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# Banana-Shaped Molecules Peculiarly Oriented in a Magnetic Field: $^2\text{H}$ NMR Spectroscopy and Quantum Mechanical Calculations

Valentina Domenici,<sup>\*,[a, b]</sup> Carlo Alberto Veracini,<sup>\*,[a]</sup> Katalin Fodor-Csorba,<sup>[c]</sup> Giacomo Prampolini,<sup>[a]</sup> Ivo Cacelli,<sup>[a]</sup> Andrija Lebar,<sup>[b]</sup> and Boštjan Zalar<sup>[b]</sup>

*The orientational properties of the banana-shaped liquid crystal 4-chloro-1,3-phenylenebis[4-(4'-(10-undecenyloxy)]benzoyloxy} benzoate (CIPbis11BB) are reported in the nematic phase under the effect of an external magnetic field. A new hypothesis, which states that the central ring of the aromatic core is oriented perpendicularly to the external magnetic field, is proposed. In support of this hypothesis, a series of studies based on  $^2\text{H}$  NMR spectroscopy, both in the bulk and in solution, are discussed.  $^2\text{H}$  NMR measurements on three selectively deuterium-labelled isotopomers*

*are presented, together with DFT results from B3LYP/cc-pvDz calculations performed on the aromatic core. The rather flat shape of the investigated intramolecular energy surface allows for several different conformations to be populated, the computed magnetic susceptibilities of which are consistent with the proposed hypothesis of peculiar orientation of banana-shaped molecules. Moreover, the orientation of the magnetic susceptibility tensor is shown to be strongly dependent on the internal conformation of the banana-shaped molecules.*

## 1. Introduction

Banana-shaped molecules<sup>[1–3]</sup> represent one of the most surprising fields of soft matter developed in the last ten years. The main reason for interest is that the biaxial smectic liquid crystalline (LC) phases formed by these molecules exhibit spontaneous polarization in the layer plane<sup>[4–6]</sup> without having any asymmetric carbon atoms. Several speculations about the origin of phase chirality have been proposed, which link the molecular structure and symmetry to the peculiar molecular packing of such bent molecules within different mesophases.<sup>[7]</sup> In this context, NMR spectroscopy can play a significant role, as demonstrated by several studies based on both deuterium NMR<sup>[8–10]</sup> and carbon-13 NMR measurements.<sup>[11]</sup> Another aspect of great interest is the fact that banana-shaped liquid crystals (BLCs) have a particular behaviour even in the nematic phase. Mesophase biaxiality,<sup>[12]</sup> slow molecular dynamics,<sup>[13]</sup> large viscosity,<sup>[14]</sup> and giant flexoelectricity<sup>[15]</sup> are some examples of experimental evidence for the unusual behaviour of these molecular systems in the nematic phase. Such properties are certainly related to the distinctive orientation and aggregation of banana-shaped mesogens in this phase, while the effect of external fields can lead to results that are not easily predictable. For instance, recent studies based on NMR spectroscopy have shown that some BLC mesogens do not align at all in a magnetic field,<sup>[16–18]</sup> while others show a good orientation in magnetic fields higher than 7 T.<sup>[19]</sup>

An original hypothesis on the alignment of BLCs in a magnetic field, supported by the semi-empirical calculation of the molecular magnetic susceptibility anisotropy  $\Delta\chi_m$  and preliminary  $^2\text{H}$  NMR experiments, has been recently proposed.<sup>[20]</sup> One of the most interesting aspects, in fact, is to understand how

banana-shaped molecules are organized and packed in the bulk and under the effect of an external magnetic field. Knowledge of the value of the anisotropy  $\Delta\chi_m$  of the total molecular magnetic susceptibility  $\chi_m$  is mandatory for the determination of how the mesophase directors align in an applied magnetic field  $\vec{H}$ . Usually, the magnetic field is not strong enough to orient single and isolated molecules: the interaction energy, due to cooperative molecular ordering, is indeed crucial.<sup>[21]</sup> Moreover, in the calamitic liquid crystal the molecular magnetic susceptibility is much different from the phase magnetic susceptibility, which is a quantity averaged over all internal motions of molecules in the nematic phase. Herein, we show that overall motions in the banana nematic phase are strongly reduced, in particular the reorientation of the central ring about its *para* axis. For this reason, the molecular magnetic susceptibility is not very different from the phase susceptibility, a fact

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resulting in a perpendicular alignment of banana-shaped molecules in the magnetic field.

At a macroscopic level, the magnetic energy density of the system can be expressed as  $g_M = -\chi_a(\vec{H} \cdot \vec{n})^2 / (2\mu_0)$ , where  $\chi_a$  is the anisotropic part of the magnetic susceptibility tensor, defined as  $\chi_a = \chi_{||} - \chi_{\perp}$ , with  $\chi_{||}$  and  $\chi_{\perp}$  denoting the components of the magnetic susceptibility tensor parallel and perpendicular to the director of the phase, respectively. The direction of preferred alignment of a system in the magnetic field depends on the sign of the quantity  $\chi_a$ . Positive  $\chi_a$  values in most liquid crystals result in the alignment of the phase director  $\vec{n}$  parallel to the magnetic field  $\vec{H}$ . The sign of  $\chi_a$  can often be easily predicted for discotic and calamitic liquid crystals based on the molecular structure, since in principle it is possible to relate the macroscopic property  $\chi_a$  to the molecular property  $\Delta\chi_m$  as well as the Saupe order parameters  $S$ .<sup>[22]</sup> The case of banana-shaped molecules is less obvious, since the molecular shape of these molecules is in a way intermediate between the previous cases. This also makes it difficult to properly choose the direction of the long molecular axis in banana-shaped molecules and may be the reason why these mesophases form biaxial phases. The implications of the shape of the average molecular conformation of banana-shaped mesogens are related not only to the phase chirality, but also to the alignment of BLC phases in a magnetic field, since, as preliminary calculations demonstrated,<sup>[20]</sup> the molecular magnetic susceptibility anisotropy  $\Delta\chi_m$  is strictly dependent on the molecular conformation. In the case of banana-shaped molecules, however, complex molecular aggregates may form, in which molecules are not completely free to rotate and molecular dynamics is scaled to the low-frequency range with respect to common calamitic liquid crystals.<sup>[9,13,18,20]</sup> In this frame, the relation between the molecular and mesophase magnetic susceptibility anisotropy is much stronger.

To support the fact that BLC molecules in the bulk behave in a very particular way, several  $^2\text{H}$  NMR studies have been performed on banana-shaped molecules<sup>[23]</sup> or their intermediates<sup>[10,24]</sup> dissolved in LC solvents, such as conventional nematic calamitic compounds. In this case, BLC molecules behave in a completely different way with respect to the bulk. In particular, in LC solutions, BLC molecules were found to align with the five-ring aromatic core parallel to the long molecular axis of calamitic mesogens. Moreover, the orientational order parameter  $S$ , referred to the local aromatic core of bent molecules, was found to be very high (up to 0.85), and the  $^2\text{H}$  spin-spin relaxation times, as well as the experimental line widths, indicate that molecules are affected by fast reorientational motions. When the same BLC molecules are in the bulk, the  $^2\text{H}$  NMR spectra are affected by much slower motions<sup>[9,13,16,25,26]</sup> and therefore show completely different features. These experimental findings support the idea that BLC molecules have a peculiar packing within the nematic phase under the effect of a magnetic field, as proposed in ref. [20] and widely demonstrated in this work, which has the main purpose to provide further elements to confirm and support such a hypothesis.

