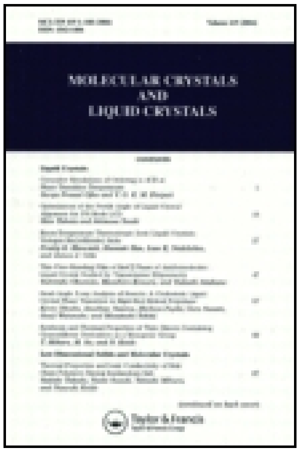

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Molecular Dynamics and Spectral Density Determination in Liquid Crystals

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Molecular Dynamics and Spectral Density Determination in Liquid Crystals

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Recently there have been an increasing number of deuterium NMR relaxation studies aiming at the separation of individual spectral densities of motion for various atomic sites in flexible liquid crystal molecules. These spectral densities contain information on the frequency spectra of fluctuations from molecular motions such as director fluctuations, anisotropic molecular tumbling and internal conformational motions. The rigid core of a rodlike mesogen is usually made up of phenyl rings (plus linkage group) whose internal motion consists of ring rotation about their para axes. To understand the spectral densities of the ring deuterons measured in different mesophases, we extend the calculations of reorientation of a mesogen in an ordering potential to include internal ring rotation. New DMR data at 15.4 MHz is presented for the nematic, smectic A, smectic C and smectic B phases of 50.7 and analyzed quantitatively using the above model.

Keywords: smectic, reorientation, ring rotation, deuterium relaxation, spectral densities

I. INTRODUCTION

Nuclear spin relaxation measurements[1,2] have been used to study molecular dynamics of liquid crystals.[3] More recently NMR pulsed techniques were applied to measure simultaneously the deuterium Zeeman (T_{1Z}) and quadrupole (T_{1Q}) spin-lattice relaxation times in deuterated or partially deuterated liquid crystals.[4–8] Some advantages of DMR are the site specificity of the deuteron probe in a flexible

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mesogen and the ease in the separation of spectral densities of motion from the deuterium spin relaxation measurements. The disadvantages are the necessity of deuterating liquid crystals and the insensitivity of the deuteron probe to intermolecular interactions arising from motions such as translational self-diffusion. It is believed that the temperature and frequency dependence of the spectral densities $J_0(\omega)$, $J_1(\omega)$ and $J_2(\omega)$ can provide a crucial test of various motional models which involve the collective motion in liquid crystal known as director fluctuations[9] and/or the non-collective motions such as molecular tumbling[10-12] and internal rotations in an anisotropic potential. Thus far the approach has been employed to investigate both rodlike[4-7] and discotic[8] liquid crystals as well as lyotropic liquid crystals.[13] It is now clear that the inability to explain the observed site dependence of J_p's by the conventional spin relaxation theory for mesogens[10-12] is due to the usual simplifying assumption that a mesogenic molecule is a rigid cylinder or disk. A theory that takes into account internal motions and segmental isomerization of alkyl chains in liquid crystals is still lacking. A simpler problem is to examine the internal rotation of phenyl rings which form part of the rigid core of most rodlike liquid crystals. There is evidence that ring rotation is fast and free in the nematic and "disordered" smectic phases such as A and C phases but is restricted to slow π flips in some "ordered" smectic phases[14] such as E, G and H phases. Calculations of molecular reorientation in a restoring potential including internal ring rotation will be outlined and discussed in terms of obtaining rotational diffusion coefficients from the measured spectral densities. Preliminary data have been reported[6] for the aniline ring of 4-n-pentyloxybenzylidene-4′-n-heptylaniline-2,3,5,6-d_4(50.7-d_4) and the spectral densities were interpreted qualitatively by restricted rotational diffusion of a symmetric top in a strong collision model. One purpose of this paper is to report new and improved results which are necessary for quantitative analysis in the mesophases of 50.7 and eliminate an apparent discrepancy between the reported data[7] on 40.8 and our 50.7 data which unfortunately suffer from difficulties associated with lack of phase-cycling[15] in the Jeener-Broekaert pulse sequence and/or poor signal-to-noise ratio from the sample.

