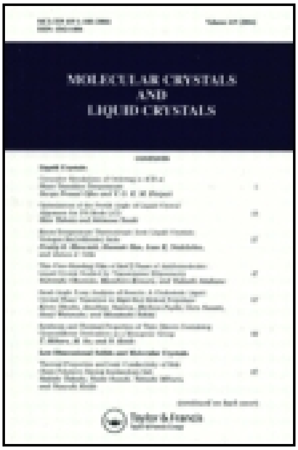

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# Orientational Properties of Banana-Shaped Molecules and their Sub-Units by Means of $^2$H NMR Spectroscopy

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# Orientational Properties of Banana-Shaped Molecules and their Sub-Units by Means of $^2$H NMR Spectroscopy

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*Several $^2$H NMR studies have been performed on two deuterium labelled banana-shaped liquid crystals, the 1,3-phenylene bis{4-4′-(11-undecenyloxy) benzoyloxy} benzoate (Pbis11BB) and its 4-chloro homologue (ClPbis11BB), in the isotropic, nematic and $B_2$ phases.*
*In this article, the state of the art of these studies is drawn and some new $^2$H NMR measurements on deuterated banana sub-units, namely the 3-(benzoyloxy)phenyl benzoate-$d_{10}$ (BOB-$d_{10}$) and its 4-chloro homologue (ClBOB-$d_{10}$), used as small probes dissolved in two banana-shaped liquid crystals in the nematic phase are reported.*
*As a general result, the orientational ordering properties of these sub-units are discussed in the frame of recent results obtained on the same banana-shaped liquid crystals dissolved in calamitic nematic solvents as well as in the bulk.*

**Keywords:** banana-shaped; $^2$H NMR; liquid crystals; nematic; orientational order; probe; solute

## INTRODUCTION

Banana-shaped liquid crystals (BLCs) have been widely studied since their discovery, ten years ago [1,2], for their peculiar chemical and physical properties [3,4] related to the bent shape, and finally the first technological applications in the field of liquid crystal displays have been recently presented [5]. However, the interest in this kind of soft materials is due not only to the possible improvements of liquid crystalline-based devices, but also to pure chemical and physical

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properties, such as the origin of phase chirality [4], related to their molecular conformation, the unusual dynamics [6–8], the still not completely understood supramolecular structure of some B phases [4] and the effect of external field on the mesophase structure [9].

Concerning the experimental techniques, Nuclear Magnetic Resonance (NMR) revealed to be particularly powerful in elucidating the conformational, orientational and dynamic properties of banana molecules.

The conformational problem has been studied first by high resolution solid state $^{13}$C NMR by Watanabe *et al.* [10] on a not-substituted sample (P-14-O-PIMB) showing a $B_2$ and a $B_4$ phases. Here, although the molecular structure is symmetric, the presence of a doublet of chemical shift of the C=O signals of the two lateral wings in the mesophases has been interpreted as the occurrence of an “average” chiral molecular conformation. Further, this experiment was considered the evidence of the twisted-propeller shape of banana molecules. This has been also confirmed by theoretical calculations [11] and other $^{13}$C NMR studies on different BLC molecules [12,13].

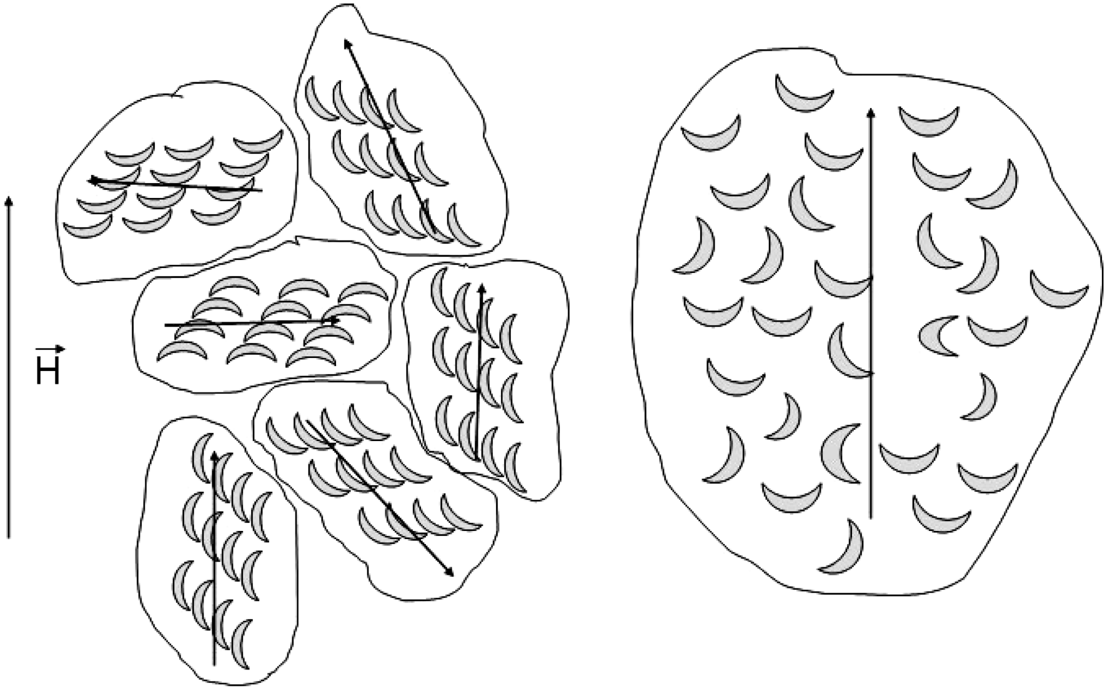
$^{2}$H NMR, on the other hand, supported these findings [12], with the addition of a more quantitative analysis based on the possibility to detect different sites of the molecule by selective deuteration. The difference between lateral wings for substituted and not substituted (thus symmetric) bent molecules was observed in different compounds, deuterium labelled on the lateral aromatic rings, showing nematic [12,14] or $B_2$ phases [13].

