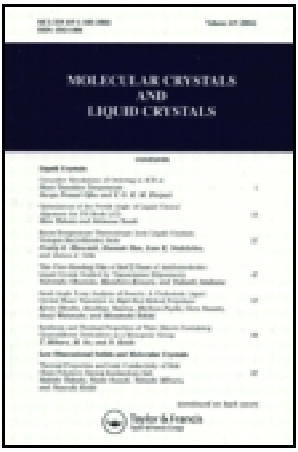


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Smectic A - Smectic C* Transition in a "de Vries" Liquid Crystal by ^{2}H NMR

Valentina Domenici [a], Mario Cifelli [a], Alessandro Marchetti [b c], Moreno Lelli [b], Vera Hamplova [d], Miroslav Kaspar [d] & Carlo Alberto Veracini [a]

[a] Dipartimento di Chimica e Chimica Industriale, via Risorgimento 35, 56126, Pisa, Italy

[b] Centre de RMN à Très Hauts Champs 5 rue de la Doua, 69100, Villeurbanne, France

[c] Scuola Normale Superiore di Pisa Piazza dei Cavalieri 7, 56126, Pisa, Italy

[d] Liquid Crystal Group, Department of Dielectrics Institute of Physics - Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21, Prague, Czech Republic

To cite this article: Valentina Domenici, Mario Cifelli, Alessandro Marchetti, Moreno Lelli, Vera Hamplova, Miroslav Kaspar & Carlo Alberto Veracini (2012): Smectic A - Smectic C* Transition in a "de Vries" Liquid Crystal by ^{2}H NMR, Molecular Crystals and Liquid Crystals, 553:1, 103-110

To link to this article: http://dx.doi.org/10.1080/15421406.2011.609440

Mol. Cryst. Liq. Cryst., Vol. 553: pp. 103–110, 2012

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.609440

Smectic A – Smectic C* Transition in a "de Vries" Liquid Crystal by ^{2}H NMR

VALENTINA DOMENICI,[1,*] MARIO CIFELLI,[1] ALESSANDRO MARCHETTI,[2,3] MORENO LELLI,[2] VERA HAMPLOVA,[4] MIROSLAV KASPAR,[4] AND CARLO ALBERTO VERACINI[1]

[1]Dipartimento di Chimica e Chimica Industriale, via Risorgimento 35, 56126 Pisa, Italy
[2]Centre de RMN à Très Hauts Champs 5 rue de la Doua, 69100 Villeurbanne, France
[3]Scuola Normale Superiore di Pisa Piazza dei Cavalieri 7, 56126 Pisa, Italy
[4]Liquid Crystal Group, Department of Dielectrics Institute of Physics - Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague, Czech Republic

Solid State ^{2}H Nuclear Magnetic Resonance (NMR) spectroscopy was applied to the structural and orientational studies of a selectively labelled 'de Vries' liquid crystal compound. Measurements were performed at five values of the magnetic field, ranging from 4.70 to 18.80 T. The trend of the orientational order S *and tilt angle θ of the ^{2}H-labeled moiety in the SmA and SmC* phases at different magnetic fields confirms previous results and allows us to better characterize the SmA-SmC* transition.*

Keywords Liquid crystal; de Vries; Phase transition; Tilt; Order; NMR

1. Introduction

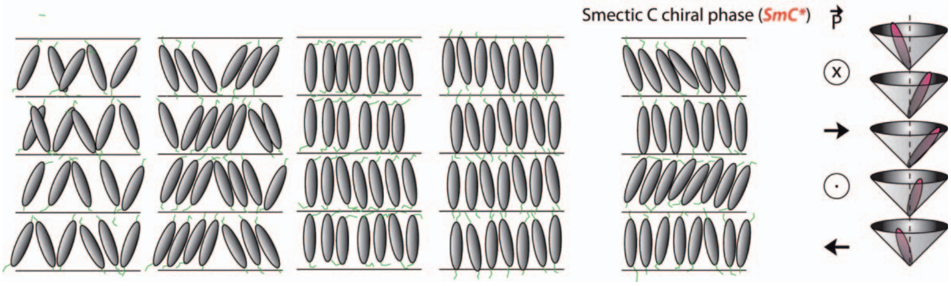
"*De Vries*" liquid crystalline (LC) smectic phases [1–3] exhibit potential applications in the field of new electro-optic devices, such as ferroelectric (FLC) and antiferroelectric (AFLC) displays. These mesophases show indeed a substantially constant layer spacing within the SmA and the SmC* phases, thus excluding the occurrence of so called *"Chevron"* defects at the SmA-SmC* transition, the main limit of the performance and the quality of current electro-optic devices [4]. For this reason, the knowledge of the molecular peculiarity of "de Vries" liquid crystals as well as the influence of external fields on their molecular organization is at the centre of interest for both industry and academia involving many research teams [5–15].

