PHYSICAL REVIEW E **74**, 030701(R) (2006)

Orientational ordering of a banana-shaped solute molecule in a nematic calamitic solvent by ^{2}H-NMR spectroscopy: An indication of glasslike behavior

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(Received 14 April 2006; published 26 September 2006)

The Saupe ordering matrix of a banana-shaped mesogenic molecule as a solute in a common nematic calamitic solvent has been determined by ^{2}H-NMR spectroscopy as a function of temperature. The temperature dependence of the Saupe ordering matrix element associated with the principal molecular axis is consistent with a glassy behavior in the reorientational motion of this particular solute molecule. The Haller expression, appropriately modified, provides a good fit to the experimental data.

DOI: 10.1103/PhysRevE.74.030701 PACS number(s): 61.30.Gd, 61.43.Fs, 61.18.Fs

Since their discovery [1], banana-shaped mesogens have attracted a constantly increasing attention. The motivation of this growing interest has been essentially twofold. Banana-shaped molecules give rise to unusual layered phases with ferroelectric and antiferroelectric properties [2,3], frequently associated with a puzzling chirality [4]. In addition, banana-shaped molecules can be a possible route to generate a biaxial nematic phase [5,6].

More recently, the interest in banana-shaped mesogens has been also directed toward the isotropic and the nematic phases exhibited by these molecules, because of their potentially curious properties. Indeed, results of recent dynamic light scattering [7] and ^{2}H-NMR [8–10] studies performed in the isotropic and nematic phases of banana-shaped mesogens are consistent with a molecular reorientational motion much slower than that observed in common liquid crystals.

The present work reports on another manifestation of the peculiar behavior banana-shaped molecules may have even in higher-symmetry phases. This Rapid Communication is concerned with the determination, by ^{2}H-NMR spectroscopy, of the temperature dependence of the Saupe ordering matrix of a mesogenic banana-shaped molecule as a solute dissolved into a common nematic calamitic solvent.

The banana-shaped molecule in question is 4-chloro-1,3-phenylene-bis{4,4′-(11-undecenyloxy)benzyloxy}benzoate, deuterated on the central ring (Fig. 1), and henceforth named ClPbis11BB-d$_3$. The nematic liquid called E7, a mixture of cyanobiphenyl nematics, has been used as solvent.

The solution was prepared as follows. First, weighed amounts of solvent and solute were poured into the NMR tube; then, several cycles of heating, until the isotropic phase was reached, and uniform mixing of the solution were performed before introducing the tube into the magnet. The solute concentration was less then 1 % wt.

The ^{2}H-NMR experiments were carried out on a 9.40 T Varian InfinityPlus400 spectrometer, working at 61 MHz for deuterium, by using a goniometric probe (5 mm) dedicated to the deuterium nucleus. The prepared solution was cooled within the magnet from the isotropic to the nematic phase. The temperature was controlled within 0.2°, and 5 min were allowed for thermal equilibration of the samples at each temperature considered. ^{2}H-NMR spectra were recorded on cooling by quadrupolar echo (QE) pulse sequences [11,12], with the exorcycle phase scheme, either with or without ^{1}H continuous-wave decoupling. A 90° pulse of 4 μs, pulse delay of 0.5 s, and QE time delay τ of 23 μs have been used. The number of scans varied from 20 000 to 100 000.

^{1}H-decoupled ^{2}H-NMR spectra of ClPbis11BB-d$_3$ in the nematic solvent E7 are characterized by two quadrupolar splittings, as shown in Fig. 2(a), where a spectrum at 25 °C, with 100 000 scans, is shown. ^{2}H-NMR spectra that are not ^{1}H-decoupled are characterized by two quadrupolar splittings, with the inner referring to the deuterium into position 2, and the outer further split in a doublet, because of the coupling between the proton in position 5 and deuterium in position 6. One example of this type of spectrum is available in Fig. 2(b).

From the spectra acquired as a function of temperature, we could get often well-resolved dipolar splittings, and always well-resolved quadrupolar splittings for the two deuterons (Fig. 3).

