $\beta_{R,Q} = 60°$, they found that $S_{xx} - S_{yy}$ is small and <0.04 in the entire nematic phase of 60CB. The quadrupolar splittings of the biphenyl rings (i = 0, 1) may be calculated[19] from

$$\Delta\nu_i = \pm \frac{3}{4} q^{(i)}_{bb}\{S_{zz}[(3l^2_{bzi} - 1) + \eta_i(l^2_{azi} - l^2_{czi})] + (S_{xx} - S_{yy})[l^2_{bxi} - l^2_{byi} + \frac{1}{3}\eta_i(l^2_{axi} - l^2_{cxi} + l^2_{cyi} - l^2_{ayi})]\} \tag{7}$$

where the direction cosines l_{axi} etc. relate the principal axes (xyz) of $\tilde{S}$ (z-axis is chosen to be parallel to the para axes) to the principal axes (abc) of the quadrupole interaction tensor $\tilde{\nu}^{(i)}_Q$. The b axis is along C—^{2}H bond. The molecular frame is assumed to be identical to the principal frame of $\tilde{S}$. Thus the Z_M axis is along the para axes, while the X_M axis is on a phenyl ring. The asymmetry parameter η_i is defined as $(q^{(i)}_{aa} - q^{(i)}_{cc})/q^{(i)}_{bb}$ with a and c chosen to give a positive η value. We have assumed that $q^{(0)}_{bb} = q^{(1)}_{bb} = \nu_Q$ and the different in $\Delta\nu_i$ is due to different η_i as the two rings have the same S_{zz}. Using the quadrupolar splittings $\Delta\nu_0$ and $\Delta\nu_1$, and the local order parameters of Poon *et al.* at $T_c - T = 10$K, we found that $\eta_0 = 0.012$ and $\eta_1 = 0.065$. Note that η was determined to be 0.064 for anthracene.[20] The asymmetry order parameter $(S_{xx} - S_{yy})$ is sensitive to the value of $\beta_{R,Q}$ but is usually small and also relatively insensitive to temperature.[9] To obtain the temperature dependence of $\bar{P}_2$ shown in Figure 2, we averaged the S_{zz}'s which were

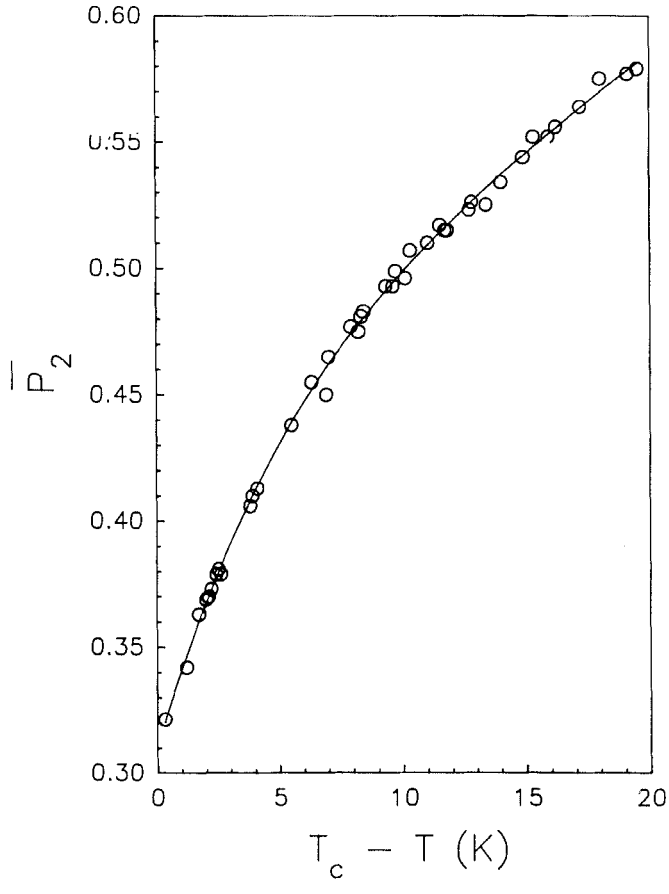

FIGURE 2 Plot of order parameter $\tilde{P}_2$ versus temperature. Data are obtained based on the deuterium splittings of both rings.

calculated from Equation (7) using the splittings of both phenyl rings, a constant value of 0.04 for $(S_{xx} - S_{yy})$, and the above η values.