Herein, the BLC 4-chloro-1,3-phenylenebis[4-[4'-(10-undecyloxy)] benzoyloxy] benzoate (CIPbis11BB) was investigated

by  $^2\text{H}$  NMR spectroscopy and quantum mechanical calculations. A complete  $^2\text{H}$  NMR study in the nematic phase, performed on three deuterium-labelled isotopomers of CIPbis11BB, is reported together with a selection of results obtained on small BLC sub-units dissolved in the CIPbis11BB itself. In this work, the values of the components of the tensor associated with the property  $\chi_m$ , calculated for a single molecule of CIPbis11BB, are reported as a function of internal coordinates. The results obtained suggest a strong dependence of the anisotropy  $\Delta\chi_m$  on the different conformations. By comparing this behaviour with that found in a conventional calamitic compound, such as 8CB, the calculated susceptibilities can help in understanding why banana-shaped molecules have difficulties in assuming a uniform alignment of directors in a very packed and organized structure, such as the  $B_2$  phase.<sup>[18]</sup>

Finally, the main result of this work is the description and validation of a new hypothesis of a peculiar aggregation of banana-shaped molecules in the nematic phase in the presence of a magnetic field, which is supported by theoretical calculations and  $^2\text{H}$  NMR experimental evidence. Moreover, our findings justify the observation that some banana-shaped compounds do not easily orient even in a high magnetic field, and under some conditions they form specific aggregates.

## Experimental Section

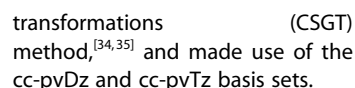
**Materials:** The sample under study is the banana-shaped mesogen CIPbis11BB. Three isotopomers, selectively labelled as indicated in Scheme 1a, namely CIPbis11BB- $C-d_3$ , CIPbis11BB- $I-d_4$  and CIPbis11BB- $O-d_4$ , were investigated by  $^2\text{H}$  NMR spectroscopy. In this way we could detect, in separate experiments, the five rings representing the central aromatic core of the BLC. The synthesis and characterization of the unlabelled and labelled samples are reported in refs. [27,28], respectively. The deuterium percentages of the CIPbis11BB- $C-d_3$  are 85, 75 and 5 for positions 2, 6 and 5, respectively. For CIPbis11BB- $I-d_4$  and CIPbis11BB- $O-d_4$  the level of deuteration is about 95%.

The sample CIPbis11BB showed the following mesophase transition temperatures on cooling, as detected by differential scanning calorimetry: Isotropic 355 K Nematic 311 K Crystal.

Note that the transition temperatures detected on the three labelled isotopomers are slightly different, due to deuteration effects and impurities.

The 3-(benzoyloxy)phenyl benzoate (BOB) probe deuterated on the two lateral rings ( $d_{10}$ ; see Scheme 1b) was used as a small deuterium-labelled solute. Its synthesis is reported in ref. [10]. BOB- $d_{10}$  was diluted in the banana-shaped mesogen CIPbis11BB (1.2% by weight) and the LC solution was mixed by heating to the isotropic–nematic transition temperature.

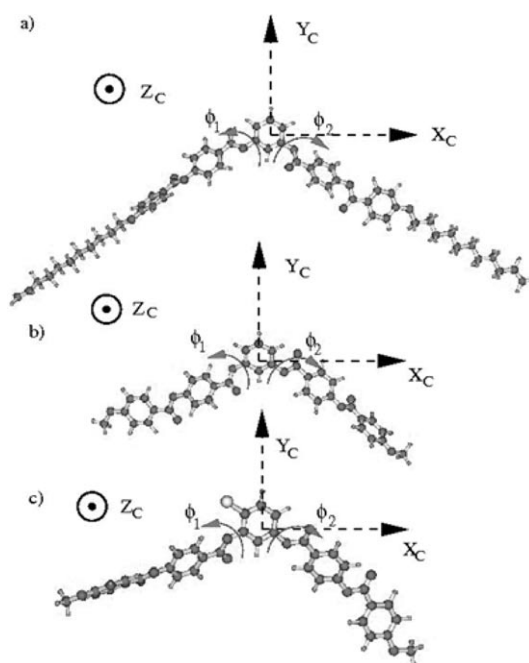
**$^2\text{H}$  NMR Measurements:** The  $^2\text{H}$  NMR experiments were performed with two different NMR spectrometers. Measurements on the CIPbis11BB- $I-d_4$  and CIPbis11BB- $O-d_4$  samples were carried out on a 9.40-T Varian InfinityPlus400 spectrometer, working at 61 MHz for deuterium, by using a goniometric probe (5 mm) dedicated to the deuterium nucleus.  $^2\text{H}$  NMR spectra were recorded, either on cooling or on heating, by single-pulse (SP) and quadrupolar-echo (QE) pulse sequences,<sup>[29]</sup> either with or without  $^1\text{H}$  continuous-wave decoupling. A 90° pulse of 4.6  $\mu\text{s}$ , a pulse delay of 1 s and a QE time delay  $\tau$  of 24  $\mu\text{s}$  were used. The number of scans varied from 400



### 2.1.1. Banana-Shaped Molecules in the Bulk

<sup>2</sup>H NMR spectra of the three isotopomers CIPbis11BB-I-d<sub>4</sub>, CIPbis11BB-O-d<sub>4</sub> and CIPbis11BB-C-d<sub>3</sub> (see Scheme 1 a) were recorded with and without proton decoupling (QE sequence) following several cooling and heating procedures and temperature equilibration times, as mentioned in Materials and Methods. It should be remembered that the nematic phase is a monotropic one, and this can cause differences in the freezing temperature. According to <sup>2</sup>H NMR investigations, the mesophase range of stability is reduced and the temperature transitions are the following:

All the considered molecular geometries were optimized with a Dunning correlation-consistent basis set cc-pvDz. The intramolecular torsional energy surface of the ClPbis1BB molecule was computed by optimizing all internal coordinates except the dihedrals  $\phi_1$  and  $\phi_2$ , defined in Figure 1. All calculations of the magnetic susceptibility tensors were performed with the complete set of gauge



**Figure 1.** Structures of a) the Pbis11BB molecule, b) the Pbis1BB molecule and c) the ClPbis1BB molecule.  $\phi_1$  and  $\phi_2$  are the torsional angles around the linkage between the central phenyl ring and the left and right wings, respectively. The  $Z$  axis is perpendicular to the plane of the central ring.

CIPbis11BB-I- $d_4$ : isotropic 353 K nematic 339 K crystal,  
 CIPbis11BB-O- $d_4$ : isotropic 361 K nematic 344 K crystal,  
 CIPbis11BB-C- $d_3$ : isotropic 361 K nematic 339 K crystal.