However, another interesting work based on $^{2}$H NMR and computational calculations [15] gave some clues in understanding the origin of different chiral conformations, with positive (+) and negative (−) chirality. A standard method to study conformational problems is the analysis of $^{2}$H NMR spectra of deuterated probes dissolved in liquid crystalline environments, by taking into account different conformations for the probe molecule [16]. This procedure has been followed for two banana-shaped sub-units, namely the 1,3-benzenediol dibenzoate (BOB-$d_{10}$) and the 4-Chloro 1,3-benzenediol dibenzoate (ClBOB-$d_{10}$), both labelled on the two lateral aromatic rings, dissolved in several common calamitic nematic solvents, such as 5CB and Phase V [15]. This approach revealed that in a completely cylindrical environment, probe molecules are free to reorient and the internal conformational motions let disappear any chirality due to averaging over all possible conformations, weighted on the basis of the computed molecular energy for each conformer. However, the energy potential surface for the BOB and ClBOB probes, as for five-rings banana molecules [17], indicates that if the geometry is restricted, as in banana mesophases, chiral or twisted conformations are the most favourite. This finding was important to state that the molecular packing, determining the symmetry and restrictions of the B phases, can induce the positive, or negative, molecular chirality to appear on a macroscopic scale, as recently demonstrated for the $B_2$ phase formed by enantiomeric/racemic banana mixtures [4].

More, $^2$H NMR experiments on banana-shaped molecules in the bulk [9,13,18] on one side and on the banana-shaped molecules dissolved in calamitic nematic environments [19] on the other, put in evidence drastic differences between a restricted system (the first case) and not-restricted one (the second one). When banana-shaped molecules are in the bulk, the molecular packing strongly influences the dynamic of the system [6,7,18] as well as the orientational properties [9,20]. In particular, the cases of the 1,3-phenylene bis{4-4′-(11-undecenyloxy) benzoyloxy} benzoate (Pbis11BB) and its 4-chloro analogue (ClPbis11BB) are quite significant. In the first case, a $B_2$ phase is formed by cooling the sample, but, even in presence of a strong magnetic field, a uniform orientation of the macroscopic sample couldn't be reached: instead, a distribution of single smectic domains occurs [13], as represented in Scheme 1. For the ClPbis11BB, having a nematic phase, the effect of the magnetic field seems to be much stronger, since the orientation of molecules in the nematic phase is perpendicular to the field [9] (see Scheme 1), contrary to the expected behaviour for common nematogens having a positive magnetic susceptibility anisotropy, $\Delta\chi_m > 0$ (only few cases are known with $\Delta\chi_m < 0$). Moreover, the molecular packing in the nematic phase, as well as the isotropic one, hinders molecular motions as widely demonstrated in Refs. [6,7,20] by means of $^2$H NMR, and in Ref. 8, by Dynamic Light Scattering on similar BLCs.

Finally, $^2$H NMR of deuterated banana molecules dissolved in liquid crystalline solvents, such as nematic phases [19], provided an interesting indication of a glasslike behaviour, with a sensitive deviation of the orientational order from the Haller trend [22] and an extremely high orientational order parameter $S_2$ for the bent core. A possible explanation is the occurrence of molecular clusters [19] among the "long" banana-shaped molecules and the "small" cyano biphenyl molecules, in the ratio of c.a. 1:300, as nicely reported in Ref. [19].

