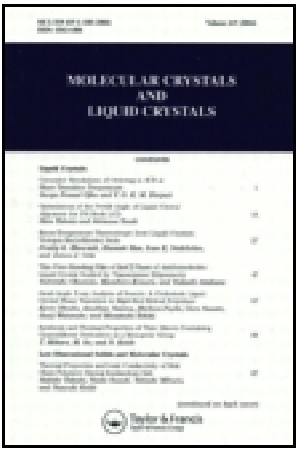

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A Brief Overview of ^{2}H NMR Experiments Used to Study the Phase Biaxiality in Nematic Liquid Crystals

Valentina Domenici [a]

[a] Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa, via Risorgimento, 35 - 56126, Pisa, Italy

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A Brief Overview of ^{2}H NMR Experiments Used to Study the Phase Biaxiality in Nematic Liquid Crystals

VALENTINA DOMENICI*

Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa,
via Risorgimento 35 – 56126, Pisa (Italy)

In this paper, some of the most relevant ^{2}H NMR experiments with the aim of determining the biaxial nature of the nematic phase in several thermotropic liquid crystals are overviewed. Advantages and disadvantages of the technique are discussed. This contribution is an extract of the lecture held in Erice (Sicily) in occasion of the "18th Course - Liquid crystal nanostructures and self-assembling: from organic electronics to metamaterials", the 2nd School of the Italian Liquid Crystal Society.

1. Introduction

Phase biaxiality in nematic systems represents one of the hot topics in the liquid crystal (LC) field, for the high potentiality in new display technology [1] and for fundamental research [2,3]. Starting from the definitions [4], this brief overview concerns the main results obtained so far by means of ^{2}H NMR spectroscopy to determine the phase biaxiality parameter in the nematic phase formed by bent-core liquid crystals (BLCs) [5], liquid crystal polymers (PLCs) and elastomers (LCEs) [6–9], as well as tetrapodes [10].

1.1. Order Parameters in the Orthorhombic Nematic Biaxial Phase

In the simplest case, when liquid crystalline molecules can be assumed uniaxial and rigid, and the mesophase has uniaxial symmetry (i.e. common nematic and SmA phases), the orientational order of the system can be described by a single parameter, the major orientational order parameter *S:*

$$S = \frac{1}{2}(3\langle\cos^2\theta_m\rangle - 1), \tag{1}$$

where θ_m is the angle between the molecular long axis and the nematic director, **n**. The brackets stand for an "average" over the molecular reorientations, which in general takes into account both space and motional averaging.

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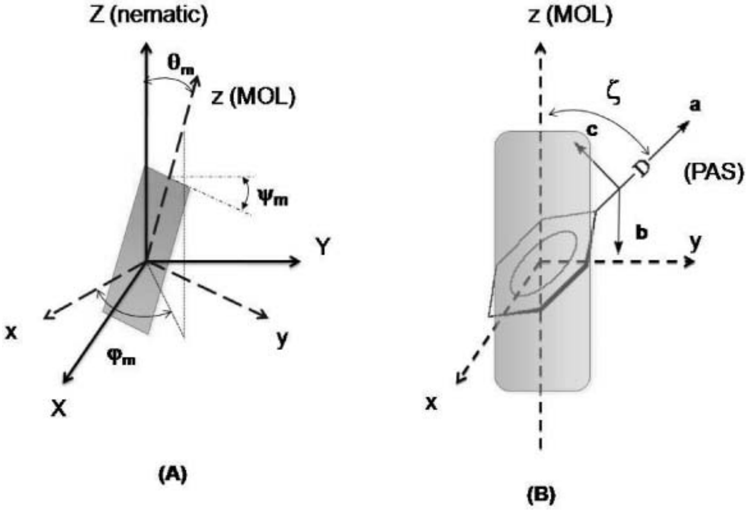
*Address correspondence to Valentina Domenici, Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa, via Risorgimento 35 – 56126, Pisa (Italy). Tel.: 0039 050 2219215; Fax: 0039 050 2219260. E-mail: valentin@dcci.unipi.it



Scheme 1. (A) Nematic phase frame (*X*, *Y*, *Z*) and molecular frame (*x*, *y*, *z*) with the relevant angles of transformation; (B) Principal axis frame (PAS) in the case of the deuterium labelled aromatic ring (*a*, *b*, *c*) and molecular frame (*x*, *y*, *z*).

