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Supporting Information

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Peculiar orientation of banana-shaped molecules in the presence of magnetic field: ^{2}H NMR and quantum mechanical calculations

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Supporting Information

The ^{2}H NMR spectra of ClPbis11BB-O-d_4 acquired without proton decoupling in the range of stability of the mesophase ($\Delta T \sim 16$ degrees) are characterized by a single quadrupolar splitting, with a line-width of about 1800 Hz. Representative spectra recorded at T=355 K are reported in **Figure 4(a)**. The quadrupolar splitting increases by decreasing the temperature, within the mesophase temperature range, without changing the spectral features, until the crystalline phase is reached.

The proton-decoupled spectrum is dominated by two partially overlapped quadrupolar doublets, with a line-width of about 1000 Hz. [25] An example of such spectra is reported in **Figure 4(a)**. The trend of the quadrupolar splittings within the temperature range of stability of the mesophase is similar to that described for the non-decoupled spectra, as reported in **Figure S1**. As a qualitative comment on these spectral features, we can assert that the two quadrupolar splittings observed for this isotopomer are ascribable to the two lateral rings, thus the two lateral wings of the banana-shaped molecule are not equivalent. This fact can be explained by observing that the molecule is not symmetric, due to the presence of the Chlorine atom on the central ring. Consequently, the two lateral wings either experience different “average” conformation and/or they have a different orientation with respect to the magnetic field. On the other hand, this finding is in agreement with Quantum Mechanical computations for the five-ring molecule [33] as well as with the observed behaviour of two banana-subunits (three-rings probes) diluted in LC solvents. [10] This finding is quite important because it is another experimental evidence of the fact that small substitutions on the molecular structure lead to substantially different mesophase behaviours and that the existence of a nematic phase, instead of a B phase for instance, can be strongly related to the different conformational, and consequently orientational, properties of the constituent molecules.

Concerning the spectral features, in the case of outer lateral rings we could not detect any dipolar couplings $D_{1H\text{-}2H}$ from the spectra acquired without proton decoupling. This means that the dipolar coupling is small, contributing only to a broadening of the two quadrupolar signals. Moreover, the fact that the dipolar splitting is small tells us that the orientational order parameters referred to the *para* axes of the lateral aromatic rings, being proportional to the dipolar coupling, are quite small as well.

The ^{2}H NMR spectra of ClPbis11BB-I-d_4 acquired by proton decoupling in the range of stability of the mesophase (ΔT ~ 14 degrees), are characterized by two quadrupolar splittings, as for the previous sample. An example of such spectra recorded at T=349 K is reported in **Figure 4(b)** and the trend of quadrupolar splittings is reported in **Figure S1**. Also in this case, we can easily assert that the two lateral rings are not equivalent and similar considerations are valid for this isotopomers.

The ^{2}H NMR spectra measured without proton decoupling are here characterized by two quadrupolar splittings, further split by a small, but still detectable, dipolar coupling. **Figure S2** shows the dipolar coupling $D_{1H\text{-}2H}$ as a function of temperature for the two quadrupolar signals. In the following analysis, however, the dipolar splittings are not taken into account because our purpose is to have the simplest expression for the quadrupolar splitting in order to compare more easily the five deuterated rings. Moreover, as shown in **Figure S2**, the large error of these values would invalidate the analysis. In fact, calculations obtained using also the dipolar splittings bring to values of S with an error of 30%.

A quantitative analysis of the recorded quadrupolar splittings for the ClPbis11BBO-d_4 and ClPbis11BB-I-d_4, can be carried out in order to determine local orientational order parameters relative to the four *para* axes of the deuterated aromatic rings.

Focusing on a single aromatic ring, the experimental quadrupolar splitting Dn_q^i (where *i* stands for the four rings) is given by Eq. (**S1**), with the averaged quadrupolar frequency adjusted for the reorientational motions of the lateral rings about their respective para-axes.

$$\left|\Delta n_q^i(T)\right| = \left|\left\langle n_q\right\rangle^i \cdot S_2(T)\cdot P_2(\cos b)\right| \tag{S1}$$

Specifically, $\left\langle n_q\right\rangle = n_q \cdot P_2(\cos j)$. If we assume that fast unbiased reorientations of the lateral ring about their respective para-axes take place, $j \approx 60°$. Consequently,

$$\left|\Delta n_q^i(T)\right| \approx \left|n_q/8 \cdot S_2(T)\cdot P_2(\cos b)\right| \tag{S2}$$

for the lateral aromatic rings' deuterons. Here $b = p/2$ like in the case of central ring deuterons. The angle j is also shown in **Scheme S1** and it is the angle between the C-D bond and the *para (=zpi)* direction. The values of the orientational order parameters S_2 for the four rings are reported in **Figure S3** in absolute values. It should be noticed here that the order parameter S_2 is not referred to the para axes but to the Z axis of the laboratory frame in the assumption that the para axes form an angle $b = p/2$ with respect to the Z axis and that a fast reorientation of the phenyl rings around their para axes takes place. Bearing this in mind some general conclusions can be drawn.