The last step, reported in this article, consists of the study of deuterated banana sub-units, namely the BOB and ClBOB probes, dissolved in banana nematic liquid crystals. This is the first study where a nematic phase formed by banana-shaped molecules, is used as solvent. The main purpose of this work is to study the orientational



a) Isotropic distribution of $B_2$ domains. In each domain, molecules are tilted and distributed in smectic layers.

b) Molecules uniformely oriented in the “nematic” phase, with plane of symmetry perpendicular to the field.

**SCHEME 1** Scheme of orientation of bent molecules in the magnetic field. a) in the $B_2$ phase formed by Pbis11BB, as reported in ref. [13]; b) in the nematic phase formed by ClPbis11BB, as reported in ref. [9].

properties of these probes in the new environment, and to compare it with that observed in common calamitic nematic [15].

On the other hand, $^2$H NMR spectra of these probes in the banana nematic help in verify orientational and dynamic properties in the banana nematics. As commented in the last part of the paper, it seems that for small probes dissolved in the nematic phases, calamitic or banana ones, the Haller behaviour is confirmed, on the contrary to the case of large probes [19].

# EXPERIMENTAL

## Materials

Two selectively deuterated molecules, the 1,3-benzenediol dibenzoate (BOB) and the 4-Chloro 1,3-benzenediol dibenzoate (ClBOB), both labelled on the two lateral aromatic rings have been used as *probe* molecules in nematic banana-shaped liquid crystals (see Fig. 1). The samples used as liquid crystalline solvents are the 4-chloro 1,3-phenylene bis{4-4′-(11-undecenyloxy) benzoyloxy} benzoate (ClPbis11BB) and the 4-chloro 1,3-phenylene bis{4-4′-(10-decenyloxy) benzoyloxy} benzoate (ClPbis10BB). The synthesis of small probes and banana-shaped liquid crystals are reported in Ref. [15] and [23], respectively. The solutions were prepared following the same procedure: the weighted amounts of solvent and solute were poured into the NMR tube; then, several cycles of heating, until the isotropic phase was reached, and uniformly mixing of the solution were performed before introducing the tube into the magnet.

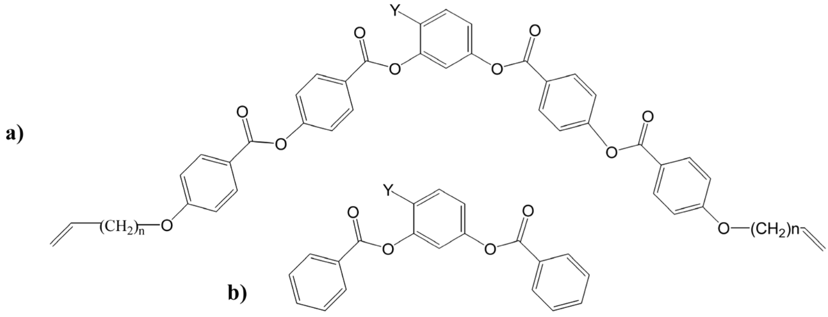


**FIGURE 1** Molecular structure of several banana-shaped mesogens and banana sub-units. a) Pbis11BB (Y=H, n = 9); ClPbis11BB (Y=Cl, n = 9); ClPbis10BB (Y=Cl, n = 8); b) BOB (Y=H); ClBOB (Y=Cl).

The solute concentrations in the prepared solutions range between 1.2 to 0.5 %wt.

## $^2$H NMR Experiments

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 solutions were cooled within the magnet from the isotropic to the nematic phase. $^2$H NMR spectra were recorded by the Quadrupolar Echo (QE) pulse sequence [24,25] ($90_x$–$\tau$–$90_y$–$\tau$), with the exorcycle [26] phase scheme, on cooling and on heating. A 90° pulse of 4.6 μs, a pulse delay of 0.8 s and QE time delay $\tau$ of 25 μs were used. The number of scans varied from 1000 to 200000, depending on the sample and kind of measurements. The temperature was controlled within 0.2 degree and 10 minutes were allowed for thermal equilibration of the samples at each temperature.