II. THEORY

Standard NMR relaxation theory[16-18] by nuclear quadrupole interaction (assume axial symmetry) for a spin $I = 1$ gives the following expressions for T_{1Z} and T_{1Q},

$$T_{1Z}^{-1}(\theta) = A[J_1(\omega_0,\theta) + 4J_2(2\omega_0,\theta)] \qquad (1)$$

$$T_{1Q}^{-1}(\theta) = 3AJ_1(\omega_0,\theta) \qquad (2)$$

where $A = (3\pi^2/2)(e^2qQ/h)^2$, e^2qQ/h is the quadrupolar coupling constant, $\omega_0/2\pi$ is the Larmor frequency, θ is the angle between the director $\hat{n}$ (optic axis of the mesophase) and the external magnetic field, and the spectral densities $J_p(p\omega)$ are given by

$$J_p(p\omega) = \int_0^\infty G_p(t)\cos(p\omega t)dt \qquad (3)$$

where $G_p(t)$ is the autocorrelation function of the fluctuating part of the second order spherical harmonic describing the orientation of electric gradient tensor in the external magnetic field. When one simultaneously measures these relaxation rates at one particular Larmor frequency using either the Jeener-Broekaert method as suggested by Vold et al.[15] or by a modification of selective inversion method as proposed by Beckmann et al.,[4] one can evaluate $J_p(p\omega_0,\theta)$ for $p = 1$ and 2. In particular, when the angle θ is zero, one obtains $J_p(p\omega_0, 0) = J_p(p\omega_0)$, the spectral densities for $\hat{n}$ being aligned along the external magnetic field. It was argued before[19] that director fluctuations would not be an effective spin relaxation mechanism for ring deuterons. Instead molecular tumbling seems to play a dominant role. Molecular reorientation has been described[11,12,20] by solving equations for small step rotation diffusion of a rigid molecule in an anisotropic restoring potential given by $U(\beta_0) = -\lambda P_2(\cos\beta_0)$. Here we extend this model to include internal ring rotation in a liquid crystal molecule. The following assumptions are used: 1. electric field gradient of a C—D bond is axially symmetric, 2. internal ring rotation is uncorrelated to molecular tumbling, 3. rotational diffusion tensor for reorientation has axial symmetry (i.e. treat molecule as a symmetric top), and 4. rotation of phenyl ring(s) is free with D' being the rotational diffusion constant for ring rotation about its para axis. The autocorrelation function can be expressed in terms of the Wigner rotation matrix elements describing successive coordinate transformations: from the C—D bond axis to the para axis, from the para axis to the molecular frame that contains the long molecular axis, from the molecular frame to the director frame, and from the director frame to the laboratory frame defined by the magnetic field. It can be shown[21] that when the director is parallel to the magnetic field the autocorrelation function for the ring deuterons is given by

$$G_p(t) = \sum_{q,b=-2}^{2} \kappa(p,q)[d^2_{qb}(\beta_{D1})]^2[d^2_{b0}(\beta_{1F})]^2 \exp(-t/\tau^2_{pqb}) \qquad (4)$$

where

$$[d^2_{00}(\beta)]^2 = (3\cos^2\beta - 1)^2/4$$

$$[d^2_{10}(\beta)]^2 = (3\sin^2 2\beta)/8$$

$$[d^2_{11}(\beta)]^2 = (1 - 3\cos^2\beta + 4\cos^4\beta)/4$$

$$[d^2_{12}(\beta)]^2 = (1 - \cos^4\beta)/4$$

$$[d^2_{20}(\beta)]^2 = (3\sin^4\beta)/8$$

$$[d^2_{22}(\beta)]^2 = (1 + 6\cos^2\beta + \cos^4\beta)/16$$

β_{1F} is the angle between the C—D bond and the para axis, β_{D1} the angle between the para axis and the long molecular axis, and

$$\kappa(p,q) = \langle[D^2_{pq}(\Omega_0)]^2\rangle - |\langle D^2_{pq}(\Omega_0)\rangle|^2\delta_{p0}\delta_{q0} \qquad (5)$$

are the mean square averages of the Wigner rotation matrices. τ^2_{pqb} is a correlation time written in terms of the correlation time τ^2_{pq} for molecular reorientation (with $D_\parallel$ and $D_\perp$ being the rotational diffusion constants about and of the long molecular axis) and the correlation time τ_b for internal ring rotation:

$$(\tau^2_{pqb})^{-1} = (\tau^2_{pq})^{-1} + (\tau_b)^{-1} = (D_\perp/\beta^2_{pq}) + (D_\parallel - D_\perp)q^2 + D'b^2 \qquad (6)$$

