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Investigating the core moiety of banana-shaped liquid crystals using ²H NMR coupled with quantum simulations

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Abstract

Bent-core or 'banana-shaped' molecules have displayed an array of novel chiral liquid crystal (LC) phases. However, the descriptions of these molecules as having well defined bend angles, and possibly exhibiting shape-chirality, have limited analytical support. Here, we present a step toward a more detailed understanding of the core moiety in banana molecules in LC phases, with the goal of guiding further molecular design and characterization efforts. We present ²H NMR studies on two of the popular banana core moieties, analyzed using ab initio structure calculations and the steric 'inertial frame' model. © 2004 Elsevier B.V. All rights reserved.

1. Introduction

A rapidly expanding area of liquid crystal (LC) research is that of 'banana-shaped' or bent-core molecules. Since the discovery of these 'banana phases' in 1996 [1], approximately 50 000 new LC-forming 'mesogen' structures [2] have been synthesized. These mesogens produce a rich variety of novel mesophases possessing chiral or achiral symmetries, and these symmetry properties give rise to various electro-optical and other physical properties, such as ferroelectricity [3-5]. These materials promise to provide new degrees of freedom in electro-optic display design as well as in other LC and 'soft materials' applications. Researchers attribute many of these novel behaviors to the mesogen core geometries, as these molecules appear to be bent when one analyzes them using simple chemical structure arguments, computational analysis, and indirect evidence from X-ray diffraction and other analytical techniques [6–8].

Recently, some have questioned the commonly accepted structures of banana molecules, namely planar and bent, in favor of more 'rod-like' [7], 'twisted' [6,8,9] or 'not totally planar' [10] structures. Some have claimed using ¹³C NMR evidence [11] that the mesogens take on chiral average conformations due to twist in the core backbone, which in turn dictates the mesophase chirality observed in this class of achiral molecules. While molecular chirality is consonant with these observations, planar *achiral* conformations are also consistent with these data. In short, there have been many assumptions made when discussing the structures of banana molecules, but little analytical data to support these assumptions.

We have begun a more detailed look at core conformations in LC phases, with the goal of improving molecular design and characterization strategies. Here, we describe NMR studies coupled with quantum structural calculations on two of the popular core moieties. We have synthesized the selectively deuterium-labeled core molecules shown in Fig. 1, 1,3-benzenediol

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Fig. 1. (A) Molecular structure of the two probe molecules ($X = {}^{1}H$, BOB; X = Cl, ClBOB). The reference frames used in the analyses are shown superimposed. (B) A planar achiral conformation of BOB that would exhibit NMR chemical shift differences between the two outer phenyls.

dibenzoate- d_{10} and 4-chloro 1,3-benzenediol dibenzoate- d_{10} and refer to them as BOB and CIBOB (derived from the common name *b*enzoyl*oxy b*enzene). Dissolving these *probe* molecules into traditional rodlike nematics and employing ²H NMR spectroscopy provides a sensitive probe of the conformational and orientational order of these molecules. Deuterium labeling on the outer phenyl rings allows for characterization of the relative conformations of these rings. We have analyzed this data with the aid of ab initio structure calculations in conjunction with the Steric 'inertial frame' (IF) model [12]. This study takes a step toward understanding the conformational preference of these structures in real mesophases.

2. Synthesis, sample preparation, and NMR measurements

Benzoic acid- d_5 (11.8 mmol, BOB and ClBOB) was refluxed in 25 mL of SOCl₂ for 4 h. Excess SOCl₂ was removed by distillation under reduced pressure. The benzoyl chloride- d_5 product was dissolved in 10 mL of dichloromethane. To this solution was added slowly with vigorously stirring a solution of resorcinol (5.90 mmol, BOB), or 4-chlororesorcinol (5.90 mmol, ClBOB) dissolved in a mixture (12 mL) of pyridine and dichloromethane (1:10 v/v, BOB, 1:5 v/v, ClBOB) at room temperature. After 5 min (30 min, ClBOB), white precipitate appeared and another 5 mL dichloromethane was added (none added for ClBOB). After stirring 10 h at room temperature, and heating at 80 °C for 1 h (10 h for ClBOB), the mixture was cooled to room temperature. After diluting with 50 mL dichloromethane (60 mL, ClBOB) and washing with 50 mL distilled water (200 mL, ClBOB), the dichloromethane soluble fraction was collected, and dichloromethane was removed using a rotatory evaporator. This product was washed with distilled water and recrystallized from a mixture of ethanol/water (1:1, BOB; 1:2, ClBOB). Yield: 73% (83%, ClBOB).