## RESULTS

$^2$H NMR spectra of the BOB-$d_{10}$ in ClPbis11BB, 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 Fig. 2a); (b) between $-45$ and $-30$ KHz and between 30 and 45 KHz, where a very broad quadrupolar splitting corresponds to the *para* deuterons [7] (see Fig. 2b). In this case, as observed for the same probe dissolved in common calamitic LCs [15], no differences can be noticed between the two lateral aromatic rings. However, the fact that the *para* signals are characterized by large broadening was not observed in common nematic LCs [15], where the line-width was about 120 Hz for all signals (see Fig. 2c). This big difference between the calamitic and banana 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 ClPbis11BB sample [6,7,18]. In fact, the *para* signals are not averaged out by the internal rotation of the phenyl rings around their *para* axes, as the *ortho/meta* signals are: for this reason, the *para* signals are sensitive probes for the overall motions of the probes as well as of the nematic environment [7].

Two sets of similar $^2$H NMR measurements were performed for the LC solutions of BOB-$d_{10}$ and ClBOB-$d_{10}$ dissolved in the banana nematic ClPbis10BB (the molecular structure is reported in Fig. 1). In this case, the amount of probe was extremely small (less than

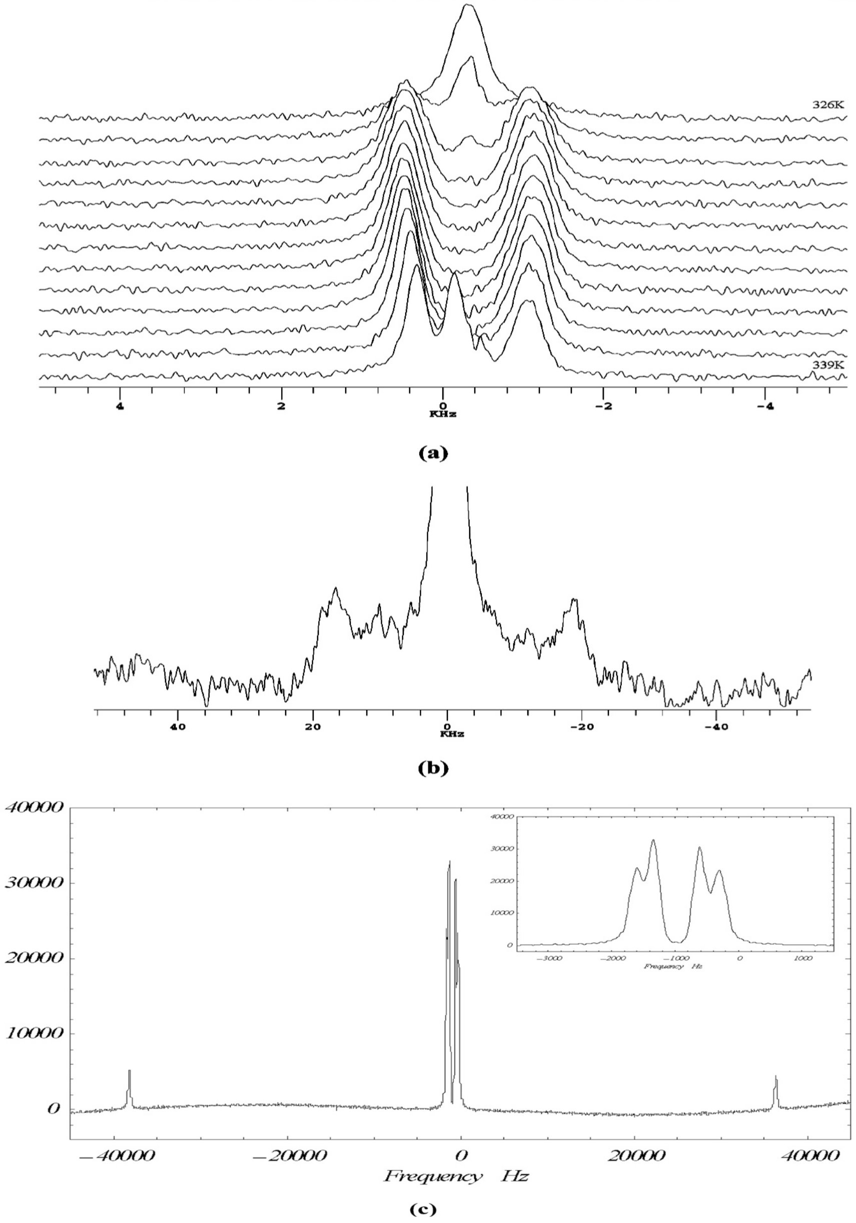


**FIGURE 2** $^2$H NMR spectra of the BOB-$d_{10}$ probe dissolved in the ClPbis11BB nematic sample (a and b), and in the calamitic nematic solvent Phase V (c). a) The region of the *ortho-meta* signals is enlarged and the spectra are reported from 339 K to 326 K every 1 degree. b) The region of the larger quadrupolar splitting, ascrivable to the *para* deuterons, is expanded at T = 332 K. c) $^2$H NMR spectrum of BOB-$d_{10}$ in Phase V at 300 K, with an enlarger window on the *ortho*/*meta* signals.