The parameters β_{pq} depend on the orientational order of the phase. Plots of β^2_{pq} versus the order parameter $\langle P_2\rangle \equiv \langle D^2_{00}(\Omega_0)\rangle$ were given in ref. (20), while $\kappa(p, q)$ were tabulated by Freed[11] in terms of order parameters $\langle P_2\rangle$ and $\langle P_4\rangle \equiv \langle D^4_{00}(\Omega_0)\rangle$ where Ω_0 is a set of Euler angles which transform between the director frame and the molecular frame. These κ factors account for effects of static order in an anisotropic medium and arise from the fact that the autocorrelation functions decay to non-zero averages which are governed by the equilibrium order parameters. It should be noted that the $\kappa(p,q)$ values with $q \neq 0$ depend on the anistropic rotational diffusion factor $R = D_{\|}/D_{\perp}$ and on the form of the restoring potential.[22] Since β_{D1} is usually small ($\sim 10°$) for rodlike mesogens, $[d^2_{qb}(\beta)]^2$ is nonzero when $q = b$. In consequence, we drop for simplicity in notation the label b in τ^2_{pqb} to give

$$(\tau^2_{pq})^{-1} = (D_{\perp}/\beta^2_{pq}) + (D_{\|} + D' - D_{\perp})q^2 \tag{7}$$

From Eq. (3), $J_p(p\omega)$ is given by

$$\begin{aligned} J_p(p\omega) = {} & \kappa(p, 0)[d^2_{00}(\beta_{D1})]^2[d^2_{00}(\beta_{1F})]^2 \frac{\tau^2_{p0}}{1 + p^2\omega^2(\tau^2_{p0})^2} \\ & + 4\kappa(p, 1)[d^2_{11}(\beta_{D1})]^2[d^2_{10}(\beta_{1F})]^2 \frac{\tau^2_{p1}}{1 + p^2\omega^2(\tau^2_{p1})^2} \\ & + 4\kappa(p, 2)[d^2_{22}(\beta_{D1})]^2[d^2_{20}(\beta_{1F})]^2 \frac{\tau^2_{p2}}{1 + p^2\omega^2(\tau^2_{p2})^2} \end{aligned} \tag{8}$$

In the limit that D' goes to zero (i.e. no ring rotation or ring rotates too fast), one recovers the spectral densities reported in the literature.[1,11,20]

The deuterium NMR spectrum of a single ring deuteron consists of a quadrupolar doublet whose splitting $\Delta\nu_Q$ is given by

$$\Delta\nu_Q = (3/2)(e^2qQ/h)P_2(\cos\beta_{D1})P_2(\cos\beta_{1F})\,\langle P_2\rangle \tag{9}$$

where $P_2(\cos\beta) = (3\cos^2\beta - 1)/2$.

III. EXPERIMENTAL

The 50.7-d$_4$ sample was same as that used earlier.[6] The transition temperatures for $S_G - S_B$, $S_B - S_C$, $S_C - S_A$, $S_A - N$, and $N - I$ phase transitions were 38, 52.4, 56, 63.2, and 76.2°C, respectively. The longitudinal relaxation times T_{1Z} and T_{1Q} were determined by means of a Jeener-Broekaert pulse sequence $[(\pi/2) - \tau - (\pi/4) - t - (\pi/4)]$ with the proper phase-cycling[15] to get rid of unwanted coherences. The preparation time τ was chosen according to $(2n + 1)/2\Delta\nu_Q$ with $n = 1$. T_{1Z} and T_{1Q} were derived from the sum