When molecules cannot be approximated to uniaxial objects (Scheme 1), a further molecular parameter is defined, namely the molecular biaxiality:

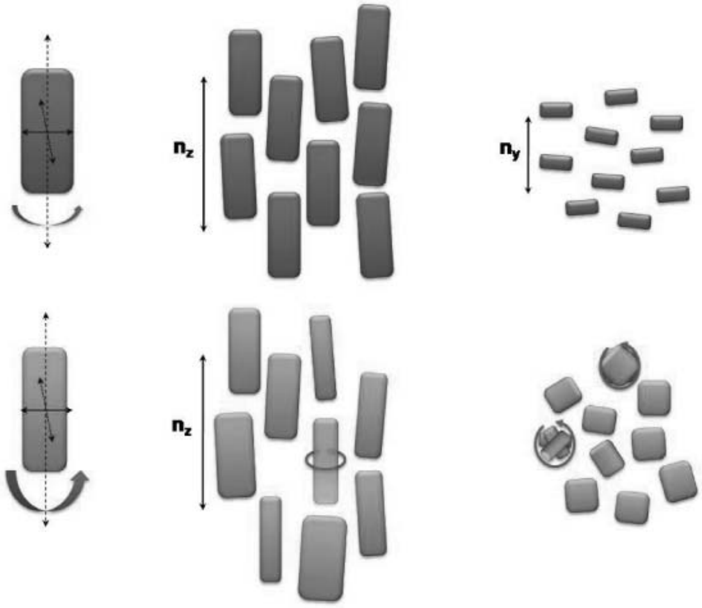
$$\Delta_{biax} = D = S_{xx}^{ZZ} - S_{yy}^{ZZ} = \frac{3}{2} \cdot \langle \sin^2 \theta_m \cdot \cos 2\psi_m \rangle \tag{2}$$

Here, Z defines the axis of the director and x, y, z is the molecular frame. For molecules deuterium-labelled in the lateral chains, the molecular biaxiality is usually small and negligible. This is in general valid for rod-like LCs in the nematic phase, while for other exotic molecular shapes, such as bent-core LCs, this is not true [10,11]. When LC molecules are selectively ^{2}H-labelled on the aromatic rings, the molecular (or fragment) biaxiality is in general higher (as observed in several nematogens [11,12]: $0 < |\Delta_{\mathrm{biax}}| < 0.05$) and the assumption of molecular uniaxiality should be considered carefully (see also refs. [13–15]).

Biaxial phases can possess different symmetries and they are characterized by different names [16]: (i) triclinic biaxial nematic phase ($\mathrm{N_{Bt}}$), (ii) monoclinic biaxial nematic phase ($\mathrm{N_{Bm}}$) and (iii) orthorhombic biaxial nematic phase ($\mathrm{N_{BO}}$). The last one corresponds to the $\mathrm{D_{2h}}$ point group and it is the most studied and the one treated in the present work.

The orthorhombic nematic phase is characterized by three phase directors, i.e. $\mathbf{n_x}$, $\mathbf{n_y}$ and $\mathbf{n_z}$, perpendicular to each other and the principal director is usually chosen along the Z direction. The occurrence of phase biaxiality is related to the not uniaxial distribution of molecules within the mesophase, as represented in Scheme 2, and the possibility to detect the phase biaxiality is also related to the dynamic processes.

Biaxial phases in principle can be formed either by uniaxial or not-uniaxial molecules. However, the cases reported in the literature in LC polymers and LC elastomers as well as in bent-core LCs, assume a not cylinder-like, but platter-like geometry of the molecules. This is in agreement with the idea of a not completely free rotation of these molecules around their long molecular axis (as drawn in Scheme 2).



Scheme 2. (top) Example of a biaxial nematogen subject to slow reorientations. The nematic phase is biaxial, as seen from the front and top views. (down) The same biaxial nematogen, subject to much faster dynamic reorientations gives rise to a uniaxial nematic phase, as seen by the schematic front and top views.