0.5%) and we could detect the sole *ortho/meta* signals, while the *para* ones are flatten under the base-line.

In both solutions, no differences among the two lateral aromatic rings could be detected, neither for BOB or ClBOB. While this is expected for the BOB-$d_{10}$ probe, different is the case of ClBOB-$d_{10,}$where in principle two sets of signals should be seen for the two lateral rings, that closer to the Chlorine atom and the other one [15]. However, in the case of ClBOB-$d_{10}$ the recorded $^2$H NMR spectra in the whole nematic range were characterized by a partial superimposition between a single quadrupolar splitting ($\Delta\nu_{h/2} \sim 500\,\mathrm{Hz}$) and a high-intensity isotropic peak, probably due to the not complete miscibility of the ClBOB in the nematic ClPbis10BB.

The experimental quadrupolar splittings of these probes dissolved in different nematic BLC solvents are reported in Figure 3.

In the present cases, the order parameters experimentally accessible are relative to the two *para* axes of the deuterated aromatic rings of the probe molecules.

Focusing on a single aromatic ring, the quadrupolar splittings, $\Delta\nu_q^i$, of the *ortho/meta* and, where they are accessible, *para* deuterons are

arameters $S_{zz}$ and $\Delta_{biax} = S_{xx} - S_{yy}$ of the

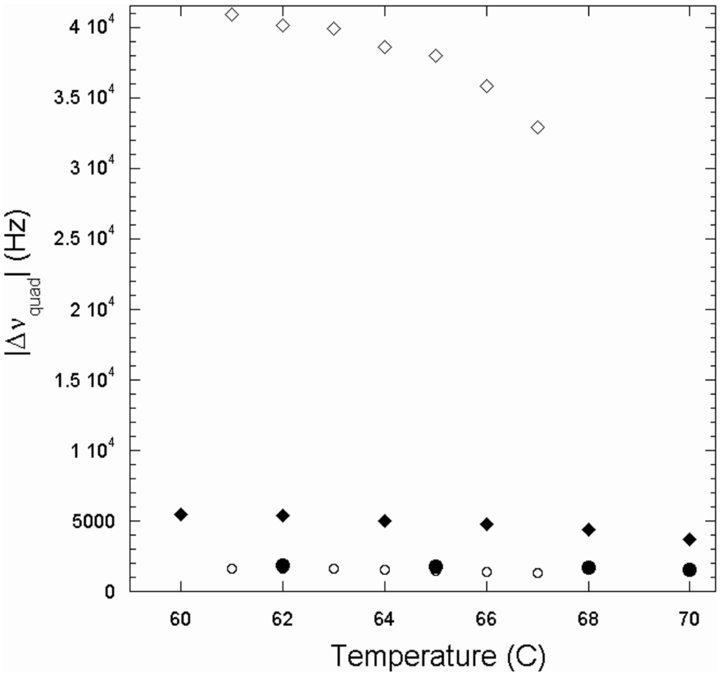


**FIGURE 3** Quadrupolar splittings (Hz) vs. Temperature (C) for the *ortho/meta* deuterons of BOB-$d_{10}$ (●) and ClBOB-$d_{10}$ (◆) dissolved in ClPbis10BB, and for the *ortho/meta* (○) and *para* (◇) deuterons of BOB-$d_{10}$ dissolved in ClPbis11BB in their nematic phases.

deuterated ring by the following Eqs. [27,28]:

$$\Delta\nu_q^i[T] = \frac{3}{2}q_{aa}\left\{S_{zz}[T]\cdot\left(\cos^2\varphi_i - \frac{1}{2}\sin^2\varphi_i - \frac{\eta}{6}\cos^2\varphi_i + \frac{\eta}{6} + \frac{\eta}{3}\sin^2\varphi_i\right)\right.$$
$$\left. + \Delta_{biax}\left(\frac{1}{2}\sin^2\varphi_i + \frac{\eta}{6}\cos^2\varphi_i + \frac{\eta}{6}\right)\right\} \tag{1}$$

where $q_{aa}$ and $\eta$ are the quadrupolar coupling constant and asymmetry parameter, respectively. The standard values of $q_{aa} = 185\,\text{kHz}$ and $\eta = 0.04$ have been used in the following analysis. The angle $\varphi_i$ between the C–D bond and the *para* ($=z$) direction has been assumed equal to 60° and 0° for *ortho/meta* and *para* deuterons, respectively.