We formed homogeneous solutions of these probe molecules in two LC solvents for NMR investigations. Merck and Aldrich, respectively, supplied the nematic mixture Phase V (I) and the nematic 4'-pentyl-4-biphenyl carbonitrile (5 CB) (II). For NMR experiments, we prepared 2.0–2.3 wt% solutions by weighing solvent and solute amounts into 5 mm NMR tubes, heating into the isotropic phase, and then mixing using a Vortex apparatus.

We acquired ²H NMR spectra at room temperature on the probe molecules in both solvents at 55.28 MHz on a Bruker DMX-360 spectrometer using a broadband 10 mm *rf* coil probe and a simple pulse-acquire sequence with a pulse of 2 μ s (<20°) and a spectral width of 100 KHz. The numbers of scans were 20 000 and 4000 for BOB and ClBOB in solvent **I**, and 100 000 in solvent **I**.

3. Quantum-mechanical structure calculations

In order to determine both the preferred conformations and the *flexibility* of these core molecules, we employed the restricted Hartree–Fock (RHF) method to build potential energy surfaces (PESs) for the internal motions in both BOB and CIBOB. Of paramount interest, especially for analysis of NMR data, was to understand what conformations are favored for the lateral wings (outer phenyl rings and carboxyls) relative to each other and to the central phenyl ring of each probe molecule. Both BOB and CIBOB yielded somewhat surprising results in terms of their conformational preferences and flexibilities.

Initially, we performed geometry optimizations using the GAUSSIAN 03 package [13] (RHF 6-31G* basis set) without imposing symmetry restrictions, starting from the molecular geometry optimised with the AMI method. Both molecules optimize to planar conformations with the torsional angles $d_{\rm R}$ and $d_{\rm L}$, shown in Fig. 1, measuring 0° and 0°, in BOB, and 0° and 180°, in ClBOB, respectively. Thus, the two carbonyl groups are on the same side of the central phenyl ring in BOB, and on the opposite side in ClBOB. Starting from these two stabilised geometries, several low resolution scans were done for both molecules, by varying the six dihedral angles $d_{\rm R}$ and $d_{\rm L}$, d_1 and $d_{1'}$, d_2 and $d_{2'}$ (see Fig. 1). According to these calculations and to reference [6], the outer phenyl rings and carbonyl groups are strongly favored to lie in the same plane, allowing us to search only the two torsional angles $d_{\rm R}$ and $d_{\rm L}$ to build PESs. Single point energy scans (with geometry re-optimization) performed by varying $d_{\rm R}$ and $d_{\rm L}$ in steps of 18°, from $d_{\rm R}^0$ to $d_{\rm R}^0 + 180^\circ$ and from $d_{\rm L}^0$ to $d_{\rm L}^0 + 180^\circ$, clearly revealed a σ symmetry with respect to the central ring plane, and Fig. 2 show the optimized PESs (100 conformations for each molecule).

Using this study, and contrary to the conventional pictures propagated in the banana LC literature, one notices the following structural properties of BOB and ClBOB. For ClBOB the PES is *not symmetric* with respect to the angles d_R and d_L in that the conformation $\{d_R, d_L\} = \{0^\circ, 0^\circ\}$, in which the chlorine is closer to the carbonyl oxygen atom, is less favored than the most stable conformation $\{d_R, d_L\} = \{0^\circ, 180^\circ\}$, by 30.75 kcal/mol. Furthermore, the $\{d_R, d_L\} = \{180^\circ, 180^\circ\}$ conformation. For BOB, the two conformations $\{d_R, d_L\} = \{0^\circ, 180^\circ\}$ and $\{d_R, d_L\} = \{180^\circ, 0^\circ\}$ clearly have the same energy, and they are less favored than the minimum en-



Fig. 2. Potential energy surfaces for BOB (A) and ClBOB (B), obtained by varying dihedral angles $d_{\rm R}$ and $d_{\rm L}$.

ergy conformation $\{d_R, d_L\} = \{0^\circ, 0^\circ\}$ by only 1.44 kcal/ mol. The PES is quite flat over the entire ranges of these two angles. Thus, BOB is a very flexible molecule in terms of d_R and d_L (and CIBOB similarly in its d_R angle), and it is reasonable to assume that its conformations may be influenced by quite subtle intermolecular (e.g., solvent-solute) interactions. Twisted chiral conformations may arise in either molecule, but only under the influence of symmetry-breaking intermolecular driving forces.