In addition to a modest layer shrinkage (less than 5%) at the SmA-SmC* transition, the "de Vries" SmA phases have a very large electroclinic effect [16]. In fact, it has been shown that the application of external electric fields determines an increase of the induced

---

[*] Address correspondence to Valentina Domenici, Dipartimento di Chimica e Chimica Industriale, via Risorgimento 35, 56126 Pisa, Italy. E-mail: valentin@dcci.unipi.it

tilt angle, or "optical tilt," whose temperature dependence is well described by the Landau mean field theory [17].



Scheme 1. (A) Sketch of the four models known for "de Vries" SmA* phase: from left to right, random diffuse cone, cluster diffuse model, conformational change model, interdigitation model; (B) Representation of the ferroelectric SmC* phase and helical arrangement of both molecules and spontaneous polarization.

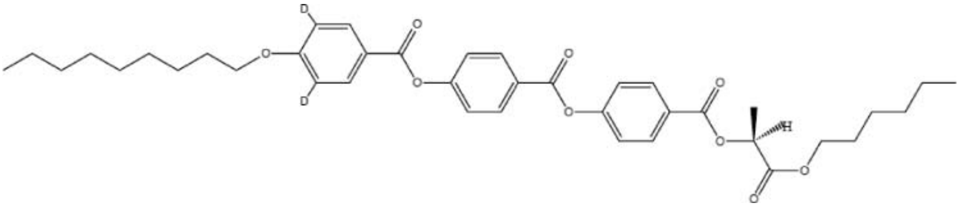
Since their first discovery, scientists have tried to explain these properties through different models (see Scheme 1). The first hypothesis, the "diffuse cone model," was proposed by Adrian de Vries himself [3]: in the SmA phase molecules are tilted with respect to the layer normal, but the azimuthal angle is randomly distributed with no correlation in the smectic layer (see Scheme 1a). A second model was proposed by Diele [8]: LC molecules would experience a different average conformation in the two smectic phases and the absence of a layer shrinkage is explained in terms of different orientations of both rigid core and lateral chains passing from the SmA to the SmC* phases (see Scheme 1a). A third model, which is particularly adapted to describe nanosegregated systems, such as fluorinate or organosiloxane derivatives, invokes a different behavior of molecules at the interface between consecutive smectic layers in the two phases. Within the "interdigitated" model [10, 11] in the SmA phase, molecules are not tilted but partially interdigitated, thus justifying a smectic layer spacing smaller than the effective molecular length. On the contrary, in the SmC* phase, molecules are tilted, but interdigitation does not occur anymore and the measured layer spacing results similar to that in the SmA phase [9]. Recently, a fourth model was proposed by us [15] based on ^{2}H NMR investigations of a deeply studied "de Vries" compound, namely **9HL**. The presence of an average tilt of the deuterated moiety in the SmA phase was indeed confirmed. Moreover, this study revealed a strong magnetic effect [18–21] on the orientational order of the aromatic fragment within the SmA phase leading us to formulate a variation of the "diffuse cone model" by substituting the "random" distribution in azimuthal angle with a "locally ordered" or "cluster" distribution in azimuthal directions.

The (S)-hexyl-lactate derivative "de Vries" LC compound, usually abbreviated as **9HL**, selectively deuterated in a phenyl moiety, has been investigated by ^{2}H NMR at five magnetic field strengths in order to extend previous studies [15]. In this paper, the trends of the orientational order parameters and molecular tilt within the SmA and SmC* phases of **9HL** are reported and discussed in the frame of the four models proposed for "de Vries" LC systems.