In the case of the BOB-$d_{10}$ dissolved in the ClPbis11BB, we could fit two quadrupolar splittings, for the *ortho/meta* and *para* deuterons, and the obtained order parameter S, as a function of temperature, is

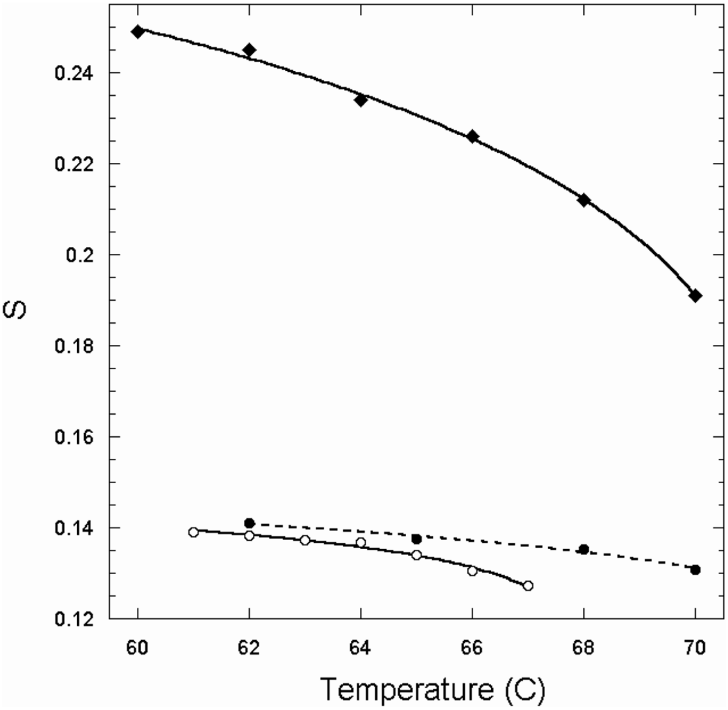


**FIGURE 4** Order parameter S, referred to the *para* axes of the lateral rings of BOB-$d_{10}$ (●) and ClBOB-$d_{10}$ (◆) dissolved in the ClPbis10BB and BOB-$d_{10}$ (○) dissolved in the ClPbis11BB in their nematic phase. Curves refer to the best-fitting of order parameters S by using Eq. (2).

reported in Figure 4 (empty circles). The best-fitting $\Delta_{biax}$ was found to be 0.024.

For the other two sets of measurements, no signals for the *para* deuterons could be detected, thus the biaxiality was fixed to 0.024, according to the value previously found for the BOB-$d_{10}$ probe, and the order parameter S could be evaluated by applying Eq. 1 at each temperature. The obtained values of *S(T)* are reported in Figure 4 (full circles and full rhombs for BOB and ClBOB, respectively).

Moreover, if we look at the trend of S as a function of temperature, the Haller Equation [22] can be used to fit experimenta data:

$$S(T) = S_0(1 - T_c/T)^{\gamma} \tag{2}$$

All sets of data are well fitted as it can be seen in Figure 4 and the best fitting parameters are: (1) $S_0 = 0.155$, $T_c = 67.97$ C and $\gamma = 0.047$ for

BOB-$d_{10}$ in ClPbis11BB; (2) $S_0 = 0.157$, $T_c = 73.58$ C and $\gamma = 0.061$ for BOB-$d_{10}$ in ClPbis10BB; (3) $S_0 = 0.302$, $T_c = 71.07$ C and $\gamma = 0.1098$ for ClBOB-$d_{10}$ in ClPbis10BB. The best fitting curves are shown in Figure 4. The orientational order parameter S(T) for the lateral wings of the banana sub-units is well described by the Haller equation.

As a general result, even though the *para* axes of the ClBOB molecule are more oriented than those of the BOB molecule, the average values of the orientational order parameter, S, are quite small: 0.13 and 0.22 for BOB and ClBOB, respectively. Small differences could be detected between the two banana nematic LCs. On the contrary, if we compare these values with those obtained for the same probes dissolved in calamitic nematic solvents [15] a sensitive difference can be noticed. In particular, the orientational order parameter S of the *para* axes of the BOB molecule was found to be 0.26, instead of 0.13, while S is equal to 0.34 and 0.27 for the *para* axis of the two lateral *para* axes for the ClBOB probe, instead of 0.22. This means that in the BLC environment these probes are less oriented than in the calamitic one.