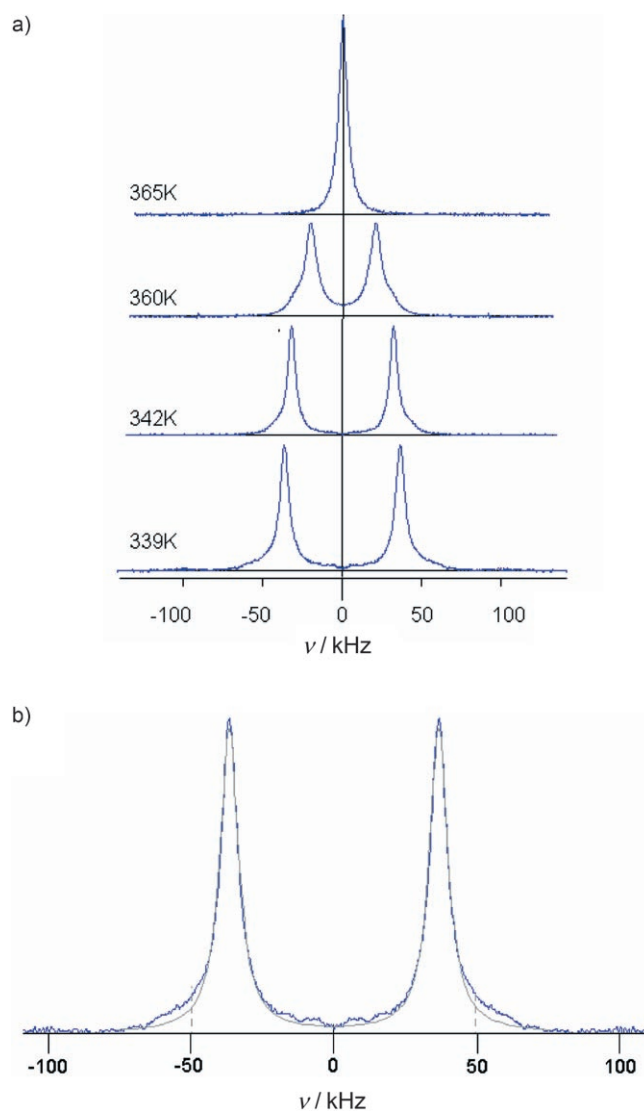
The two isotopomers labelled on the lateral aromatic rings (CIPbis11BB-I- $d_4$ , CIPbis11BB-O- $d_4$ ) yield quite similar  $^2\text{H}$  NMR spectra that differ very much from those typical of the isotopomer labelled on the central ring (CIPbis11BB-C- $d_3$ ). The main features of the recorded spectra are summarized and discussed here.

**CIPbis11BB-C- $d_3$  Sample:** Several  $^2\text{H}$  NMR measurements were performed on this sample under different experimental conditions. The first  $^2\text{H}$  NMR spectra of CIPbis11BB-C- $d_3$  were acquired with a spectrometer working at 61 MHz for deuterium, and preliminary results were reported in ref. [8]. Herein, we present new  $^2\text{H}$  NMR measurements acquired with a very high reproducibility, which test the effect of different cooling and heating rates. However, the fundamental features of the spectra could be confirmed and they can be summarized as follows.

Despite the presence of three different deuterium sites, as shown in Scheme 1 a, the  $^2\text{H}$  NMR spectra in the oriented nematic phase show a single quadrupolar doublet, with a splitting  $\Delta\nu_q^C$  whose value is extremely high (from 45 to 73 kHz). Each doublet peak has a very broad line width, which remains substantially constant within the investigated temperature range ( $\Delta\nu_{h/2} \approx 7500$  Hz), as reported in Figure 2.<sup>[13]</sup> No differences were observed between spectra acquired with and without proton decoupling.

As concerns the interpretation of the spectral features, the observation of a single quadrupolar doublet with three different, that is, physically and chemically inequivalent, deuterium sites was first explained<sup>[8]</sup> when we proposed a very particular orientation of the central ring with respect to the magnetic field  $H$ . In fact, the previously proposed explanation requires that the three deuterons retain a peculiar geometry in order to have the same quadrupolar splitting, in absolute values, with a different sign. A slight deviation from such a particular orientation would lead to completely different values of the quadrupolar splitting among the different aromatic deuterons. The offered interpretation was then very artificial, even if in agreement with the commonly accepted picture of bent molecules oriented similarly to rodlike ones (a conjecture never verified experimentally and based on a rather arbitrary selection of the long molecular axis). These elements are important to understand why we started to consider an alternative orientation of the CIPbis11BB molecules in the presence of magnetic fields.

A simpler and more plausible explanation of the  $^2\text{H}$  NMR spectral features described above was proposed recently:<sup>[20]</sup> the central ring of the CIPbis11BB sample orients perpendicularly to the magnetic field; thus, all aromatic C–D bonds form an average angle of  $90^\circ$  with respect to the external field  $H$  and also experience the same orientational order. In this hypothesis, depicted in Figure 3, we introduce several assumptions: 1) the mesophase is well-aligned in the magnetic field; 2) the mesophase is uniaxial, with a cylindrical symmetry axis parallel to the magnetic field; and 3) the central ring is as-



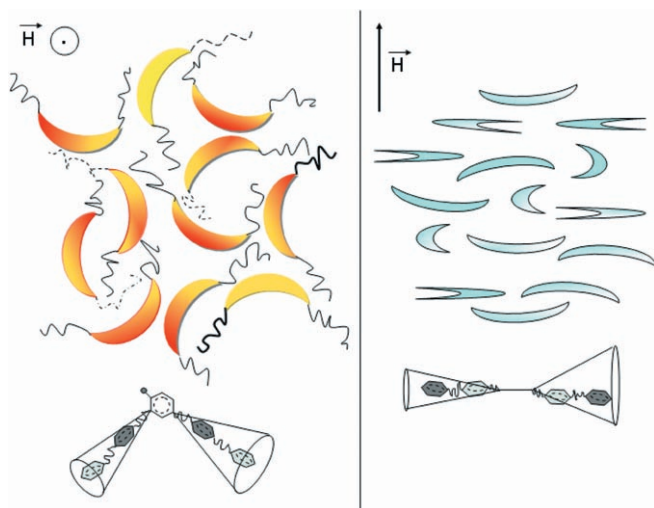
**Figure 2.** a) A selection of  $^2\text{H}$  NMR spectra of CIPbis11BB-C- $d_3$  at different temperatures. b) Experimental (blue) and fitted (grey)  $^2\text{H}$  NMR spectrum of CIPbis11BB-C- $d_3$  at  $T = 339$  K.

sumed to possess on average the same symmetry as the mesophase.