$S(t)$ and difference $D(t)$ of the doublet component intensities obtained by the third monitoring pulse, respectively:

$$S(t) \propto \sqrt{2}(1 - \exp(-t/T_{1Z})) \tag{10}$$

$$D(t) \propto -(3/2)\exp(-t/T_{1Q}) \tag{11}$$

The home-built superheterodyne coherent pulsed spectrometer[6] was operated at 15.4 MHz for DMR and used a $\pi/2$ pulse width of 6 μs. The signal-to-noise ratio was improved by a new single-coil-tuned probe which was placed in a temperature oven. The sample temperature was monitored by a copper-constantan thermocouple and the thermal gradient across the sample was estimated to be better than 0.3°C. The 4k quadrature FFT spectrum was achieved with a BNC 12 (Nicolet) by averaging signals starting at a time τ after the third monitoring pulse, over 400–1600 scans at repetition times of $\geqslant$200 ms. The observed doublet splitting was used to calculate $\langle P_2\rangle$ in Figure 1 using e^2qQ/h = 183 kHz, β_{D1} = 15° and β_{1F} = 60°. The value of $\langle P_4\rangle$ in Figure 1 was estimated from the Raman data of 40.8[23] and the DMR data of 40.8-d$_4$.[24] The relaxation time measurements had an experimental error of $\pm5\%$.

IV. RESULTS AND DISCUSSION

The spectral densities of motion, $J_1(\omega_0)$ and $J_2(2\omega_0)$, for the aniline deuterons of 50.7-d$_4$ were calculated from T_{1Z} and T_{1Q} using eqs. (1–2) and $A = 0.5 \times 10^{12} s^{-2}$. These are plotted versus the reciprocal temperature in the N, S_A, S_C and S_B phases in Figure 2. Both spectral densities increase with decreasing temperature and show a small discontinuity similar to $\Delta\nu_Q$ at the $S_C - S_B$ phase transition. The observations are similar to those reported[7,24] for another smectogen of the nO.m series (viz. 40.8). This is not surprising despite differences in the sequence of phases, since molecular reorientation is probably governed mainly by the length of molecule and the rotational viscosity. It was speculated[6] that ring rotation may play a significant role in relaxing the aniline deuterons in the S_B phase of 50.7 as there is a S_G phase beneath the S_B phase. The present data does not support such interpretation. Furthermore it will be seen that both molecular reorientation and internal ring rotation are fast on the NMR scale ($\sim10^{-8}$ s) in all the mesophases of 50.7 except perhaps the S_G phase which is excluded in the present study. In examining τ^2_{pq} of eq. (7),

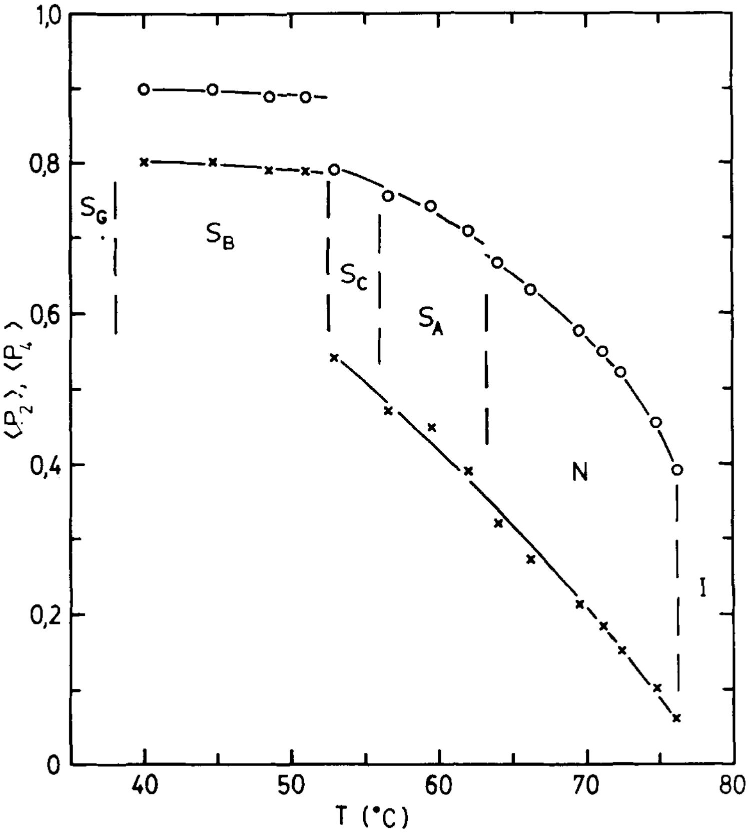

FIGURE 1 Plots of order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for 50.7 versus temperature. $\langle P_2 \rangle$ is calculated from the quadrupolar splitting, while $\langle P_4 \rangle$ is estimated (see text). ○ and × denote $\langle P_2 \rangle$ and $\langle P_4 \rangle$, respectively.