2. Materials and Methods

2.1 Liquid Crystalline Material Compound

The synthesis and chemical physical characterization of the “de Vries” liquid crystal compounds (the (S)-hexyl-lactate derivative abbreviated as **9HL** and the analogous LC selectively labelled in the aromatic core, namely **9HL-d$_2$**, shown in Scheme 2) are reported in [5–7]. The mesophase transitions of **9HL-d$_2$**, as detected by means of DSC by cooling the sample at 5°C/min rate and by polarized optical microscope are: Isotropic - 128°C - SmA - 74°C - SmC* - 35°C - crystal.



Scheme 2. Molecular structure of the deuterium labelled **9HL-d$_2$** compound.

2.2 NMR Measurements

^{2}H NMR measurements were carried out with the following instruments: (a) Bruker DMX 200 MHz WB, (b) Varian VXR 300 MHz (5 mm liquid state probe), (c) Bruker 500 MHz Avance III WB (5 mm double channel static probe), (d) Bruker 700 MHz Avance II SB (BBO 5 mm liquid probe) and (e) Bruker 800 MHz Avance III SB (5 mm liquid probe). Magnetic fields are respectively: 4.70 T, 7.05 T, 11.75 T, 16.45 T and 18.80 T. All the ^{2}H NMR spectra were acquired by means of single pulse or quadrupolar echo sequences by cooling the sample from the isotropic to the crystalline phase.

3. Results and Discussion

Five sets of ^{2}H NMR measurements were performed in the whole mesophasic temperature range of the **9HL-d$_2$** at five different magnetic fields. Two sets of data were previously published in [15] and they are those recorded at 7.05 T and 16.45 T. Additional three new sets of ^{2}H NMR data were then recorded: at a lower field, 4.70 T, at an intermediate field, 11.75 T, and at an higher field, 18.80 T. Figure 1 reports a series of ^{2}H NMR spectra as a function of temperature, recorded at the intermediate field of 11.75 T (without proton decoupling) by cooling the sample from the isotropic to the crystal phase.

The ^{2}H NMR spectra are characterized by a doublet (^{2}H quadrupolar splitting) further split by the ^{1}H-^{2}H dipolar coupling between the deuterium and protons in ortho position on the labeled ring of **9HL-d$_2$**. The experimental quadrupolar ($\Delta\nu_{\mathrm{q}}$) and dipolar ($\Delta\nu_{\mathrm{d}}$) splittings determined at each temperature can be analyzed through equations (1) and (2), which relate these experimental quantities to the local orientational order parameters [22, 23]:

$$\Delta\nu_d\,[T] = -2K_{DH}\frac{S_{zz}\,[T]}{r_{DH}^{3}}, \tag{1}$$

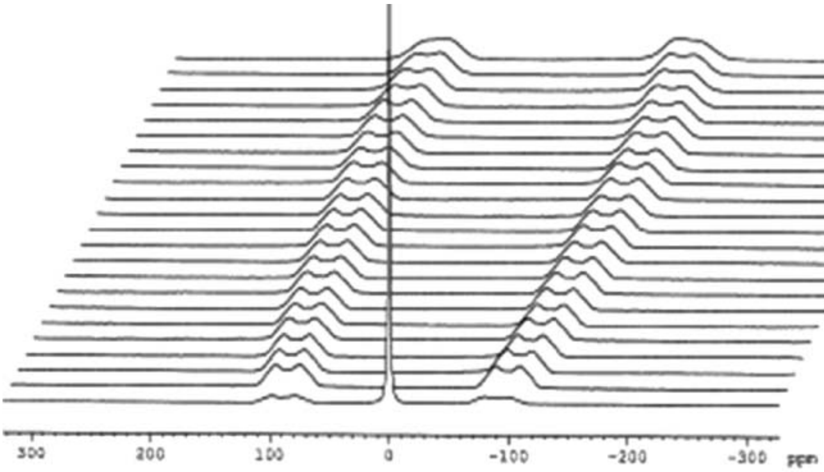


Figure 1. ^{2}H NMR spectra of **9HL-d$_2$** recorded from 127.5°C to 70°C every 2.5°C at 11.75 T.