Several experimental observations support these assumptions:

a) Due to the geometry of the NMR experiment it is not possible to discriminate between the uniaxial or biaxial phase. In fact, only angle-dependent measurements can in principle give a clue. Assumption of a perfectly uniaxial phase, as we do for simplicity in the following treatment, does not affect the conclusions of the analysis. Unfortunately, angular dependence measurements could not be performed because the sample re-oriented with the magnetic field. However, preliminary angular measurements on confined samples show that the orientation of bent molecules with respect to the confining surfaces is such that the central aromatic ring lies flat at the surface, thus giving an indication of the orientation of CIPbis11BB molecules.<sup>[36]</sup>

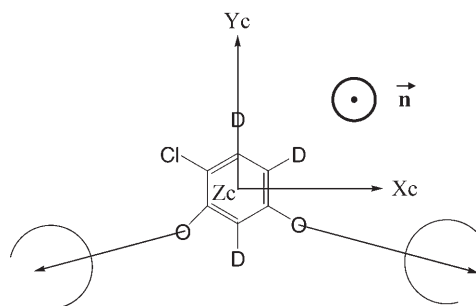




**Figure 3.** Schematic illustration of the orientation of banana-shaped CIPbis11BB molecules in a magnetic field  $H$ , in the bulk. Two views, perpendicular (left) and parallel (right) to the field, are shown. This picture is consistent with both the  $^2\text{H}$  NMR spectra and quantum mechanical computations, as discussed in the text. The average orientation of a single molecule (limited to the five-ring core) is also presented.

b)  $^2\text{H}$  NMR spectra of CIPbis11BB- $d_3$  are characterized by unusual line broadening. The simulation of the line shapes by using a Lorentzian function was quite satisfactory, as reported in Figure 2b. This is quite unusual for spectra recorded in the nematic phase formed by calamitic liquid crystals, where the line has a Gaussian shape in most of the cases reported in the literature. The spectra of CIPbis11BB- $d_3$  are indeed characterized by a single doublet well-fitted by two symmetric Lorentzian functions in the whole mesophasic range. A small inhomogeneity in the orientation justifies the small shoulders visible at the edge of the doublet at certain temperatures, which correspond to less than 2% over the total integral. From this experimental finding we can confirm that the sample is well-oriented and that the origin of the line broadening is not static, due to inhomogeneities in the nematic order, but dynamic.

c) A complete study<sup>[13, 14, 26]</sup> based on a theoretical treatment of the spin–spin relaxation times, measured in this mesophase of the same sample, proves that the origin of the unusual line broadening can be quantitatively evaluated by considering, as the main contribution, the reorientation of the molecule around an axis perpendicular to the molecular plane ( $D_\perp$ ), namely parallel to  $Z_c$  in Figure 4. The reorientation of the molecule out of the central ring plane  $D_\perp$  is the most important since it is the slowest ( $D_\perp < 10^6 \text{ s}^{-1}$ ). This extremely low value confirms that in our case, banana-shaped molecules are affected by very slow motions, thus validating our hypothesis of an incomplete averaging over molecular conformations, at least in the  $^2\text{H}$  NMR timescale. Small fluctuations of the molecule, and in particular of the central ring around the molecular plane ( $\perp$  to  $\vec{n}$ ), can be taken into account, but their characteristic time is quite long. On average, the central ring of CIPbis11BB is perpendicular to the magnetic field, and thus to  $Z_c$  in Figure 4.



**Figure 4.** Central ring frame ( $F_c = X_c, Y_c, Z_c$ ). According to this picture the angles formed by the CD bonds of deuterons in position 2 ( $\phi_1$ ), position 6 ( $\phi_2$ ) and position 5 ( $\phi_3$ ) and the  $Z_c$  axis are equal to  $90^\circ$ . The orientation of the central ring frame with respect to that of the nematic phase director  $\vec{n}$  is also indicated. This frame is in agreement with that chosen for quantum mechanical calculations (see Figure 1).

According to the previous considerations, we can analyse the experimental quadrupolar splitting  $\Delta\nu_q^c$  to evaluate the orientational order parameter referring to the ring. The quadrupolar splitting can be defined by the following equation [Eq. (1)].<sup>[37]</sup>

$$|\Delta\nu_q^c(T)| = |\langle \nu_q \rangle^c \cdot S_2(T) \cdot P_2(\cos\beta)| \quad (1)$$

where  $\langle \nu_q \rangle^c$  is the averaged quadrupolar frequency for the specific deuterium and  $S_2$  is the mesophase orientational order parameter.  $\langle \nu_q \rangle^c$  is equal to  $\nu_q$ , where  $\nu_q = 3e^2qQ/2h$  is the quadrupolar frequency of the C–D bond deuteron. For aromatic deuterons we take  $\nu_q = 275 \text{ kHz}$ . The angle  $\beta$  is equal to  $\pi/2$ , being the angle between the C–D bonds (all of them) of the central ring and the director  $\vec{n}$  (see Figure 4a or Figure 1). We then have [Eq. (2)]:

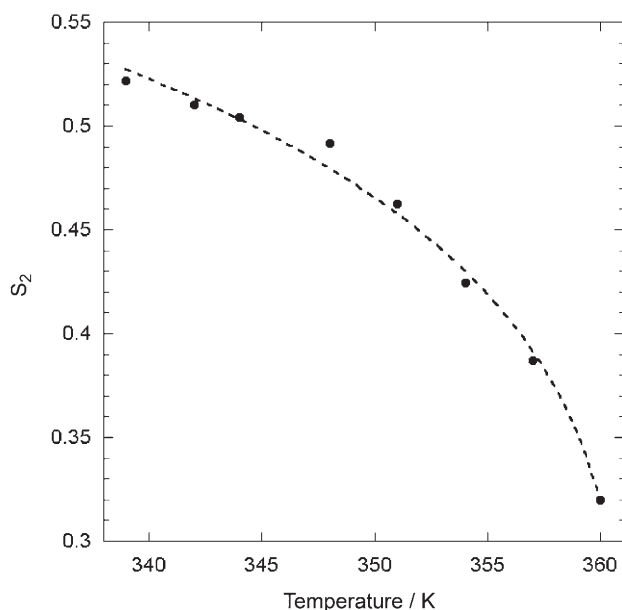
$$|\Delta\nu_q^c(T)| = |\nu_q/2 \cdot S_2(T)| \quad (2)$$

Given the above relation,  $S_2(T) < 1$  reflects fluctuations of the central ring's orientations away from a perfect perpendicularity. By applying Equation (2) to the experimental quadrupolar splittings, the orientational order  $S_2$  can be calculated and it ranges between 0.32 and 0.52, as reported in Figure 5. If we look at the trend of  $S_2$  as a function of temperature, the Haller equation can be used to fit the experimental data [Eq. (3)]:

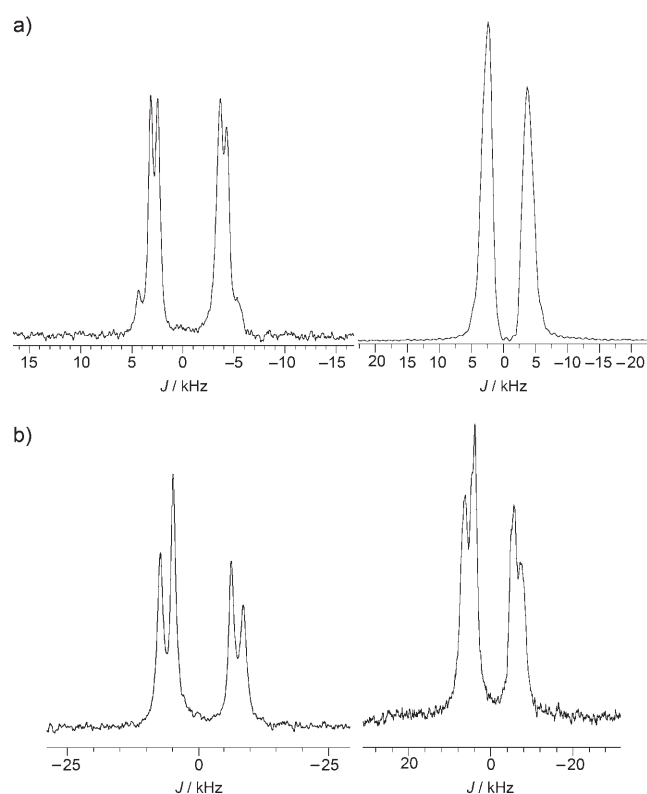
$$S(T) = S_0(1 - T_c/T)^\gamma \quad (3)$$

These data are well-fitted, as can be seen in Figure 5, and the best-fitting parameters are  $S_0 = 0.88$  and  $\gamma = 0.18$ .