The extremely high values of the order parameter S_2, obtained by applying Eq. **S2** to the external rings simply indicate that the assumption of fast motions, in particular, the unbiased reorientation of deuterons around their para-axes is an oversimplification. This seems to be in agreement with recent results obtained by ^{2}H NMR relaxation on the same molecule, [26] in which an anomalous behaviour in the quadrupolar echo intensity has been found for the deuterons in the lateral rings.

Moreover, equation **S2** is based on very rough assumptions which include the perfect knowledge of the relative positions of the lateral rings with respect to the central one. But this knowledge is not available. The comparison between the values shown in **Figure S3** and those reported in **Figure 3** can be thus misleading. Moreover, it should be pointed out that even a small deviation from the $j = 60°$ angle could result in values of S_2 very different from those reported in **Figure S3**.

Nevertheless, some conclusions can be drawn by comparing the relative values of S_2 among the lateral rings, for instance the inner (full symbols) and outer (empty symbols) rings reported in **Figure S3**. The inner rings appear to be more ordered. 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. On the other hand, this behaviour is also confirmed by the quantum-mechanical calculations reported in refs. [10] and [33], showing that the energy surface potential of the external rings is extremely flat as a function of dihedral angles. As recent computations have shown, [33] the more oriented rings are those on the lateral wing closer to the Chlorine atom.

As it is shown in the paragraph 3.1.2, similar conclusions can be drawn from the measurements of three-ring molecular probe, namely ClBOB, diluted in a LC solvent. Here the local order parameters, referred to the para-axes, were found to be |S| ~ 0.35 and |S| ~ 0.25 for the ring closer to or on the other side of the Chlorine atom, respectively. [10,16]