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

where $K_{DH} = 18434.4$ Hz $\cdot$Å^3, $r_{DH} = 2.5$ Å, $\eta = 0.04$, $q_{aa} = 185$ kHz. The angle ϕ can be safely assumed equal to 60° for the undistorted phenyl ring geometry [23–26]. The fitting variables are the order parameters (S_{zz} and $\Delta_{biax} = S_{xx} - S_{yy}$) relative to the deuterated phenyl ring (with *z* being along the *para* axis). For the three sets of measurements performed at lower magnetic fields (4.70 T, 7.05 T and 11.75 T), two separate fitting procedures have been performed for the SmA and the SmC* phases, respectively. The reproduction of the experimental quadrupolar and dipolar splitting is very good (with error less than 2%). The observed trends of both splittings from the SmA to the SmC* phase are typical of ferroelectric LCs [23–26], in particular, the helical axes of the SmC* domains are oriented parallel to the external magnetic field and molecular longitudinal axis (as well as the rigid aromatic cores) are tilted with respect to the magnetic field. The behavior of the splittings is different at higher magnetic fields, namely 16.45 T and 18.80 T: both quadrupolar and dipolar splitting increase continuously within the whole mesophasic temperature range without any discontinuity at the SmA-SmC* transition. This behavior has been observed in other "normal" ferroelectric LCs when the external magnetic field exceeds the critical value needed to unwind the SmC* helical axis [18–26].

The trends of the splitting vs temperature at various magnetic field strengths reflect in the trends of the order parameter S_{zz} obtained by fitting the experimental data, as shown in Fig. 2. The values of the fragment biaxiality, Δ_{biax}, in the SmA and SmC* phases of **9HL** have been found similar to other LC smectogens, ranging between zero to 0.05. This is quite typical for deuterated phenyl moieties of LC cores. The most peculiar property concerns the value of the local order parameter S_{zz} in the SmA* phase of **9HL**. As seen in Fig. 2, the values of S_{zz} increase significantly by increasing the magnetic field strength. This effect, first reported in ref. [15], was never observed in "normal" SmA phases. Interestingly, the two trends at lower fields are almost coincident, thus indicating that values of the magnetic

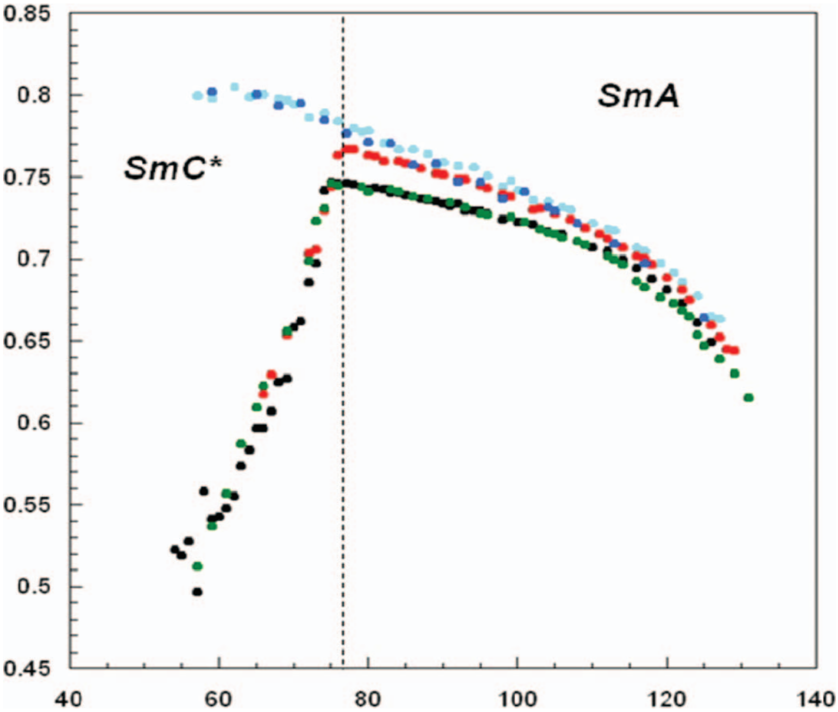


Figure 2. Main orientational order parameter, S$_{zz}$, *vs* Temperature (°C) of the ^{2}H-labeled phenyl ring of **9HL-d$_2$** as obtained by analyzing ^{2}H NMR spectra recorded at 4.70 (●), 7.05 (●), 11.75 (●), 16.45 (●) and 18.80 (●) Tesla.