4. Steric inertial frame model of mesogen conformation

The computation of second-rank properties of nonrigid molecules in uniaxial phases through equilibrium statistical procedures [12,14] has a long history and here, we summarize the main features, focusing on our NMR analysis needs. We detail these calculations for quadrupole spin interactions, but they are easily extended to other NMR observables [15].

The ordering matrix element S, which describes the average orientation of a cartesian frame fixed to the molecule and relative to the nematic director, can be defined as

$$S_{\alpha\beta} = 1/2 \big(3l_{\alpha}l_{\beta} - \delta_{\alpha\beta} \big), \tag{1}$$

where the number of independent elements in S depends on the shape anisotropy of the solute [16], which depends on the configuration. For qualitative modeling, we adopt the coarse approximation that $S\{\phi\}$ is assumed diagonal in the molecular frame (X, Y, Z) that diagonalizes the moment of inertia tensor $I\{\phi\}$, where the masses are replaced with the van der Waals radii [17,18], giving

$$I_{\alpha\beta} = \sum_{i} R^{i} \Big(r^{i} \cdot r^{i} \cdot \delta_{\alpha\beta} - r^{i}_{\alpha} r^{i}_{\beta} \Big), \qquad (2)$$

where R^i and r^i are the radius and the position of the *i*-atom, respectively.

According to this model, the three diagonal components of *S* can be calculated for each conformation $\{\phi\}$ from the equivalent ellipsoid semiaxes A_{γ} that are related to the principal moments of inertia of said configuration $\{\phi\}$ [19]. Once $S_{\alpha\beta}\{\phi\}$ is known, the quadrupolar splitting can be calculated using the general expression

$$\Delta v_i = \frac{2}{3} \sum_{\{\phi\}} \sum_{\alpha,\beta}^{X,Y,Z} P\{\phi\} \cdot q^i_{\alpha\beta}\{\phi\} \cdot S_{\alpha\beta}\{\phi\}, \qquad (3)$$

where $q_{\alpha\beta}^i\{\phi\}$ is the quadrupole interaction tensor defined in the molecular frame for the *i*-CD bond, and $P\{\phi\} = Z^{-1} \exp[-E\{\phi\}/kT]$ is the Boltzmann probability that the molecule has configuration $\{\phi\}$. The IF model assumes the energy of a single molecule $E\{\phi\}$ depends only on the configuration $\{\phi\}$, where we used the energy evaluated for each conformation $\{d_{R}, d_{L}\}$ in the ab initio study described above.

Since it is more convenient to describe the quadrupole interaction tensor in the CD bond local frame (x', y', z'), where it is diagonal and independent of the conformation $\{\phi\}$, we used

$$\Delta v_{i} = \frac{2}{3} \sum_{\alpha,\beta}^{x',y',z'} q_{\alpha\beta}^{i} \sum_{\{\phi\}} P\{\phi\} \cdot s_{\alpha\beta}^{i}\{\phi\} = \frac{2}{3} \sum_{\alpha,\beta}^{x',y',z'} q_{\alpha\beta}^{i} \left\langle s_{\alpha\beta}^{i} \right\rangle,$$
(4)

where $\langle s_{\alpha\beta}^i \rangle$ is the ordering matrix element defined in the CD bond frame and averaged over all configurations.

A simple way to include contributions to the energy due to the anisotropic environment of a locally uniaxial mesophase consists of assuming that the molecule with conformation { ϕ } is contained in a hypothetical cylinder of radius r_c , whose axis is coincident with the Z-axis, which is the direction of the minor principal moment of inertia [12,20]. In this coarse model, the configuration { ϕ } is accepted if all atoms are contained in the cylinder, otherwise it is discarded. This procedure is repeated for each value of the radius r_c , calculating all properties, such as the quadrupole splittings $\Delta v^i (r_c)$, and orienting matrices $\langle s^i_{\alpha\beta}(r_c) \rangle$, in different frames, e.g., for different rings or CD bonds.