**CIPbis11BB-I- $d_4$  and CIPbis11BB-O- $d_4$  Samples:** The  $^2\text{H}$  NMR spectra of CIPbis11BB-I- $d_4$  and CIPbis11BB-O- $d_4$ , acquired with and without proton decoupling, are reported in Figure 6. These spectra are commented on and the analysis is reported in detail in the Supporting Information. The main features of the spectra are summarized here:



**Figure 5.** Orientational order parameter  $S_2$  as a function of temperature [K] for the mesophase formed by CIPbis11BB, as obtained by the analysis of quadrupolar splittings of the isotopomer CIPbis11BB- $C-d_3$ , evaluated by applying Equation (2). The dashed curve is the best-fitting curve of the orientational order parameter, according to the Haller equation [Eq. (3)].



**Figure 6.** Selection of  $^2H$  NMR (QE) spectra of the two labelled isotopomers with (left) and without (right) proton decoupling: a) CIPbis11BB- $O-d_4$  at  $T = 355$  K and b) CIPbis11BB- $I-d_4$  at  $T = 349$  K.

1) At each temperature the  $^2H$  NMR spectra of both CIPbis11BB- $I-d_4$  and CIPbis11BB- $O-d_4$  are dominated by two

quadrupolar splittings ascribable to the two lateral wings of the banana-shaped molecule. In fact, the molecule is not symmetric due to the presence of the chlorine atom on the central ring. Consequently, the two lateral wings experience a different orientation with respect to the magnetic field. This finding is in agreement with quantum mechanical computations for the five-ring molecule,<sup>[33]</sup> as well as with the observed behaviour of two banana-shaped sub-units (three-ring probes) diluted in LC solvents.<sup>[10]</sup>

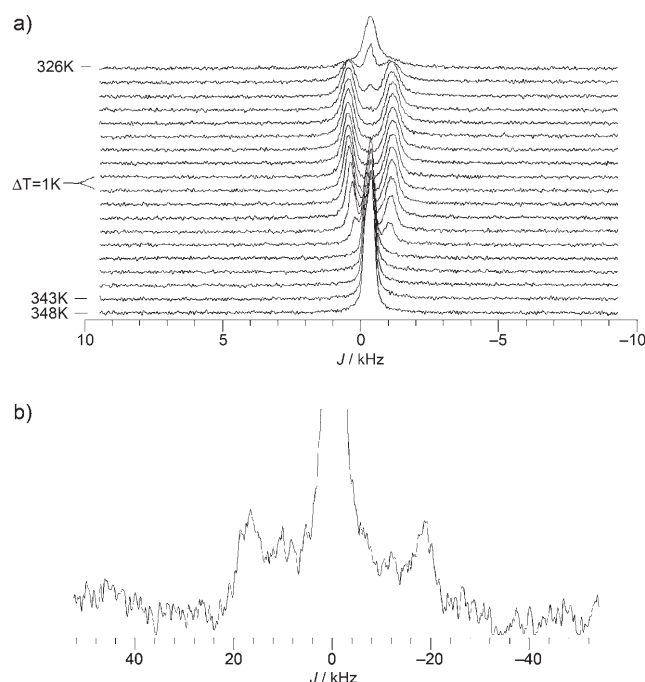
2) The inner rings appear to be more ordered than the outer rings. This fact is not surprising since the molecular orientational order usually decreases by moving away from the central rigid core closer to the lateral chains, which are more flexible, thus averaging the parameter  $S$  to smaller values. This behaviour is also confirmed by the calculations reported in refs. [10,33], which show that the energy surface potential of the external rings is extremely flat as a function of dihedral angles. As recent computations have shown,<sup>[33]</sup> the more oriented rings are those on the lateral wing closer to the chlorine atom.

3) The analysis (see Supporting Information) performed on the quadrupolar splittings of these two isotopomers with the assumption of a cylindrical symmetry, assuming that the four rings are averaged out with respect to fast reorientation around the *para* axis and conformational arrangements, give extremely high values of the order parameter  $S_2$ , referred to the mesophase director. The assumption of fast motions appears to be an oversimplification and this is in agreement with  $^2H$  NMR relaxation on the same labelled compounds.<sup>[26]</sup> This fact prevents us from directly comparing the values of the order parameters obtained for the central and lateral rings.

### 2.1.2. Banana-Shaped Sub-Units in Different Nematic Solvents

The  $^2H$  NMR spectra of BOB- $d_{10}$  diluted in the nematic CIPbis11BB (see Figure 7a and b), recorded by using the QE sequence, are characterized by two regions: 1) between  $-5$  and  $5$  kHz, where a quadrupolar splitting with typical line width  $\Delta\nu_{h/2}$  of  $400$  Hz is ascribable to the *ortho/meta* deuterons (see Figure 7a); and 2) between  $-45$  and  $-30$  kHz and between  $30$  and  $45$  kHz, where a very broad quadrupolar splitting corresponds to the *para* deuterons (see Figure 7b).<sup>[37]</sup>

For this molecule, similar to the case where it is dissolved in common calamitic liquid crystals,<sup>[10]</sup> no differences can be noticed between the two lateral aromatic rings, due to the symmetry of the molecule. However, the fact that the *para* signals are characterized by a large broadening in CIPbis11BB was not observed in common nematic liquid crystals, where the line width was about  $120$  Hz for all signals. This big difference between the calamitic and banana-shaped environment confirms that in the last case, the *para* deuterons are sensitive to the slow motion observed in the banana-shaped nematic formed by the CIPbis11BB sample.<sup>[25]</sup> In fact, the *para* signals are not averaged out by the internal rotation of the phenyl ring around its *para* axis, as the *ortho/meta* signals are: for this reason, the *para* signals are sensitive probes for the overall motions of the molecules as well as the BLCs used as solvent.

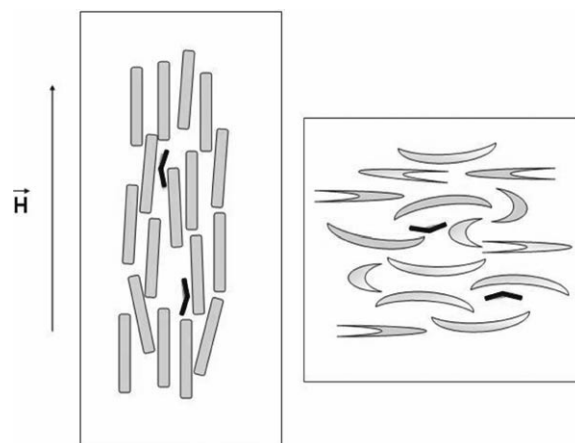


**Figure 7.** a)  $^2\text{H}$  NMR spectra of BOB- $d_{10}$  dissolved in CIPbis11BB as a function of temperature, which focus on the region  $\pm 10$  kHz. b) Detail of the  $^2\text{H}$  NMR spectrum of BOB- $d_{10}$  dissolved in CIPbis11BB, which focuses on the *para* signals.