field lower than 7.05 T do not influence the SmA structure and molecular organization. Moreover, the two trends of S$_{zz}$ at higher magnetic fields are also coincident, implying that the saturation of S$_{zz}$ is reached with magnetic fields higher than 11.75 T and lower or equal to 16.45 T (namely, the critical magnetic field is in this interval). The main orientational order of the deuterated ring in the SmA* phase at the intermediate field of 11.75 T is indeed lower than that observed at 16.45 T and higher than that observed at 7.05 T.

From these observations, several important conclusions arise:

1. The strong effect of the magnetic field on the orientational order of the **9HL** in the SmA phase indicates, analogously to the case of SmC* phases, that LC molecules of **9HL** are tilted with respect to the SmA layer normal. The molecular tilt, in particular the tilt of ^{2}H-labeled phenyl rings, can be determined by direct comparison between the main order parameters obtained at higher fields, S_{zz}^{hf}, (18.80 T and 16.45 T) and those obtained at lower fields, S_{lf}^{zz}, (4.70 T and 7.05 T), through equation:

$$S_{ZZ}^{lf}(T) = S_{ZZ}^{hf}(T) \cdot \left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right) \qquad (3)$$

In the case of intermediate fields, such as 11.75 T, the "not complete alignment" of molecules is responsible of the lower value of the tilt, when equation (3) is applied (see

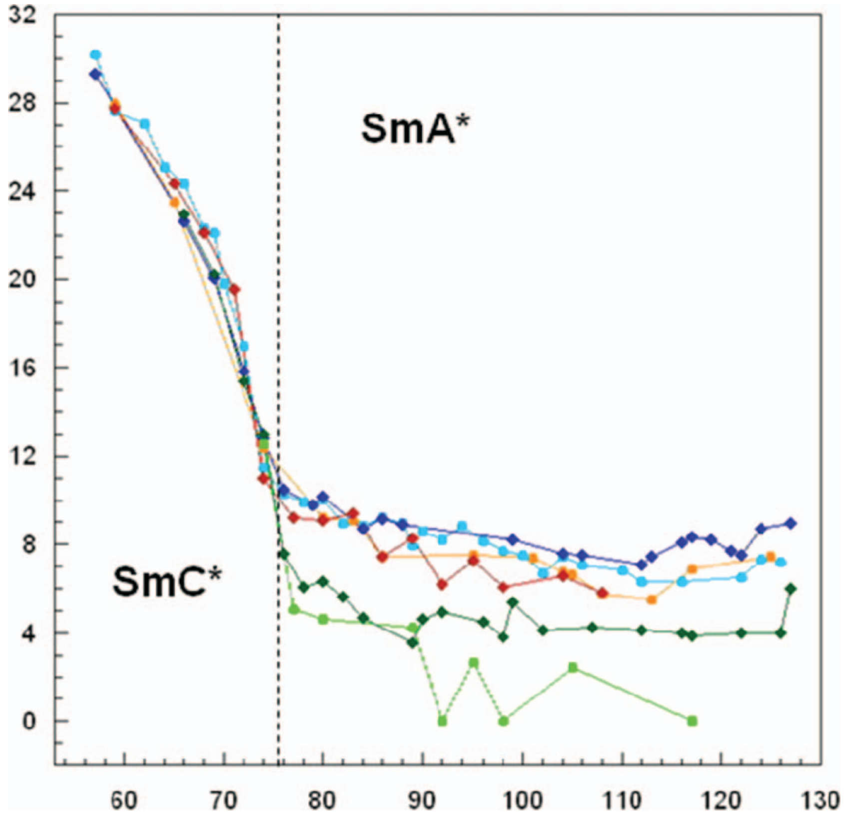


Figure 3. Tilt angle θ (degrees) *vs* Temperature (°C) directly evaluated from ^{2}H NMR data by using Equation 3. The saturation values of S_{zz} (corresponding to data recorded at 16.45 T and 18.80 T) are compared with those obtained at low fields: 18.80 T *vs* 7.05 T (◆), 16.45 T *vs* 7.05 T (■), 18.80 T *vs* 4.70 T (◆), 16.45 T *vs* 4.70 T (■), 18.80 T *vs* 11.75 T (◆) and 16.45 T *vs* 11.75 T (■).