The experimental values of the dipolar $\Delta\nu_{dip}$ and quadrupolar splitting $\Delta\nu_{qua}$, obtained from the experimental data, have been analyzed by using the following equations [13]:

$$\Delta\nu_{dip}(T) = -K_{HD}[S_{zz}(T)(3\cos^2\vartheta_{zHD}-1)+\Delta_{biax}(T) \times(\cos^2\vartheta_{yHD}-\cos^2\vartheta_{xHD})]/r_{HD}^3, \quad (1)$$

$$\Delta\nu_{qua}(T) = \frac{3}{2}q_{ad}\left[S_{zz}(T)\left(\cos^2\varphi_i-\frac{1}{2}\sin^2\varphi_i-\frac{\eta}{6}\cos^2\varphi_i+\frac{\eta}{6}+\frac{\eta}{3}\sin^2\varphi_i\right)+\Delta_{biax}(T)\left(\frac{1}{2}\sin^2\varphi_i+\frac{\eta}{6}\cos^2\varphi_i+\frac{\eta}{6}\right)\right]. \quad (2)$$

The meanings of the quantities entering Eqs. (1) and (2) are defined next. K_{HD} is the ^{1}H-^{2}H dipolar coupling constant, equal to 18 434.4 Hz Å^3, r_{HD} is the distance between the two coupled atoms, equal to 2.5 Å, q_{ad} is the quadrupolar constant for aromatic deuterons, equal to 185 kHz, and η is the quadrupolar biaxiality, equal to 0.04. The angles φ_1 and φ_2 are depicted in Fig. 1, and define the geometry of the central

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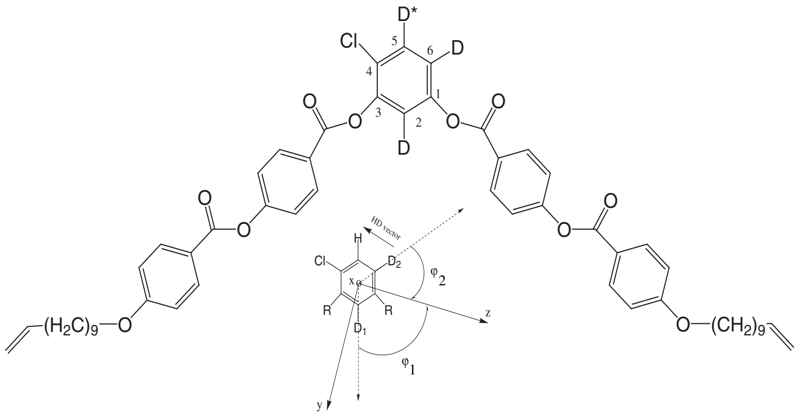

FIG. 1. Molecular structure of the banana-shaped mesogenic solute molecule. The asterisk means that the deuteration at position 5 is less than 10%, and, consequently, it could not be detected. The inset shows quantities used to define the geometry of the central ring and the molecular reference frame.

ring, as well as the directions of the three axes x,y,z of the molecular frame (Fig. 1). They are taken such that $\varphi_1+\varphi_2=120°$. The angles ϑ_{xHD}, ϑ_{yHD}, and ϑ_{zHD} are equal to, respectively, 90°, $150°-\varphi_1$, and $120°+\varphi_1$. **S** is the Saupe ordering matrix, which is diagonal in the above-mentioned molecular frame; S_{zz} is the element associated with the principal molecular axis, while S_{xx} and S_{yy} are such that $\Delta_{biax}=S_{yy}-S_{xx}$.

At each temperature considered, Eqs. (1) and (2) ave been used to fit the experimental data, thus determing the angle φ_1 and the elements of **S**. In these fittings, Δ_{biax} has been assumed to be linearly related to S_{zz} at the same temperature.

