

Chain dynamics in a chiral C phase by deuteron spin relaxation study

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Abstract

Molecular reorientations and internal conformational transitions of an aligned chiral liquid crystal (LC) 10B1M7 are studied by means of deuterium spin-lattice relaxation in its smectic A (SmA) and smectic C* (SmC*) phase. The motional model which is applicable to uniaxial phases of many LCs is found to be adequate even when the phase is a tilted SmC* phase. The deuterium NMR spectrum in this phase cannot discern rotations of the molecular director about the pitch axis. The basic assumption is that the phase biaxiality is practically unobservable. However, the relaxation rates can be accounted for by the tilt angle between the molecular director and the layer normal in the SmC* phase. The tumbling motion appears to show a higher activation energy upon entering from the uniaxial SmA into the SmC* phase.

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1. Introduction

Chiral liquid crystals (LCs) have attracted much attention [1–6] because their ferroelectric, antiferroelectric and/or ferrielectric properties shown in tilted smectic phases can lead to potential technical applications. One consequence of molecular chirality from an asymmetric carbon site(s) is the occurrence of polar order, giving electric polarization in the layer due to the alignment of molecular lateral electric dipoles. The in-layer polarization can change synclinically (chiral SmC*) or anticlinically (SmC_A*) as the molecules form a helical superstructure with its axis perpendicular to the layer planes. Among the different approaches to study molecular dynamics of LCs, deuterium spin relaxation measurements have been exploited successfully in achiral LC compounds [7–9]. In particular, the corre-

lated internal rotations within a flexible end chain(s) can best be studied by ²H NMR because of the site specificity of deuterium doublets observed in an aligned sample. However, specifically deuterated LC can often be expensive and time consuming to produce. ¹³C NMR spectrum also has the advantage of site specificity to some extent, but quantitative interpretation of relaxation rates can often be more problematic. Experimentally, site specificity is sometimes not easily achieved in chiral phases due to broad doublets observed in deuterium spectra [10–12] or broad aromatic carbon peaks [13–16] when dealing with ferroelectric phases. The reason for such line broadening effects is still an open question. While motional models for the interpretation of spin relaxation in uniaxial [17–19] and biaxial phases [20,21] are available, the biaxial phase studied theoretically thus far has a D_{2h} symmetry such as observed in biaxial nematic. Thus, a suitable spin relaxation theory for chiral (C_{2v}) phases is still lacking. As a consequence, quantitative analyses of spectral densities in chiral phases have been rather limited.

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Recently, a new approach based on some simplifying assumptions has been proposed to interpret the core dynamics in the SmC* phase of 8BEF5 [22]. Analyses of several sites in the same molecule have also been successful [23]. The present work aims to test the application of this approach on a deuterated achiral chain of 1-methylheptyl 4'-(4-*n*-decyloxy-benzoyloxy) biphenyl-4-carboxylate (10B1M7). This compound has been studied by us in the SmA phase at 15.1 and 46 MHz [11], and the decoupled model [24,25] was used successfully to gain motional parameters such as spinning (D_{\parallel}) and tumbling (D_{\perp}) diffusion constants of the molecule, as well as internal jump rates. The present investigation extends the study to a new frequency (61.4 MHz) by measuring the deuterium spin-lattice relaxation in the SmA and SmC* phases of 10B1M7. For completeness and direct comparison with findings in the SmC* phase, we have reanalyzed the data in the SmA phase by using all three different Larmor frequencies. The new analysis should provide more reliable motional information for 10B1M7 in the SmA phase, but the aim of the present study is to carry out an analysis of the SmC* phase data. The paper is organized as follows. Section 2 summarizes the decoupled model to give the spectral densities of chain deuterons and its application in the chiral SmC* phase. Section 3 outlines the experimental method, and the last section gives the results and discussion.