Another important observation concerns the value of the quadrupolar splitting of the *para* signal in CIPbis11BB and in Phase V, or 4-cyano-4'-pentybiphenyl (5CB). In the former case, it is about 38–40 kHz while in the latter it is about 76–80 kHz, depending on the temperature and on the nematic solvent (in 5CB or Phase V, for example). As the *para* signals are not averaged by the reorientation around the *para* axis, this means that this axis has a different order in the two solvents. Moreover, the fact that the quadrupolar splitting, as well as the local orientational order of the *para* axis in CIPbis11BB, is exactly half of that in common calamitic solvents can be interpreted as an indirect confirmation of the orientation proposed for the CIPbis11BB molecules, as represented in Figure 8.

## 2.2. Quantum Chemical Results

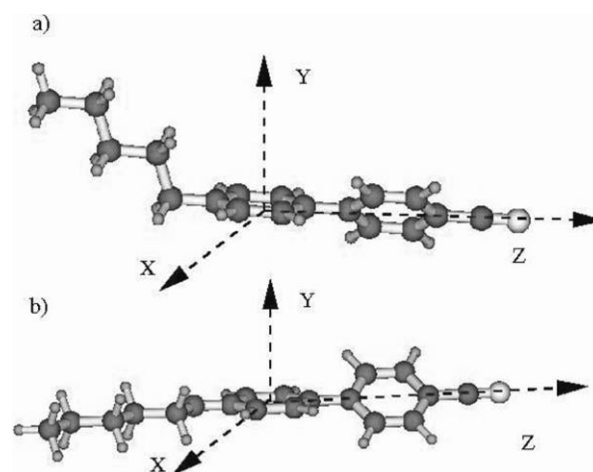
A first set of magnetic susceptibility calculations was performed on the optimized geometries of two typical nematogenic rodlike molecules, namely 5CB and 4-cyano-4'-pentoxybiphenyl (5OCB). The aim of such computations was both to evaluate the effect of the basis set and to verify the orientation of the magnetic susceptibility principal axes with respect to the molecular long axis. From the results reported in Table 1, one can see that, despite a relevant basis set dependence, the use of



**Figure 8.** Orientation of the small probe BOB in two nematic solvents: common calamitic, such as Phase V (left), and the banana-shaped nematic CIPbis11BB (right).

the smaller basis set does not alter the relative order of the computed susceptibilities.

As is clear from Table 1, the off-diagonal elements are small, thus confirming that the eigenvalues and eigenvectors are not much different from those reported in the molecular frame ( $X, Y, Z$ ) shown in Figure 9. As expected, if the two molecules are oriented with the molecular long axis parallel to the  $Z$  axis, the most negative (the larger in absolute value) component of the magnetic susceptibility tensor lies perpendicular to the  $Z$  direction and the other components are almost equal in magnitude.



**Figure 9.** Structure of a) the 5CB molecule and b) the 5OCB molecule.

**Table 1.** Computed magnetic susceptibilities of nematogenic rodlike molecules. All calculations were performed on a geometry completely optimized at the B3LYP/cc-pvDz level.

Molecule	Basis set	$\chi_{xx}$ [ppm]	$\chi_{yy}$ [ppm]	$\chi_{zz}$ [ppm]	$\chi_{xy}$ [ppm]	$\chi_{yz}$ [ppm]	$\chi_{xz}$ [ppm]
5CB	cc-pvDz	−130.8	−213.7	−125.8	−26.6	0.56	0.0
5CB	cc-pvTz	−139.4	−224.6	−140.8	−27.8	2.0	0.0
5OCB	cc-pvDz	−145.2	−219.3	−128.6	26.5	0.1	5.7
5OCB	cc-pvTz	−154.4	−229.1	−144.6	27.8	0.1	2.8



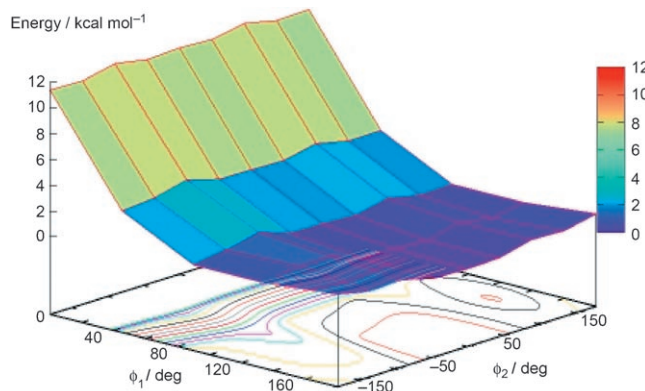
In particular, as for the benzene molecule, the main tensor component lies in between the two  $C_6$  axes of the two nearly coplanar aromatic rings (i.e. along the  $Y$  axis in Figure 9). As the interaction with the field is repulsive, this will cause these diamagnetic molecules to orient their long axis parallel to the applied magnetic field. Notice that the uniaxial symmetry of such calamitic systems allows us to average the susceptibility over rotations about the long molecular axis.

A second set of calculations was performed on the banana-shaped molecules Pbis11BB, Pbis1BB and CIPbis1BB (Figure 1). Considering the large dimensions of the (CI)-Pbis11BB molecule, it would be desirable, for computational reasons, to perform all the calculations only on the central core of such molecule, that is, on (CI)-Pbis1BB. This approach can be followed only if the lateral aliphatic chains do not alter the relative order of the components of the magnetic susceptibility tensor, as we are interested in the orientation of CIPbis11BB with respect to the field. A comparison of the results of calculations performed on the Pbis11BB and Pbis1BB molecules is reported in Table 2 and confirms this possibility. In fact, the inclusion of the chains only produces a shift of  $\approx 180$  ppm on the susceptibilities, which indicates that the lateral chain contribution is essentially isotropic. As this finding was also verified for different chain conformations, we are confident that calculations may be performed on the smaller Pbis1BB molecule.

On comparing the data of Tables 1 and 2, it emerges that rodlike and banana-shaped molecules have sensitively different magnetic properties. In the fully optimized geometry of three banana-shaped molecules, the greatest component (in absolute value) of the magnetic susceptibility tensor lies perpendicular to the central phenyl ring, but the other two components are rather different, thus showing a certain degree of biaxiality. This feature suggests that a more complex orientational behaviour in the presence of a magnetic field should be expected for banana-shaped mesogens, and rules out the possibility of performing an average over rotation around any molecular axis.

Domenici et al. have shown, through a semi-empirical approach,<sup>[20]</sup> that the magnetic susceptibility tensor  $\chi$  strongly depends on the relative orientation of the lateral phenyl rings, that is, on the values of the  $\phi_1$  and  $\phi_2$  dihedrals shown in Figure 1. On the other hand, recent calculations on banana-shaped cores<sup>[30,38]</sup> Pbis1BB and CIPbis1BB have shown that the minimum region of the torsional energy surface  $E(\phi_1, \phi_2)$  of such molecules is very flat, so that at room temperature many internal conformations are populated. Therefore, a detailed analysis of the behaviour of the molecular magnetic properties versus the possible internal conformations was performed on the CIPbis1BB molecule.