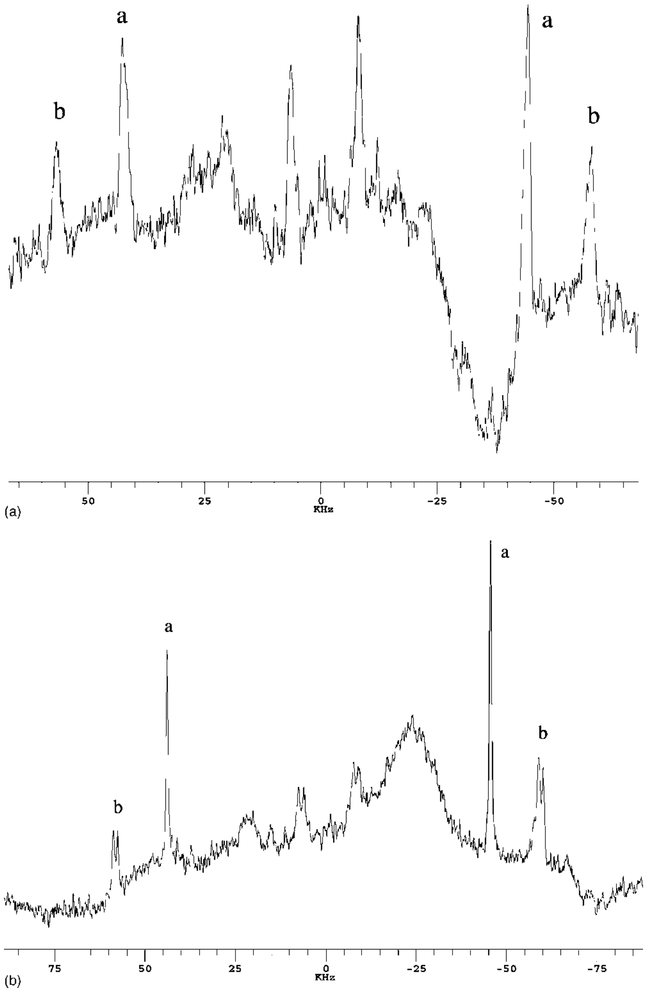

FIG. 2. Spectra at 25 °C, acquired by ^{2}H-NMR QE sequence (a) with and (b) without ^{1}H decoupling. *a* and *b* indicate the quadrupolar doublets due to deuterons in positions 2 and 6 of ClPbis11BB-d$_3$, respectively. Signals not indicated are due to the ^{2}H signals of natural abundance of the E7 solvent. 100 000 scans have been acquired.

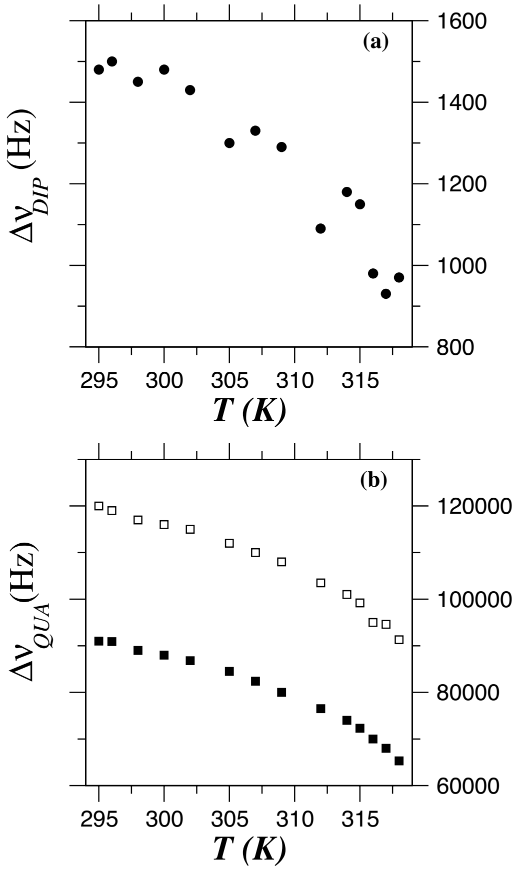

FIG. 3. (a) Temperature dependence of the dipolar splittings in absolute value from the ^{2}H-NMR spectra of ClPbis11BB-d$_3$ dissolved in E7. Experimental error is ±75 Hz. (b)Temperature dependence of the qudrupolar splittings in absolute value from the ^{2}H-NMR spectra of ClPbis11BB-d$_3$ dissolved in E7. Full and empty symbols refer to the NMR signal *a* and *b* in Fig. 2, respectively. Experimental error is ±100 Hz for the inner splittings (*a* in Fig. 2), and ±150 Hz for the outer splittings (*b* in Fig. 2).