one has two unknowns $D_\perp$ and $D_{\parallel\text{eff}} + D'$, an effective rotational diffusion coefficient (including internal ring rotation) for the molecule rotating about its long molecular axis. Using eq. (8), one can solve for these two unknowns from $J_1(\omega_0)$ and $J_2(2\omega_0)$. It should be noted that the assumptions used in the calculations to give eq. (8) would not permit separate determination of D' even if ring rotation becomes effective in relaxing the aniline deuterons.

In the following, we have used the small step rotational diffusion model of a symmetric top (eq. (8)) by setting $D' = 0$ and $\omega\tau_{pq}^2 << 1$ and have used β_{pq}^2 and $\kappa(p, q)$ given by Agostini et al.[20] and Freed,[11] respectively. It should be realized that the $\langle P_4 \rangle$ value used here may not be exact but this is the best one can do without Raman data on

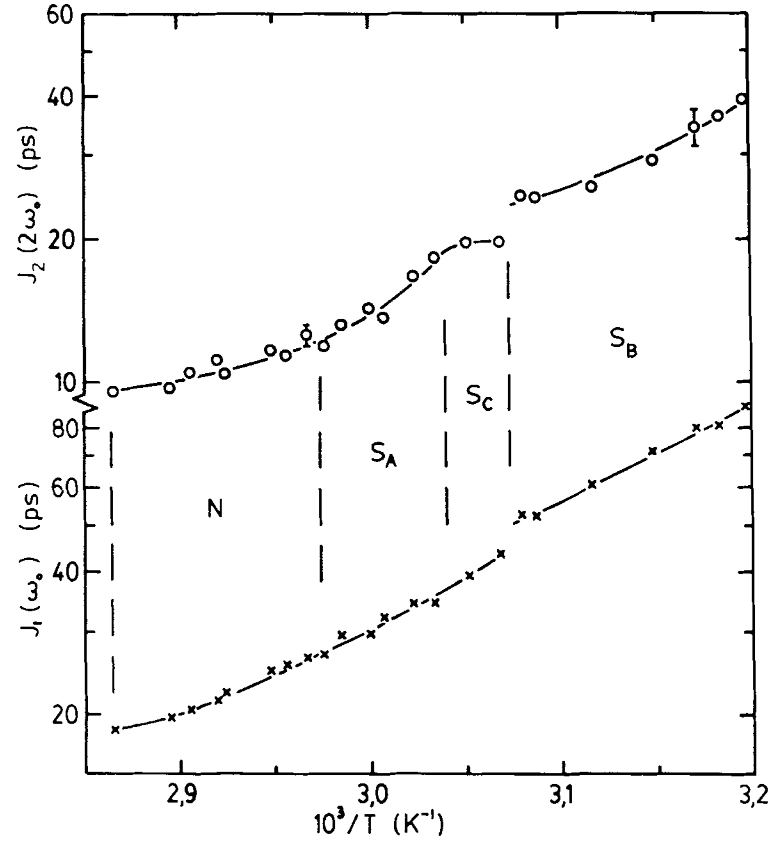

FIGURE 2 Plots of spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ versus the reciprocal temperature in the mesophases of 50.7.

50.7. The equations for $J_1(\omega_0)$ and $J_2(2\omega_0)$ were reduced to a quartic in R and $D_\perp$ which was solved by the method of bisection. The calculated rotational diffusion coefficients of 50.7 molecule are plotted in Figure 3 versus the reciprocal temperature. These values are consistent with the fast motion limit used above. It is noted that the derived $D_\perp$ is extremely sensitive to the accuracy of the spectral densities (i.e., relaxation data) and as a consequence has a much larger uncertainty than the derived $D_\parallel$ value. The values of $D_\parallel$ and $D_\perp$ were calculated from the smoothed out spectral density data, while the corresponding error bars are indicative of limits obtained from the actual $J_1(\omega_0)$ and $J_2(2\omega_0)$ data given in Figure 2. Given the large uncertainty in the relative magnitude of $D_\perp$, one should be cautious in interpreting the temperature behaviour of $D_\perp$. As seen in the figure, the anisotropic factor R is much larger than one; ranging from a value of ~20 at the low temperature end to a few hundreds at the high temperature end. In addition, $D_\parallel$ follows an Arrhenius temperature dependence with an activation energy E_a of 58 kJ/mole in the nematic, smectic A and C phases and of 40 kJ/mole in the smectic B phase. There seems to be a small drop in $D_\parallel$ at the $S_C - S_B$ phase transition. It is however not as easy to decide what E_a is for $D_\perp$. Nevertheless, $D_\perp$ obeys an Arrhenius temperature dependence in the S_B phase (E_a = 55 kJ/mole) and perhaps in the S_C