The torsional energy profile of the CIPbis1BB molecule has been computed at the B3LYP/cc-pvDz level as a function of the two dihedrals  $\phi_1$  and  $\phi_2$ . A 2D plot of the obtained surface is reported in Figure 10. The repulsion between the chlorine



**Figure 10.** Torsional energy surface for CIPbisBB. Angles  $\phi_1$  and  $\phi_2$  are defined in Figure 1 c and reported in degrees. Energies are in  $\text{kcal mol}^{-1}$ .

atom and the carbonyl oxygen atom of the left wing causes a high barrier for  $\phi_1 < 90^\circ$ .<sup>[30]</sup> On the other hand, the profile along  $\phi_2$  is rather flat, and the right wing can assume different conformations even at room temperature. These features agree well with the non-equivalency of the two wings resulting from the  $^2\text{H}$  NMR measurements previously discussed.

Finally, for all the considered geometries, the susceptibility tensor  $\chi$  was computed and diagonalized. The three resulting eigenvalues were ordered from the less negative value, thus smaller in absolute value ( $\chi^{\min}$ ) to the largest in absolute value ( $\chi^{\max}$ ). Considering its diamagnetic nature, the CIPbis1BB molecule will tend to align the eigenvector  $u^{\min}$  corresponding to  $\chi^{\min}$  along the direction of the external magnetic field. The angle  $\theta$  between  $u^{\min}$  and the  $Z_c$  axis (defined as perpendicular to the central phenyl ring, as shown in Figure 1) was plotted as a function of the dihedral  $\phi_2$  at different  $\phi_1$  angles (see Figure 11).

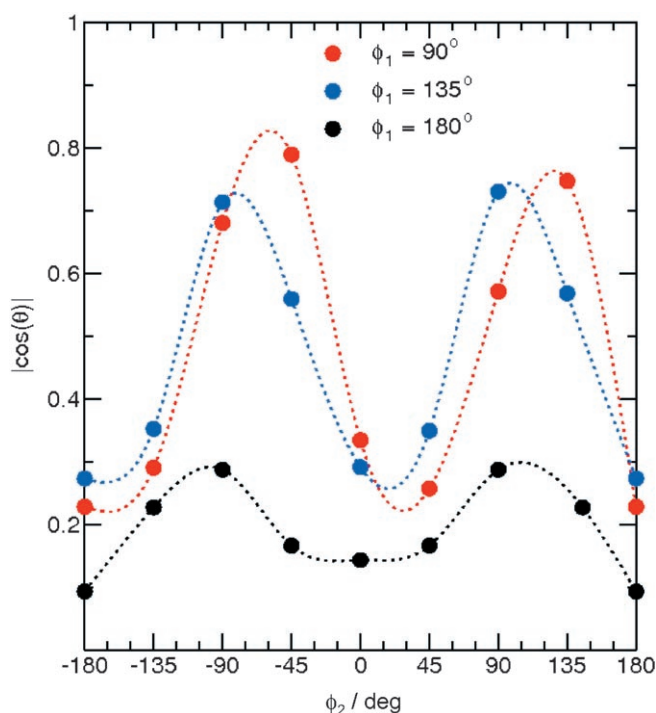
The strong dependence of the magnetic susceptibility tensor, and in particular of its minimum eigenvalue, on the torsional dihedrals  $\phi_1$  and  $\phi_2$  appears clearly from Figure 11, and confirms the preliminary calculations of ref. [10]. In particular, it may be observed that when the  $\phi_1$  dihedral is fixed to  $90^\circ$  or  $135^\circ$ , the  $\cos(\theta)$  function may assume values very close to unity, which corresponds to an alignment of  $u^{\min}$  with the  $Z_c$  molecular axis, in accordance with the hypothesis of a discotic-like behaviour of the banana-shaped molecules in the presence of a magnetic field. As one can see from Figure 10, such

conformations can be populated at room temperature, by considering the flatness of the torsional energy surface in the region  $\phi_1 = 90^\circ, 135^\circ; -180^\circ \leq \phi_2 \leq 180^\circ$ .

Unfortunately only incomplete conclusions can be drawn

**Table 2.** Computed (B3LYP/cc-pvDz) magnetic susceptibilities of banana-shaped molecules. All calculations were performed on a geometry completely optimized at the B3LYP/cc-pvDz level.

Molecule	$\chi_{xxc}$ [ppm]	$\chi_{ycyc}$ [ppm]	$\chi_{zxc}$ [ppm]	$\chi_{xcyc}$ [ppm]	$\chi_{yzc}$ [ppm]	$\chi_{xczc}$ [ppm]	$\phi_1$	$\phi_2$
Pbis11BB	-441.0	-494.3	-578.3	39.7	-81.9	-10.4	132	45
Pbis1BB	-267.2	-317.1	-394.6	34.3	-80.0	-10.7	132	45
CIPbis1BB	-282.9	-318.7	-434.0	-47.0	-13.7	-37.2	180	45



**Figure 11.**  $\cos(\theta)$  versus the torsional angle  $\phi_2$ , computed at different values of  $\phi_1$ .  $\theta$  is defined as the angle between the eigenvector corresponding to the minimum (less negative) eigenvalue of the magnetic susceptibility tensor  $\chi$  and the  $Z_c$  molecular axis. The latter, as shown in Figure 1, is chosen perpendicular to the plane of the central phenyl ring.

on the molecular behaviour in the bulk, because this analysis lacks any information about the influence of the surrounding molecules. Indeed, intermolecular interactions between neighbours in the condensed phase may sensitively alter the distribution of the intramolecular conformations (and, therefore, the  $\chi$  tensor). Clearly this cannot be predicted by single-molecule quantum calculations, but other techniques, such as computer simulations, could be employed in more accurate investigations of the proposed hypothesis.

### 3. Summary and Conclusions

We have reported a complete  $^2\text{H}$  NMR study of the banana-shaped mesogen CIPbis11BB in its nematic phase, supported by quantum mechanical calculations on the isolated single molecule. The aim of this comparative study was to elucidate the structural and orientational properties of the nematic phase formed by this banana-shaped mesogen, since previous studies have revealed some peculiar and unusual behaviour. In the investigation reported here, the analysis of  $^2\text{H}$  NMR spectra recorded on three deuterium-labelled isotopomers of CIPbis11BB enabled us to describe the whole molecular core. The orientation of the central aromatic core with respect to the magnetic field is perpendicular, as confirmed also by the comparison between  $^2\text{H}$  NMR spectra of banana-shaped subunits diluted in common LC nematic solvents and in the nematic phase formed by CIPbis11BB. Quantum mechanical calculations of the molecular magnetic susceptibility tensor revealed

that the CIPbis11BB molecule may assume such an orientation with respect to the magnetic field, since the minimum-energy conformation has an orientation of the molecular magnetic susceptibility tensor that is compatible with the picture we have proposed.

Moreover, this molecular property may have a high impact on the related mesophase property  $\chi_a$ , which has been experimentally measured in a similar banana-shaped mesogen.<sup>[14]</sup>  $\chi_a$  was found to be two orders of magnitude less than that in calamitic compounds ( $\approx 10^{-8}$  instead of  $\approx 10^{-6}$ ), and this low value could be explained by its dependence on the orientation and particular aggregation of banana-shaped molecules in the mesophase. The dependence of the molecular magnetic susceptibility anisotropy on the internal conformations, demonstrated in this work, could also be used to explain the small experimental value found for the property  $\chi_a$ .