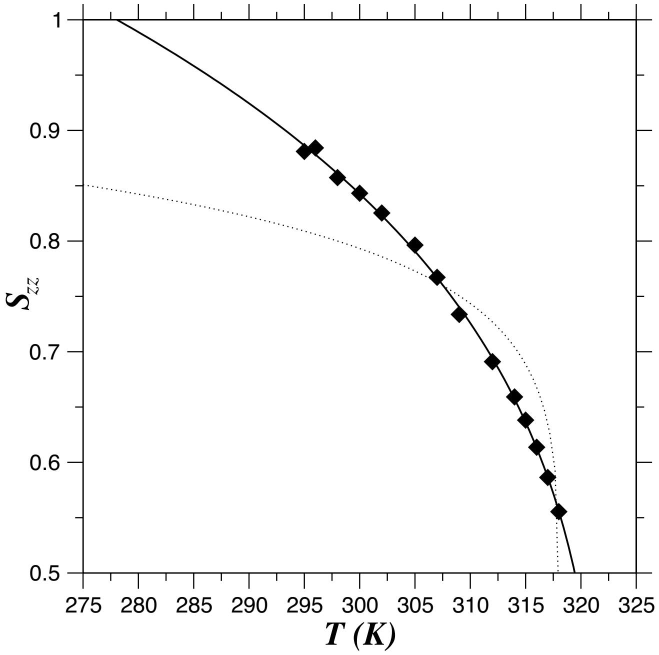

FIG. 4. Temperature dependence of the orientational order parameter S_{zz} as obtained from the analysis of the ^{2}H-NMR spectra. The dotted line is the fit via Eq. (3), while the solid line is the fit via Eqs. (4) and (6).

The value of φ_1 has been seen to vary between 86.3° and 86.4°. This means that the principal molecular axis is slightly tilted toward the chlorine atom, contrary to what happens in the unsubstituted phenyl ring, where $\varphi_1 = 90°$.

The values of S_{zz} as a function of temperature are reported in Fig. 4. Their rise upon decreasing T is considerable, and S_{zz} tends to the limiting value of unity quite rapidly. Usually, the temperature dependence of orientational order parameters in a nematic phase is effectively fitted with the Haller expression [14]

$$S_{zz}(T) = \left(1 - \frac{T}{T^*}\right)^{\gamma} \tag{3}$$

with T^* a characteristic temperature close to the nematic-to-isotropic phase transition temperature, and γ an exponent. Fitting the data of Fig. 5 with Eq. (3) have produced a mediocre result (Fig. 4). The ascent of S_{zz} upon lowering the temperature suggests that an *ad hoc* modification of Eq. (3), which may produce a noticeable improvement of the fitting quality, is the following:

$$S_{zz}(T) = \Sigma\left(1 - \frac{T}{T^*}\right)^{\gamma}. \tag{4}$$

The optimized parameters entering Eq. (4) have taken the values $\Sigma = 1.64$, $T^* = 322.2$ K, and $\gamma = 0.25$. The curve generated from Eq. (4) employing these parameters is also plotted in Fig. 4. Unsurprisingly, Σ is significantly larger than 1. This fact means that S_{zz} tends to saturate at a finite and relatively large temperature. Consequently, the *ad hoc* parameter Σ may be written as follows:

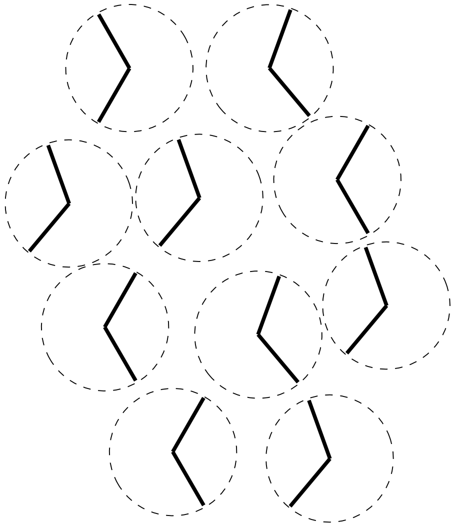

FIG. 5. Schematic representation of the solution formed by a banana-shaped solute and a nematic calamitic solvent. The dotted circles represent the borders of the aggregates of rodlike solvent molecule around a banana-shaped solute molecule, the latter represented by a bent line.