green symbols in Fig. 3). The values of the tilt angle θ found by comparing the orientational order parameter S_{zz} at various fields are reported in Fig. 3. The tilt angle θ ranges between 5° and 12° in the SmA phase (see blue, cyan, red and orange symbols in Fig. 3), while it increases by decreasing the temperature within the SmC* phase reaching the higher value of about 30°.

2. Data reported in this study confirm that the molecular cores of the "de Vries" **9HL** are tilted with respect to the SmA layer normal. However, the strong magnetic field effect in aligning molecules implies the presence of ordered aggregates and, as a consequence, it is not consistent with a completely random or uncorrelated diffuse cone model. As already observed in other LC systems [27–29], the contribution of the magnetic energy of single, isolated molecules is indeed negligible with respect to other contributions, because of the very low molecular susceptibility anisotropy of LCs [27]. In the present case [15], the observed effect of the high magnetic field, even in the SmA phase, is justified by the presence of spatial modulations or local periodicities in the azimuthal angle distribution. A schematic picture of this not

random distribution of azimuthal orientations is summarized in the "cluster diffuse cone" model (see Scheme 1).

3. At the SmA-SmC* transition the tilt angle of the ^{2}H-labelled phenyl ring with respect to the layers' normal increases rapidly with a discontinuity in the slope (see Fig. 3). This observation is apparently in disagreement with the previously reported X-ray diffraction layer spacing data [5] and optical properties [7], which show a substantial continuous behavior passing from SmA to SmC* phases. However, the orientational order parameters determined by ^{2}H NMR at various magnetic fields are local molecular properties and the sudden change of the tilt can be explained by assuming two different 'average' conformations in the two mesophases. This has been shown by recent ^{13}C NMR studies [30] applied to the same **9HL** sample and it is in agreement with a detailed computational and ^{13}C NMR study in a ferroelectric LC [31].

4. Conclusions

In the present work, ^{2}H NMR measurements on a ^{2}H-labeled "de Vries" compound, namely **9HL**, were performed at five values of the magnetic field strength, extending a previous work [15] in which NMR data were recorded at two magnetic fields. The results reported here confirm the presence of an "average" tilt angle of the molecular core of **9HL** not only in the SmC* phase, but also in the SmA phase. In particular, the tilt angle ranges between 5° to 12° by decreasing the temperature within the SmA phase. Moreover, NMR data recorded at five magnetic field strengths validated the method used to calculate the tilt angle. Molecules in the SmA phase are indeed completely aligned by a magnetic field $H \geq 16.45$ T, while the SmA phase structure as well as the average molecular orientation are not influenced by a magnetic field at least lower than 7.05 T. The magnetic field effect described in this paper is compatible with the presence of cluster or aggregates of LC molecules with the same azimuthal and tilt angles, thus the "random diffuse cone" model is replaced by the new "cluster diffuse model."

Acknowledgments

We acknowledge the support of Egide (programme Galilée), from the Università Italo-Francese (Programma Galileo 2009/2010). This work was partially funded by the COST D35 WG13–05 project (between the Italian and Czech groups). We would like to thank Dr. Sergey V. Dvinskikh for NMR measurements at 4.70 T and Prof. Anne Lesage for helpful discussions.