5. NMR results and analysis

Figs. 3a, b show the ²H NMR spectra of BOB in the two nematic solvents. In all spectra reported here, we show only half of the frequency axis, since the spectra are symmetric about zero frequency. These spectra are characterized by 3 quadrupolar splittings, with the largest splitting ascribable to the para CD bonds of the outer phenyl rings, and the inner splittings to the *meta* and ortho CD bonds. Due to the equivalence of the quadrupole splittings between the 2 rings to within our resolution (peak widths), these rings must be orientationally and conformationally equivalent. Thus, there is no evidence that these molecules exhibit average chiral conformations in nematic solvents. Prior to conducting this study, we also dissolved BOB (undeuterated) into conventional liquid solvents (CDCl₃) and into chiral liquid solvents ((-)-acetoxy-*p*-menthane). In these cases, BOB exhibited no outer ring inequivalence as observed in ¹H and ¹³C chemical shifts or *J*-couplings.

As anticipated from our quantum-structural study above, the deuterium spectra of ClBOB showed quite different behavior in the two solvents, as shown in Figs. 3c,d. The appearance of six quadrupolar splittings, the outermost two splittings ascribable to the *para* CD bonds of the two outer phenyl rings and the four inner splittings to the *meta* and *ortho* CD bonds, shows that these rings are not conformationally equivalent



Fig. 3. 2 H NMR spectra for BOB (a) and (b) and for ClBOB (c) and (d).

 $(d_{\rm R} \neq d_{\rm L})$. We cannot comment from this analysis directly on the chirality of this molecule.

As a first analysis of these NMR data, and with the goal of understanding the orientational and conformational structures of these molecules, we performed computations using the Steric IF model of the quadrupolar splittings as a function of the cylinder radius r_c from 3 to 10 Å by introducing our calculated ab initio energies $E\{\phi\}$ into Eq. (4) (see Fig. 4). We note that in this simplistic model of the nematic environment, there is not a large difference in volume of the cylinder of radius $r_{\rm c}$ given by different conformations of the molecules so that for BOB, r_c is restricted. That is, for $r_c < 4.54$ Å, no conformations are accepted, while for $r_c > 5.16$ Å, all 100 initial conformations are accepted. For ClBOB, this range is 4.16 Å $< r_c < 6.36$ Å, and this extension of the sensitive range of r_c is clearly due to the chlorine atom, which dramatically influences the molecular shape. These computations qualitatively coincide with the ²H spectra, where BOB exhibits equivalent splittings for the outer phenyl rings, while ClBOB does not.

To quantitatively fit the spectra to extract values of r_c shown in Fig. 4, we used the ratios of the quadrupole splittings since the absolute values of the calculated



Fig. 4. Plots of scaled quadrupole splittings vs. r_c for BOB (a) and ClBOB (b). Vertical lines represent best fits to r_c .

splittings will be scaled down due to LC averaging. Due to the well defined geometry of ²H nuclei on the phenyl rings, we have a fully defined system (in terms of splitting ratios) with which to fit r_c . We reproduced the experimental spectra exactly for ClBOB in both solvents (I and II) where r_c was 4.66 and 4.62 Å for the two solvents with 17 and 18 conformers rejected, respectively, and for BOB in 5CB (II), where r_c was 5.06 Å (with 11 conformers rejected), indicating that these probe molecules experience a calamitic mean field due to the host solvents. Indeed, these values of r_c found for BOB and ClBOB, are in good agreement with the IF literature on less rigid molecules [21,22].

The IF model fails to generate a fit for any value of r_c for the solute BOB in Phase V (I). The conformational space for BOB is inherently larger than that of ClBOB because of the intramolecular steric interactions in the latter. In BOB, rotations about the d_R and d_L angles are virtually unimpeded (see Fig. 2). Hence, the orientational ordering of the solute BOB may be more susceptible to specific (electrostatic) solute–solvent interactions than ClBOB [23]. Additionally, it should be emphasized that the IF model was introduced merely as a crude way to identify the so called long-molecular-axis of elongated

molecules [24]. And, a cursory look at the conformer shapes depicted in Fig. 2 show that BOB does not correspond to simple elongated molecules thereby rendering the utility of the IF model less reliable for this class of molecules. Nevertheless, the IF model can serve as a zero-order approximate description of the conformer preferences exhibited by these important constituents of banana liquid crystals.

In sum, these observations are a first step to bringing a more discerning eye to the study of banana mesogens in mesophases. In the uniaxial solvents employed herein, there is no apparent propensity for chiral conformations of the central core moiety of banana mesogens. Applying more complex and discerning models of excludedvolume interactions (than the crude shape selection of the IF model), e.g., bent-core models [25–27], as well as implementing different ²H-labeling schemes holds promise for providing insights into the complicated structure-property correlations in banana phases.

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