## REMARKS AND CONCLUSIONS

With the experiments reported in this work, several cases have now been examined by means of $^2$H NMR:

1) small banana sub-units dissolved in nematic solvents formed by calamitic compounds [15];
2) banana-shaped mesogens themselves dissolved in nematic solvents formed by calamitic compounds [19];
3) banana-shaped mesogens in their nematic phase in the bulk, in presence of the magnetic field [12,13,14,20];
4) small banana sub-units dissolved in nematic solvents formed by banana-shaped mesogens (present case).

At this step, several observations can be done.

The molecules used as small probes in case (1) and (4) are the BOB and ClBOB molecules. In case (1), the availability of very sharp $^2$H NMR signals (see Fig. 2c) allows us the conformational study by applying a semi-empirical approach [15]. The orientational order parameters were also obtained.

On the contrary to that study, here (case 4) the conformational analysis could not be applied due to the larger lines and to the absence of *para* signals in the case of the ClPbis10BB solvent. As a general remark, the solubility of these probes in ClPbis11BB and ClPbis10BB is much smaller than in common calamitic nematic. This fact may be partially ascribed to the high viscosity of the nematic phases formed by BLC samples, where molecules may form aggregates, or entanglements, as shown in Refs. [6–9,20,21].

Concerning the orientational order, the parameter S referred to the external aromatic rings, could be determined for BOB ($S \sim 0.13$) and ClBOB ($S \sim 0.22$): they are found to be relatively small, as it is typical of small molecules, but they are much smaller than in calamitic solvents [15] (about 1/2 and 2/3 for the BOB and ClBOB probes, respectively). This finding is quite interesting in order to confirm the fact in the BLC environment these small probes are less oriented and that, probably due to the peculiar molecular packing, there are some difficulties for these probes in orienting uniformly in the BLC nematic phase. It is interesting to notice that the ratio between the quadrupolar splitting of the *para* signals of BOB probe in the banana ClPbisBB11 and calamitic nematic environments ($\Delta\nu_q^{ban}/\Delta\nu_q^{cal}$) is approximately 0.5 (see Fig. 2). This allows us to do a hypothesis of averaged orientation of the probe molecules in the LC solvents, as well as to confirm the perpendicular alignment of the ClPbis11BB molecules respect to the magnetic field, proposed in refs. [9,14].

Another important observation concerns the disappearance, or extremely broadening, of the *para* signals of BOB and ClBOB in the BLC nematic phase. This fact is probably due to dynamic reasons, as reported in Ref. [7]. In particular, the *para* signals, having a very large quadrupolar splitting, are more sensitive to molecular motions of the BLC solvent, namely overall molecular motions as well as collective motions. Slow dynamics is the reason of the large broadening of the *ortho/meta* signals as well, respect to the situation observed in calamitic LC solvents [15].

Moreover, the Haller Equation, which well describes the orientational order trend within the temperature range of stability of the nematic phase, is satisfied in all the examined cases.

On the other hand, this Equation was not confirmed only in one system involving BLCs, where the banana-shaped molecules ClPbis11BB are used as probes in a nematic calamitic, the commercial E7 solvent [19]. However, in this last case (2), evidences of glassy behaviour were found, thus justifying the not applicability of the Haller equation itself, in favour of a modified Haller Equation.

Very different is the situation of BLCs in the nematic phase in the bulk.

As reported in Scheme 1, BLCs studied by $^2$H NMR revealed peculiar orientational properties [9,13]. It is clear that when banana molecules or their sub-units are dissolved in a liquid crystal the degrees of freedom are much more than in the bulk, due to the different symmetry of these systems as well as to the presence of physical restrictions, such as the formation of molecular clusters, entanglements or aggregates.

The experiments reported in this work can help only partially since the small probes here used are still too large to be used in order to get information about the structure and orientational properties of the nematic phase formed by BLCs. On the other hand, the structural features of BLCs in the bulk are still under investigation and further studies are needed to elucidating this aspect, also by using different techniques complementary to NMR. However, the presence of the magnetic field itself should not be neglected, since recent papers [9,20] underlined the role of the external field in determining orientation and aggregation properties of BLC systems.

To conclude, the study of deuterated probes dissolved in banana nematic phases was useful to (1) get other evidences of the slow dynamics, as shown also in Refs. [7,18] (2) confirm the high viscosity and the small solubility respect to common nematic solvent.

Moreover, the order parameters S of the small probes could be determined and they are found to follow the Haller trend, with $\gamma$ coefficients typical for nematic phases.

## REFERENCES

[1] Niori, T., Sekine, T., Watanabe, J., Furukawa, T., & Takezoe, H. (1996). *J. Mater. Chem.*, *6*, 1231.