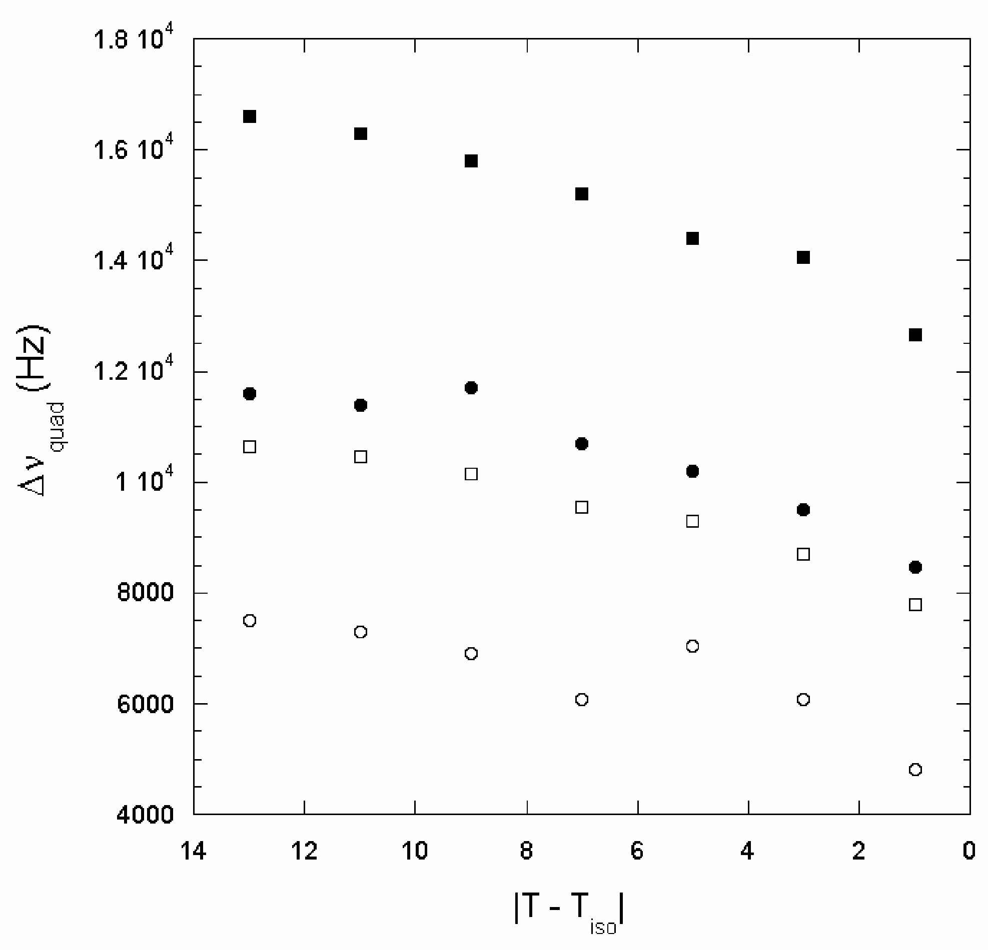


Figure S1. Quadrupolar splittings (Hz) in absolute value as a function of the reduced temperature, for the two labeled samples: ClPbis11BB-I-d_4 (full symbols) and ClPbis11BB-O-d_4 (empty symbols). Experimental error is ± 50 Hz.

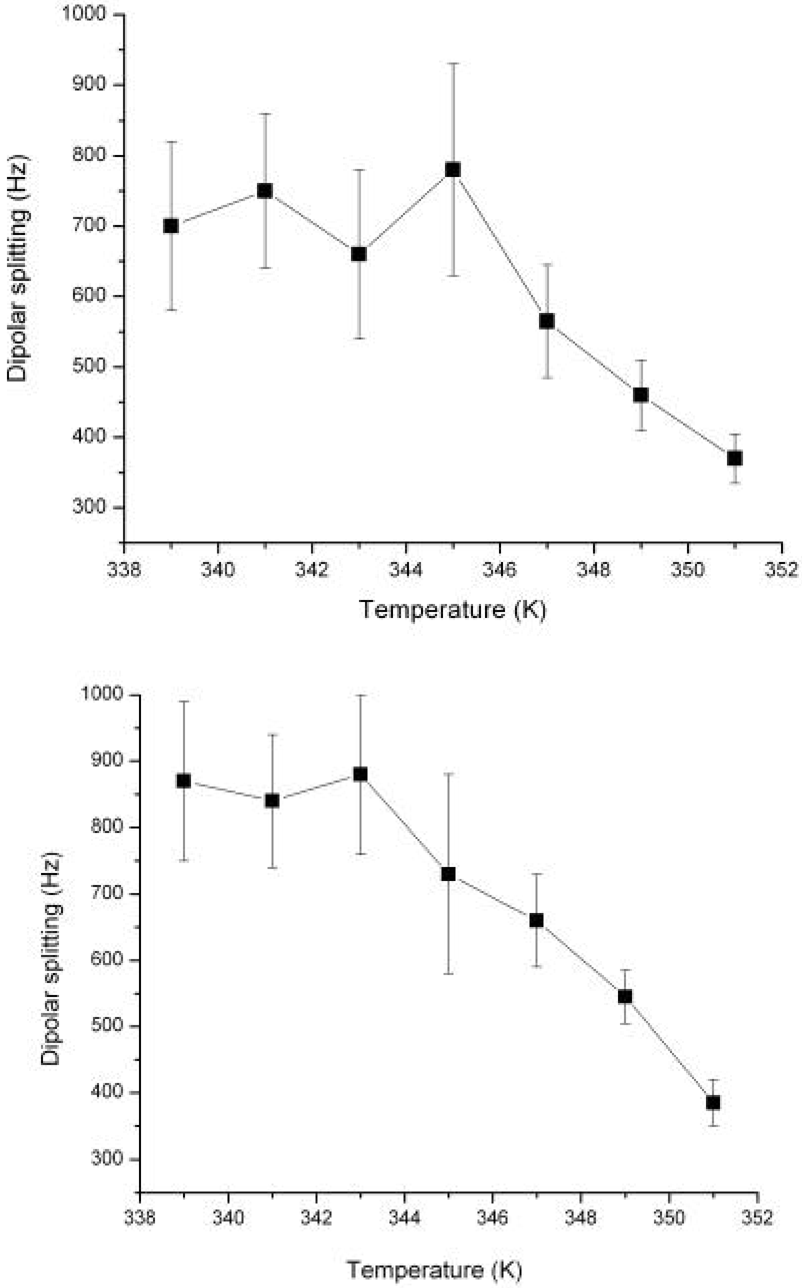


Figure S2. Dipolar splittings (Hz) as a function of temperature (K) for the two deuteron type of the sample ClPbis11BB-I-d_4. Experimental errors are also shown.