$$\Sigma = \left(\frac{1}{1 - \tilde{T}/T^*}\right)^{\gamma} \tag{5}$$

with $\tilde{T}$ a second characteristic temperature, which in the present case takes the value of 278.1 K. Equation (5) thus leads to the following extension of the original Haller expression:

$$S_{zz}(T) = \begin{cases} \left(\dfrac{1 - T/T^*}{1 - \tilde{T}/T^*}\right)^{\gamma}, & T \geqslant \tilde{T}, \\ 1, & T \leqslant \tilde{T}. \end{cases} \tag{6}$$

The fact that S_{zz} tends to unity on approaching $\tilde{T}$ may mean that the reorientational motion of the banana-shaped mesogen becomes, on decreasing temperature, not only progressively slower and of smaller amplitude, as happens commonly, but also particularly sluggish, until it freezes completely at and below $\tilde{T}$. This behavior is reminiscent of that of a glass [15]. Presumably, significant interlockings among the banana-shaped solute and the rodlike solvent molecules are responsible for the hindered solute motion and the formation of solute-solvent clusters. These clusters are harder to disentangle as temperature approaches $\tilde{T}$. It may be of interest to note that a concentration of 1 wt % is consistent with a composition of one banana-shaped solute molecule every ~340 solvent molecules, *i.e.*, roughly the number of solvent molecules contained in a sphere centered in the middle of the central ring of the banana-shaped solute and with a radius as long as one of its arms [16]. One may view the solution as formed by these aggregates which play the role of the above-mentioned solute-solvent clusters (Fig. 5).

These considerations are consistent with results of computer simulations performed on systems of model V-shaped particles, which report increasing difficulties in equilibrating the sample as the angle between the two arms deviates from 180° because of significant particle interlockings [17–19]. They are also in agreement with recent experimental studies performed on banana-shaped mesogens [7–10,21]. In particular, the unusually slow dynamic behavior of them has been tentatively explained by formulating the hypothesis of the existence of local molecular entaglements, a sort of smectic domains [7,20], preventing fast reorientational motion, while vitrified banana-shaped liquid crystals have been recently observed, albeit at such low temperature that the system is in a layered state [21].

It is worth noticing that there has been an amount of recent work leading to the hypothesis of a similarity in the reorientational dynamics of glass-forming, supercooled liquids and conventional isotropic liquid crystals [22–26], two types of fluid system which are highly packed and locally structured. The results of this Rapid Communication, certainly not in contrast with this picture, may be taken in support of it; with due caution, however, because of the peculiarities of the system investigated here, which prevent a straightforward generalization. Of more specific relevance to the present work are Refs. [23,26]. In Ref. [23] an indication of two ideal glass transitions was reported for nematogenic liquids, one occurring at a temperature, labeled T_{CH}, very close to the nematic-to-isotropic transition temperature and related to the onset of a nonzero orientational order parameter, and the other occurring at a much lower temperature, labeled T_{CL}, and related to the formation of a nematic glass. One is tempted to identify T_{CH} with T^* and T_{CL} with $\widetilde{T}$, although further work is certainly needed to verify this conjecture. In Ref. [26], apart from observing that the exploration of the potential energy surface of a model liquid-crystalline system is similar to that undertaken by a glass-forming model liquid, it has been noted that particle configurations corresponding to local potential energy minima possess a smecticlike structure even in the nematic phase. It might be that presumably intimately related features like the formation of smecticlike clusters and glassy reorientational dynamics are particularly accentuated in systems containing banana-shaped mesogenic molecules.

The possibility that the addition of banana-shaped mesogenic solutes to conventional nematic solvents induces the formation of a nematic glassy state appears interesting. It would be nice to further test this possibility with other techniques. Computer simulations, currently in progress, appear particularly suited to this purpose.

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