[2] Kruerke, D. & Heppke, G. (1997). *Presented at Banana-Shaped Liquid Crystals Workshop*, Berlin.

[3] Reddy, R. A. & Tschierske, C. (2005). *J. Mater. Chem.*, *15*, 1.

[4] Takezoe, H. & Takanishi, Y. (2006). *Jpn. J. Appl. Phys. Part 1*, *45*, 597.

[5] Takezoe, H. (2006). *Presented at International Liquid Crystals Conference*, Keystone: Colorado.

[6] Domenici, V., Geppi, M., Veracini, C. A., Lebar, A., Zalar, B., & Blinc, R. (2005). *J. Phys. Chem. B*, *109*, 769.

[7] Domenici, V., Fodor-Csorba, K., Frezzato, D., Moro, G., & Veracini, C. A. (2006). *Ferroelectrics*, *344*, 263.

[8] Wiant, D., Gleeson, J. T., Eber, N., Fodor-Csorba, K., Jakli, A., & Toth-Katona, T. (2005). *e-Liq. Cryst. Comm., Phys. Rev. E*, *72*, 041712.

[9] Domenici, V., Veracini, C. A., & Zalar, B. (2005). *Soft Matter*, *1*, 408.

[10] Kurosu, H., Kawasaki, M., Hirose, M., Yamada, M., Kang, S., Thisayukta, J., Sone, M., Takezoe, H., & Watanabe, J. (2004). *J. Phys. Chem. A*, *108*, 4674.

[11] Imase, T., Kawauchi, S., & Watanabe, J. (2001). *J. Mol. Struct.*, *560*, 275.

[12] Dong, R. Y., Fodor-Csorba, K., Domenici, V., Xu, J., Prampolini, G., & Veracini, C. A. (2004). *J. Phys. Chem. B*, *108*, 7694.

[13] Xu, J., Dong, R. Y., Domenici, V., Fodor-Csorba, K., & Veracini, C. A. (2006). *J. Phys. Chem. B*, *110*, 9434.

[14] Domenici, V., Zalar, B., Fodor-Csorba, K., Prampolini, G., Cacelli, I., & Veracini, C. A. *J. Phys. Chem. B,* submitted.

[15] Domenici, V., Madsen, L. A., Choi, E. J., Samulski, E. T., & Veracini, C. A. (2005). *Chem. Phys. Lett.*, *402*, 318.

[16] (a) Emsley, J. W. & Lindon, J. C. (1975). *NMR Spectroscopy Using Liquid Crystal Solvent*, Pergamon Press: Oxford.
  (b) Samulski, E. T. (2003). In: *NMR of Ordered Liquids*, Burnell, E. E. & de Lange, C. A. (Eds.), Kluwer Academic Publishers: Dortrecht, chap. 13.

[17] Cacelli, I. & Prampolini, G. (2005). *Chem. Phys.*, *314*, 283.

[18] Domenici, V., Frezzato, D., & Veracini, C. A. (2006). *J. Phys. Chem. B*, *110*, 24884.

[19] Cinacchi, G. & Domenici, V. (2006). *Phys. Rev. E, Rapid Comm.*, *74*, 030701(R).

[20] Domenici, V. (2005). *Pure Appl. Chem.*, *79*, 21; Domenici, V. Ph.D. thesis, University of Pisa.

[21] Wiant, D., Stojadinovic, S., Neupane, K., Sharma, S., Fodor-Csorba, K., Jakli, A., Gleeson, J. T., & Sprunt, S. (2006). *e-Liq. Cryst. Comm. Phys. Rev. E*, *73*, 030703.

[22] Haller, I. V. (1975). *Prog. Sol. St. Chem.*, *10*, 103.

[23] Fodor-Csorba, K., Vajda, A., Galli, G., Jakli, A., Demus, D., Holly, S., & Gacs-Baitz, E. (2000). *Macromol. Chem. Phys.*, *203*, 1556.

[24] Powles, J. G. & Strange, J. H. (1963). *Proc. Phys. Soc.*, *82*, 6.

[25] Luz, Z. & Meiboom, S. (1963). *J. Chem. Phys.*, *39*, 366.

[26] Bodenhausen, G., Freeman, R., & Turner, D. L. (1977). *J. Magn. Reson.*, *27*, 511.

[27] Luckhurst, G. R. & Veracini, C. A. (1994). *The Molecular Dynamics of Liquid Crystals, NATO ASI Series*, Kluver Academic Publishers: Boston, London.

[28] Veracini, C. A. (1985). In: *Nuclear Magnetic Resonance of Liquid Crystals*, Emsley, J. W. (Ed.), Reidel: Dordrecht, 99.