2. Theory

It is well-known [7] that molecules with flexible side chain(s) can exist in many different conformational states, and on the NMR time scale the observed deuteron doublets also reflect a time average over these different conformations in addition to other motional processes. It is noted that these conformations are aligned differently by the nematic mean field [26]. The number (N) of possible conformations in the decyloxy chain generated by Flory's rotameric model [27] is overwhelming, and we have followed our previous treatment by keeping only 683 conformational states, which possess relatively high probabilities of occurrence [11]. Furthermore, to solve the overall rotational dynamics of the molecule with many possible conformations it is assumed that an 'average' conformer exists, which has a particular rotational diffusion tensor. In principle, different conformations not only have their own order matrices, but also have their own rotation diffusion tensors [7]. The assumption is necessary to make the solution of the rotational diffusion equation tractable, and is a good approximation if the principal values of these diffusion tensors do not deviate much from each other. The decoupled model based on a master rate equation to describe the correlated internal

motion has been given in the literature [24,25]. Four phenomenological jump constants k_1 , k_2 , k_g and k'_g , which describe configurational transitions among different conformations are used to construct the transition rate matrix R . Suppose the carbon-carbon backbone of a pentyl chain is in a configuration given by $\{ijklm\}$. The internal energy for a configuration is governed by the number of *gauche* linkages (N_g) in the chain, and E_{tg} , the energy difference between a *gauche* linkage and the *trans* (t). The one-bond (k_1) motion is given by $\{ijklm\} \rightarrow \{ijklm'\}$, while the two-bond motion is for $\{ijklm\} \rightarrow \{ijkl'm\}$ and $\{ijkl'm'\}$. These two motions are called type-III motion by Helfand [28], while type-II motion consists of kink formation ($tttt \rightarrow g^{\pm}tg^{\mp}t$) described by a jump rate k'_g and *gauche* migration ($tttg \rightarrow tgtt$) described by k_g . Here E_{tg} used to fit the quadrupolar splittings, and the derived orientational order parameters of an average "conformer" in the SmA phase are those given previously [11]. Using the notation of Tarroni and Zannoni to describe the overall motion, the spectral densities of the C_i deuterons on the chain when the director \mathbf{n} is along the \vec{B} field can be written as [7]

$$\begin{aligned}
 J_m^{(i)}(m\omega, 0^0) = & \frac{3\pi^2}{2} (q_{CD}^{(i)})^2 \sum_n \sum_{n'} \sum_{k=1}^N \left(\sum_{l=1}^N \sum_p d_{n'l}^2(\theta_{N,Q}^{(i)l}) d_{np}^2(\theta) \right. \\
 & \times \exp \left[-i(n\varphi_{N,Q}^{(i)l}) x_l^{(1)} x_p^{(k)} \right] \\
 & \times \left(\sum_{l'=1}^N \sum_{p'} d_{n'l'}^2(\theta_{N,Q}^{(i)l'}) d_{n'p'}^2(\theta) \right. \\
 & \times \exp \left[-i(n'\varphi_{N,Q}^{(i)l'}) x_{l'}^{(1)} x_{p'}^{(k)} \right] \\
 & \times \sum_j \frac{(\beta_{mmn'}^2)_j \left[(\alpha_{mmn'}^2)_j + |\lambda_k| \right]}{m^2\omega^2 + \left[(\alpha_{mmn'}^2)_j + |\lambda_k| \right]^2}, \quad (1)
 \end{aligned}$$

where $q_{CD}^{(i)} = 165$ kHz is the quadrupolar coupling constant, $\theta_{N,Q}^{(i)l}$ and $\varphi_{N,Q}^{(i)l}$ are the polar angles for the C_i -D bond of the conformer l in the molecular N frame fixed on the phenyl ring core, θ is the angle between the Z_N -axis (or para axis) and the long molecular axis (Z_M) of 10B1M7, λ_k and $\bar{x}^{(k)}$ are the (negative) eigenvalues and eigenvectors from diagonalizing the R matrix, and $(\alpha_{mmn'}^2)_j/D_{\perp}$, the decay constants, and $(\beta_{mmn'}^2)_j$, the relative weights of the exponentials in the autocorrelation functions, are the eigenvalues and eigenvectors from diagonalizing the matrix of the rotational diffusion operator. A θ value of 8° was used [11]. The rotational diffusion constants D_{\parallel} and D_{\perp} , which appear in $(\alpha_{mmn'}^2)_j$, are for diffusive rotations of the molecule about its long axis, and about one of its short axes, respectively. The above equation, strictly speaking, is valid for a biaxial probe reorienting in a uniaxial environment. In the

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