References

[1] de Vries, A. (1970). *Mol. Cryst. Liq. Cryst.*, *11*, 361.
[2] de Vries, A. (1977). *Mol. Cryst. Liq. Cryst. Lett.*, *41*, 27.
[3] de Vries, A., Ekachai, A., & Spielberg, N. (1979). *Mol. Cryst. Liq. Cryst. Lett.*, *49*, 143.
[4] Lagerwall, J. P. F., Giesselmann, F., & Radcliffe, M. D. (2002). *Phys. Rev. E*, *66*, 031703.
[5] Krueger, M., & Giesselmann, F. (2005). *Phys. Rev. E*, *71*, 041704.
[6] Kaspar, M., Hamplova, V., Pakhomov, S., Bubnov, A., Guittard, F., Sverenyak, H., Stibor, I., Vanek, P., & Glogarova, M. (1998). *Liq. Cryst.*, *24*, 599.
[7] Giesselmann, F., Zugenmaier, P., Dierking, I., Lagerwall, S. T., Stebler, B., Kaspar, M., Hamplova, V., & Glogarova, M. (1999). *Phys. Rev. E*, *60*, 598.
[8] Diele, S., Brand, P., & Sackmann, H. (1972). *Mol. Cryst. Liq. Cryst.*, *16*, 105.

[9] Bartolino, R., Doucet, J., & Durant, G. (1978) *Ann. Phys. (Paris)*, *3*, 389.

[10] Roberts, J. C., Kapernaum, N., Song, Q., Nonnenmacher, D., Ayub, K., Giesselmann, F., & Lemieux, R. P. (2010). *J. Am. Chem. Soc.*, *132*, 364.

[11] Prasad, S. K., Rao, D. S. S., Sridevi, S., Lobo, C. V., Ratna, B. R., Naciri, J., & Shashidhar, R. (2009). *Phys. Rev. Lett.*, *102*, 147802.

[12] Manna, U., Jang-Kun Song, Vij, J. K., & Naciri, J. (2008). *Phys. Rev. E*, *78*, 041705.

[13] Osipov, M. A., Gorkunov, M. V., Gleeson, H. F., & Jaradat, S. (2008). *Eur. Phys. J. E*, *26*, 395.

[14] Saunders, K. (2009). *Phys. Rev. E*, *80*, 011703.

[15] Marchetti, A., Domenici, V., Novotna, V., Lelli, M., Cifelli, M., Lesage, A., & Veracini, C. A. (2010). *Chem. Phys. Chem.*, *11*, 1641.

[16] Garoff, S., & Meyer, R. B. (1977). *Phys. Rev. Lett.*, *38*, 848.

[17] de Gennes, P. G., Prost, J., In *"The Physics of Liquid Crystals"*; Claredon press, New York, 1993, pp. 57–58.

[18] Catalano, D., Cifelli, M., Domenici, V., Fodor-Csorba, K., Richardson, R., & Veracini, C. A. (2001). *Chem. Phys. Lett.*, *346*, 259.

[19] Domenici, V., *Master Thesis*, University of Pisa, 2001.

[20] Domenici, V., Marini, A., Veracini, C. A., Zhang, J., & Dong, R. Y. (2007). *Chem. Phys. Chem.*, *8*, 2575.

[21] Domenici, V., Veracini, C. A., Novotna, V., & Dong, R. Y. (2008). *Chem. Phys. Chem.*, *9*, 556.

[22] Domenici, V., Geppi, M., & Veracini, C. A. (2007). *Prog. Nucl. Magn. Reson. Spectrosc.*, *50*, 1.

[23] Domenici, V. (2007). *Pure Appl. Chem.*, *79*, 21.

[24] Cifelli, M., Domenici, V., Marini, A., & Veracini, C. A. (2010). *Liq. Cryst.*, *37*, 935.

[25] Domenici, V. (2011). *Pure Appl. Chem.*, *83*, 67.

[26] Domenici, V., & Marini, A. (2010). *Ferroelectrics*, *395*, 46.

[27] Domenici, V., Veracini, C. A., Fodor-Csorba, K., Prampolini, G., Cacelli, I., Lebar, A., & Zalar, B. (2007). *Chem. Phys. Chem.*, *8*, 2321.

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

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

[30] Domenici, V., Marchetti, A., Cifelli, M., Lelli, M., Lesage, A., & Veracini, C. A. manuscript in preparation.

[31] Domenici, V., & Marini, A. (2010). *J. Phys. Chem. B*, *114*, 10391.