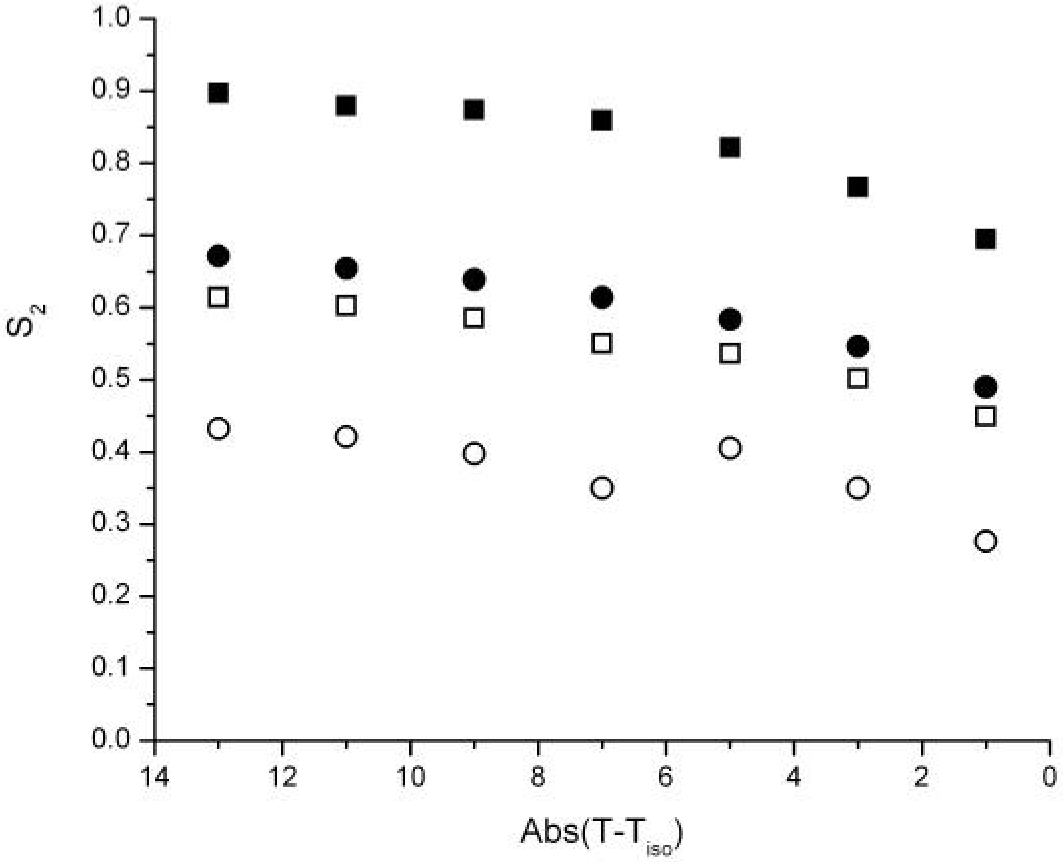
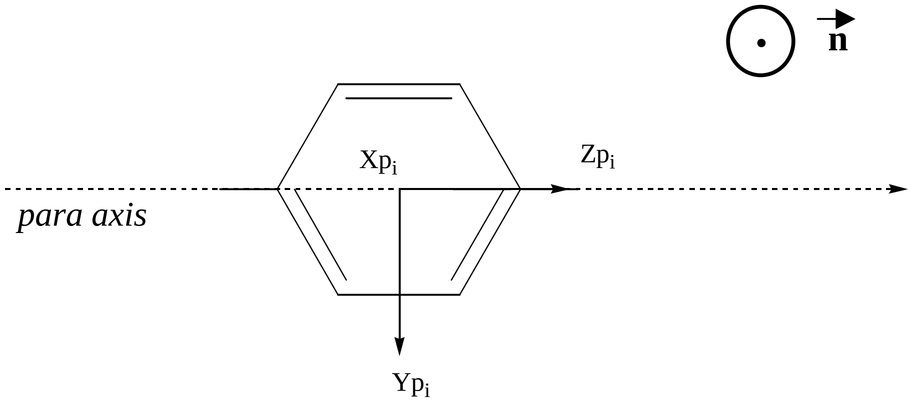


Figure S3. Orientational order parameters S_2, in absolute value, as a function of the reduced temperature for the four rings of the the banana-shaped liquid crystal ClPbis11BB, as obtained by the analysis of quadrupolar splittings. Full and empty symbols refer to the inner and outer aromatic rings, respectively. Squares and circles refer to the rings on the lateral wing on the Chloro side (12', 14', 19', 21' of **Scheme 1a**) and on the other side (12, 14, 19, 21 of **Scheme 1a**).



Scheme S1. Local phenyl frame (Fpi= Xp$_i$, Yp$_i$, Zp$_i$) for the four lateral aromatic rings. For each ring, the local frame can be fixed with the Zp$_i$ axis coincident with the para axis of the phenyl ring. *i* stays for the numbers 1, 2, 3 and 4 corresponding to the four rings. The relative orientation of the para axis with respect to the local director **n** is also shown.