Figure 3 shows the spectral densities versus $T_c - T$ for ring 0 and ring 1 of the biphenyl core of 60CB. It was observed that the spectral densities for deuterons on ring 0 are less than the corresponding values of ring 1, indicating that the rates of internal ring rotation for these rings may not be identical. Note that both $J_1(\omega_0)$ and $J_2(2\omega_0)$ increase with decreasing temperature in the nematic phase and that $J_1(\omega_0) > J_2(2\omega_0)$ for both rings. At the same temperature, the J_1/J_2 ratio is larger for ring 0 than that of ring 1. Furthermore, this ratio increases with decreasing temperature for both rings. Given four spectral densities of motion, one can in principle derive four model parameters.

In applying the third rate anisotropic viscosity model (Equations 4 and 6), one encounters difficulty with the present data set since the model requires five rotational diffusion constants. One may incorporate internal rotation of one ring into the γ-motion by fixing the molecular frame on one of these rings. However there

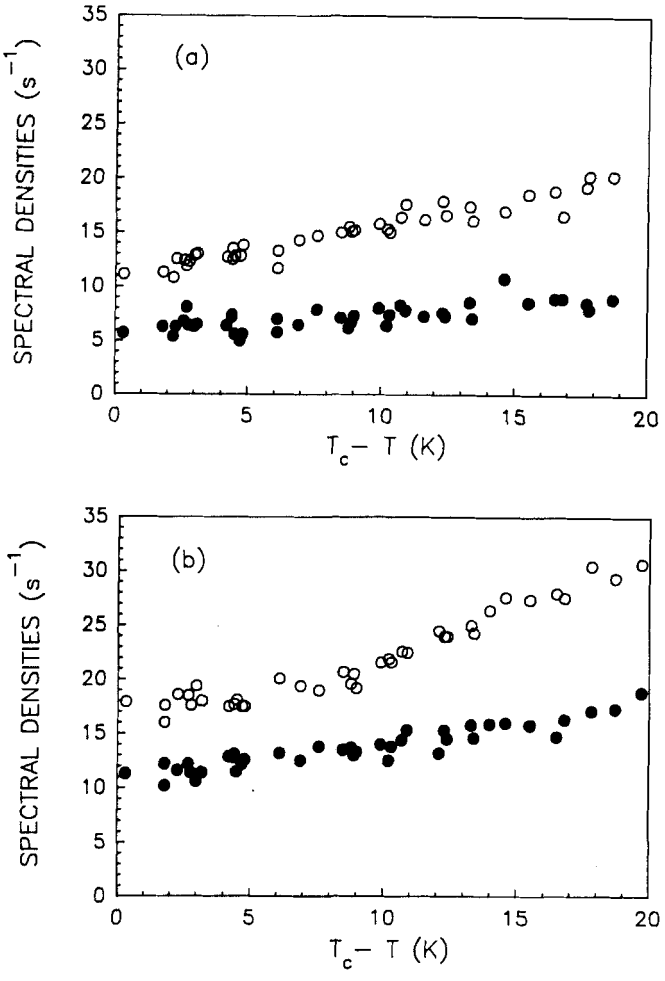

FIGURE 3 Plots of spectral densities versus $T_c - T$ in the nematic phase of 60CB. Graph (a) is for ring 0 while (b) is for ring 1. Open and closed circles denote $J_1(\omega_0)$ and $J_2(2\omega_0)$, respectively.

remains a fundamental problem in the application of either the third rate anisotropic viscosity model or the Nordio model to ring deuterons, that is, the dominant contribution in the spectral density (Equation (4)) corresponds to $m_M = 0$ term involving $d^2_{m,0}$ ($\beta_{M,Q}$) which is close to zero as $\beta_{M,Q} \simeq 60°$. In the Nordio model, the correlation time τ_{mL0} is governed by $D_\perp$, while in the third rate anisotropic viscosity model, it is dominated by D_α. Hence the ring deuterons are not a good candidate to study motion of the long molecular axis. Because of large uncertainty in deriving the rotational diffusion constant for molecular tumbling, unphysically high activation energies were found for $D_\perp$ and in particular D_β in these models. We therefore await experimental data from the chain deuterons of 60CB and ring deuterons data at another frequency for testing these models for molecular reorientation. Since $D_\perp$ or D_β are smallest among the rotational diffusion constants,

the frequency dependences in spectral densities will also aid us in deriving $D_\perp$ or D_β with better accuracy. This report presents preliminary results and outlines two existing motional models to describe reorientation of the biphenyl core in 60CB. We conclude that additional spectral densities from the chain deuterons in 60CB are needed to shed light on the reorientational motion once a realistic model[21] of internal dynamics is formulated for liquid crystals.

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