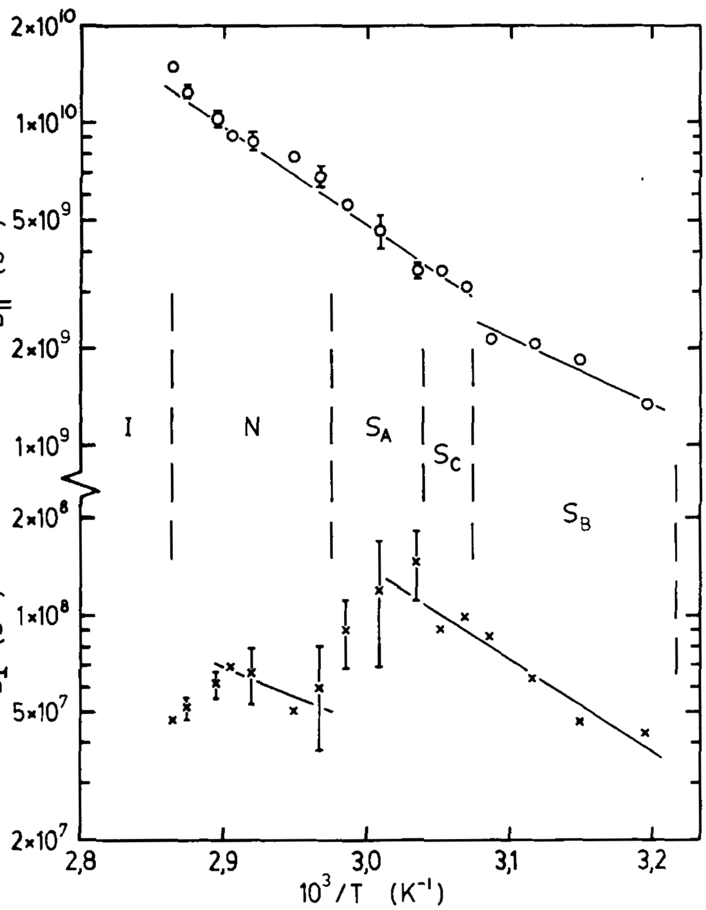

FIGURE 3 Plots of rotational diffusion coefficients $D_\parallel$ and $D_\perp$ versus the reciprocal temperature in the mesophases of 50.7.

and even in part of the S_A phase. There seems to be an increase in the $D_\perp$ value at the $N - S_A$ phase transition which is not observed in 40.8 when applying the same model.[24] Such an increase may however not be real as one may argue that $D_\perp$ increases gradually as temperature decreases from the nematic to the smectic A phase. This kind of temperature dependence seems quite unlikely. In the nematic phase except near T_C, $D_\perp$ may also be described by a thermal activation process but with a lower activation energy of 36 kJ/mole. It is not clear why the model predicts a decrease in $D_\perp$ near T_C as one would expect that R is one in the isotropic phase.

In conclusion, it would appear that the spectral densities of the aniline deuterons in the nematic, smectic A, C, and B phases of 50.7-d_4 may be quantitatively described by the small step rotational diffusion model of a symmetric top, and the rotational diffusion coefficients $D_\parallel$ and $D_\perp$ are obtained as a result. It should be noted that these coefficients are extremely sensitive to the relative magnitude of the spectral densities and the model parameters such as β^2_{pq}.[24] The internal ring rotation has been considered theoretically and may not be easily separated from the molecular reorientation experimentally in order to get the rotational diffusion constant D'.

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