The main results obtained from this study can be summarized as follows. 1) The sample CIPbis11BB is well-aligned and uniformly oriented in the presence of the external magnetic field. 2) The mesophase is assumed to be uniaxial and the orientational order parameter  $S_2$  was determined by analysing the quadrupolar splittings of the central ring:  $S_2$  ranges between 0.32 and 0.52, which is typical of nematic liquid crystals. 3) This result confirms that the central ring of the molecule is oriented perpendicular to the external magnetic field; banana-shaped LC molecules thus orient differently from rod-shaped LC molecules in the external magnetic field. 4) The analysis of the quadrupolar splitting of the lateral rings in terms of orientational order is much more complicated. Our analysis shows that the assumption of fast and unbiased reorientations of the lateral rings about the *para* axis is not valid. 5) The values of the order parameters for the four lateral rings indicate that the inner rings are more ordered than the outer rings; moreover, there is a different average conformation of the lateral wing closer to the chlorine atom with respect to the other wing. 6)  $^2\text{H}$  NMR measurements on a small probe dissolved in common nematogens, such as 5CB, and in the CIPbis11BB itself (used as solvent), confirm that the calamitic and banana-shaped environments are completely different. In particular, the relative orientation of the small probes within the two kinds of nematic phase confirms our hypothesis of a peculiar orientation of the bent molecules with respect to the magnetic field. 7) Quantum mechanical calculations of the magnetic susceptibility tensor reveal strong dependence of the anisotropy  $\Delta\chi$  on the internal conformations. 8) The favourite conformations correspond to  $\Delta\chi$ , which agrees with the orientation arrangement of BLC CIPbis11BB proposed here.

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- [1] T. Niori, F. Sekine, J. Watanabe, T. Furukawa, H. Takezoe, *J. Mater. Chem.* **1996**, 6, 1231–1233.
- [2] R. A. Reddy, C. Tschierske, *J. Mater. Chem.* **2006**, 16, 907–961.
- [3] H. Takezoe, Y. Takanishi, *Jpn. J. Appl. Phys. Part 1* **2006**, 45, 597–625.
- [4] J. Prost, P. Barois, *J. Chem. Phys.* **1983**, 80, 65–68.
- [5] R. G. Petschek, K. M. Wiefeling, *Phys. Rev. Lett.* **1987**, 59, 343–346.
- [6] F. Tournilhac, L. M. Blinov, J. Simon, S. V. Yablonski, *Nature* **1992**, 359, 621–623.
- [7] H. Niwano, M. Nakata, J. Thisayukta, D. R. Link, H. Takezoe, J. Watanabe, *J. Phys. Chem. B* **2004**, 108, 14889–14896.
- [8] R. Y. Dong, K. Fodor-Csorba, J. Xu, V. Domenici, G. Prampolini, C. A. Veracini, *J. Phys. Chem. B* **2004**, 108, 7694–7701.
- [9] V. Domenici, M. Geppi, C. A. Veracini, R. Blinc, A. Lebar, B. Zalar, *J. Phys. Chem. B* **2005**, 109, 769–774.
- [10] V. Domenici, L. A. Madsen, E. J. Choi, E. T. Samulski, C. A. Veracini, *Chem. Phys. Letts.* **2005**, 402, 318–323.
- [11] W. Weissflog, Ch. Lischka, S. Diele, G. Pelzl, I. Wirth, S. Grande, H. Kresse, H. Schmalfuss, H. Hartung, A. Stettler, *Mol. Cryst. Liq. Cryst.* **1998**, 333, 203–223.
- [12] L. A. Madsen, D. J. Digemans, M. Nakata, E. T. Samulski, *Phys. Rev. Lett.* **2004**, 92, 145505.
- [13] V. Domenici, D. Frezzato, C. A. Veracini, *J. Phys. Chem. B* **2006**, 110, 24884–24896.
- [14] D. Wiant, S. Stojadinovic, K. Neupane, S. Sharma, K. Fodor-Csorba, A. Jakli, J. T. Gleeson, S. Sprunt, *Phys. Rev. E* **2006**, 73, 030703(R).
- [15] J. Harden, B. Mbanga, N. Éber, K. Fodor-Csorba, S. Sprunt, J. T. Gleeson, A. Jakli, *Phys. Rev. Lett.* **2006**, 97, 157802.
- [16] V. Domenici, PhD thesis, University of Pisa (Italy), **2005**.
- [17] V. Domenici, *Pure Appl. Chem.* **2007**, 79, 21–37.
- [18] J. Xu, R. Y. Dong, V. Domenici, K. Fodor-Csorba, C. A. Veracini, *J. Phys. Chem. B* **2006**, 110, 9434–9441.
- [19] R. Y. Dong, J. Zhang, K. Fodor-Csorba, *Chem. Phys. Lett.* **2006**, 417, 475–479.
- [20] V. Domenici, B. Zalar, C. A. Veracini, *Soft Matter* **2005**, 1, 408–411.
- [21] P. G. de Gennes, J. Prost in *The Physics of Liquid Crystals*, Clarendon, New York, **1993**, pp. 57–58.
- [22] A. Saupe, G. Englert, *Mol. Cryst. Liq. Cryst.* **1966**, 1, 503–527.
- [23] G. Cinacchi, V. Domenici, *Phys. Rev. E* **2006**, 74, 030701(R).
- [24] V. Domenici, C. A. Veracini, *Mol. Cryst. Liq. Cryst.* **2007**, 465, 327–340.
- [25] V. Domenici, K. Fodor-Csorba, D. Frezzato, G. Moro, C. A. Veracini, *Ferroelectrics*, **2006**, 344, 19–28.
- [26] M. Cifelli, V. Domenici, *Phys. Chem. Chem. Phys.* **2007**, 9, 1202–1209.
- [27] K. Fodor-Csorba, A. Vajda, G. Galli, A. Jakli, D. Demus, S. Holly, E. Gacs-Baitz, *Macromol. Chem. Phys.* **2002**, 203, 556–563.
- [28] L. Calucci, C. Forte, K. Fodor-Csorba, B. Mennucci, S. Pizzanelli, *J. Phys. Chem. B* **2007**, 111, 53–61.
- [29] Z. Luz, S. Meiboom, *J. Chem. Phys.* **1963**, 39, 366–370.
- [30] Gaussian 03 (revision A.1), M. J. Frisch et al., Gaussian, Inc., Pittsburgh, PA, **2003**.
- [31] A. Becke, *J. Chem. Phys.* **1993**, 98, 5648–5652.
- [32] R. Wrzalik, K. Merkel, A. Kocot, *J. Mol. Model.* **2003**, 9, 248–258.
- [33] I. Cacelli, G. Prampolini, *Chem. Phys.* **2005**, 314, 283–290.
- [34] T. A. Keith, R. F. W. Bader, *Chem. Phys. Lett.* **1993**, 210, 223–231.
- [35] T. A. Keith, R. F. W. Bader, *Chem. Phys. Lett.* **1994**, 194, 1–8.
- [36] V. Domenici, B. Zalar, unpublished results.
- [37] C. A. Veracini in *Nuclear Magnetic Resonance of Liquid Crystals* (Ed.: J. W. Emsley), Reidel, Dordrecht, **1985**, p. 99.
- [38] T. Imase, S. Kawachi, J. Watanabe, *J. Mol. Struct.* **2001**, 560, 275–281.

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