The phase biaxial parameter is usually called η and depends on the spatial and time averaging of molecules with respect to the nematic frame (X, Y, Z in Scheme 2). The complete description of the orientational order in the orthorhombic phase includes the dependence by the PAS to MOL polar angles (i.e. ζ, χ, γ, are known from the literature, or determined by experiments or by *ab initio* computations) and by four order parameters, which can be written in terms of the polar angles θ_m, ψ_m and φ_m, related to the 'MOL' to 'nematic' frame transformation. The four order parameters are S, D (or Δ_{biax}), P and C. The latter two ones are here defined as reported in [17]:

$$P = S^{XX}_{zz} - S^{YY}_{zz} = \frac{3}{2}\langle \sin^2\theta_m \cdot \cos 2\varphi_m \rangle, \tag{3}$$

$$\begin{aligned} C &= \left(\left(S^{XX}_{xx} - S^{YY}_{xx}\right) - \left(S^{XX}_{yy} - S^{YY}_{yy}\right)\right) \\ &= \left\langle \frac{3}{2}(1 + \cos^2\theta_m)\cos 2\varphi_m \cos 2\psi_m - 3\cos\theta_m \sin 2\varphi_m \sin 2\psi_m \right\rangle. \end{aligned} \tag{4}$$

If the molecular biaxiality is zero ($\Delta_{biax} = 0$), the order parameter C is also null and the phase biaxiality parameter η reduces to this ratio:

$$\eta = \frac{P}{S}. \tag{5}$$

It should be noticed that all these parameters are averaged quantities, where the average is within the ensemble of molecules (in the various domains in the macroscopic system) and it is a "time average". When dealing with experimental methods, a fundamental condition to measure phase biaxiality is that the characteristic time of the measurement is shorter than the correlation times of the motional processes responsible of the time averaging.

2. ^{2}H NMR Experiments

It is known that single and isolated deuterons in partially oriented systems contribute to the ^{2}H NMR spectrum with a double peak characterized by the quadrupolar splitting [18]:

$$\overline{\Delta\nu_q} = \frac{3}{2} q_{aa} \left[S_{aa} + \frac{\eta_q}{3} \left(S_{cc} - S_{bb} \right) \right] \tag{6}$$

The terms S_{aa}, S_{bb} and S_{cc} are the diagonal elements of the orientational order tensor (Saupe matrix) which is assumed to be uniaxial in the PAS frame, where the Electric Field Gradient (EFG) tensor, responsible of the quadrupolar interaction, is uniaxially symmetric with the main axis along the C—D bond (see Scheme 1). The quadrupolar constant and the asymmetry parameter of the ^{2}H quadrupole are q_{aa} and η_q, respectively.

The measured quadrupolar splitting $\overline{\Delta\nu_q}$ is related to the mesophase order parameters (i.e. the *P* and *S* parameters seen in the previous page) in a more complicate way than Eq. 6, and in general several assumptions are needed.

If the 'LAB' and 'nematic' frames coincide, namely the phase director, **n**, is parallel to the external magnetic field, **H**, the measured quadrupolar splitting is not influenced by the phase biaxiality parameter η, but only by the molecular biaxiality, Δ_{biax}, and by the major orientational order, *S*. The measured quadrupolar splitting is indeed a function of Δ_{biax}, *S* and the angular quantities (Ω) relating the PAS to the MOL frames:

$$\overline{\Delta\nu_q}(0) = F(\Delta_{biax}, \Omega) \cdot S \tag{7}$$

However, if angular-dependent measurements are performed the quadrupolar splitting depends also on the biaxial parameter η:

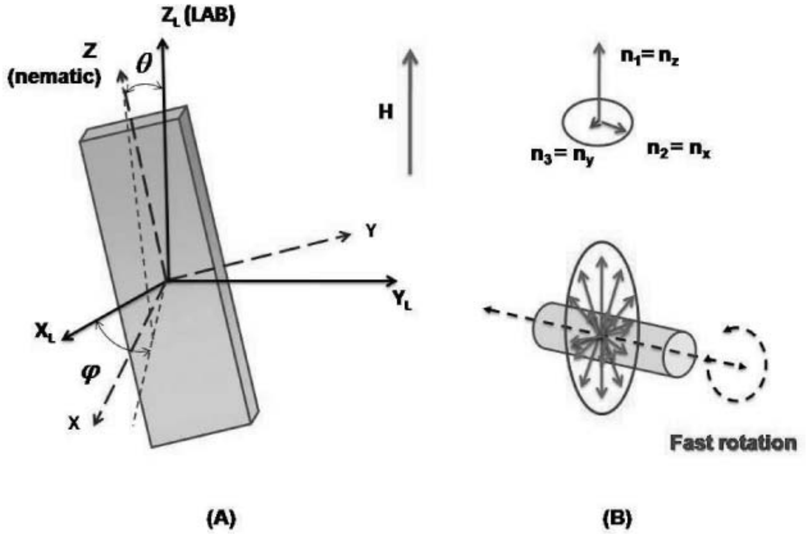
$$\overline{\Delta\nu_q}(\theta, \varphi) = \overline{\Delta\nu_q}(0) \cdot \left[\left(\frac{3}{2} \cos^2\theta - \frac{1}{2} \right) + \frac{\eta}{2} \cdot \left(\sin^2\theta \cos 2\varphi \right) \right]. \tag{8}$$

Angular NMR measurements are usually performed by varying the angle θ (see Scheme 3). They have been used for the first time to investigate the phase biaxiality in lyotropic liquid crystals by Yu and Saupe [19]. During the last years, the reliability of this method has been object of several criticisms, in particular, when spin probes are used [20].

The essential condition to use angular NMR measurements is that the rotation of the macroscopic sample with respect to the magnetic field does not alter the average alignment of molecules and that director reorientations or redistributions do not occur. To take into account this last eventuality, two methods have been optimized in the last years:

1. Fast jump rotation of the sample of an angle θ for the time of the experiment (repositioning the sample at $\theta = 0$ between consecutive acquisitions) to prevent the main director reorientation;
2. Continuous rotation of the sample in a direction perpendicular to $\mathbf{n_z}$ and consequent induced spatial distribution of the second main director $\mathbf{n_x}$.

If the main director reorientation is a very slow process with respect to the time needed to acquire a good spectrum, angular measurements can be safely performed by varying the angle θ of consecutive small steps (standard angular measurements).



Scheme 3. (A) Relative orientation of the nematic frame (X, Y, Z) with respect to the LAB frame (X_L, Y_L, Z_L) in angular NMR measurements; (B) Sketch of the continuous rotation experiment. The relative orientation of the three directors and the external magnetic field, H, is also reported.

3. Overview of Some Real Experiments

In 2004, several fundamental works were published concerning the evidence of phase biaxiality in the nematic phase formed by LC polymers and LC elastomers [9] and bent-core LCs [5]. In the first letter [9], deuterated probes were used and their molecular biaxiality neglected ($\Delta_{biax} = 0$), thus reducing the number of order parameters to S and P (or η). This approximation was justified by the fast reorientation of the small probes around their long molecular axis.

The phase biaxiality of the nematic phase formed by LCPs and LCEs was evaluated by measuring the quadrupolar splitting in the spectra at $\theta = 0°$ and at $\theta = 90°$ measured by using the fast jump rotation approach (*1*) as well as by standard angular measurements [9]. In recent works, full angular measurements (in the range $0° < \theta < 90°$) by varying θ in small steps have been performed for a careful determination of the values of phase biaxiality parameter [6–8] in LCPs and LCEs.

In the case of monodomain LCEs, also called Liquid Single Crystal Elastomers (LSCEs), the orientation of the three directors $\mathbf{n_x}$, $\mathbf{n_y}$ and $\mathbf{n_z}$ is known and the value of θ and ϕ is fixed according to the geometry of the macroscopic sample. In these samples, if we assume that the presence of the external magnetic field does not alter the orientation of the three directors, Equation (8) can be safely used to determine the parameter η from angular measurements. For instance, the following relationships can be easily derived for the ratio between the quadrupolar splittings measured at $\theta = 90°$ and at $\theta = 0°$, with fixed geometry $\varphi = 0$ or $\varphi = 90°$:

$$\frac{2\left|\Delta\nu_q(90°, 0°)\right|}{\left|\Delta\nu_q(0°, 0°)\right|} = 1 - \eta \tag{9}$$

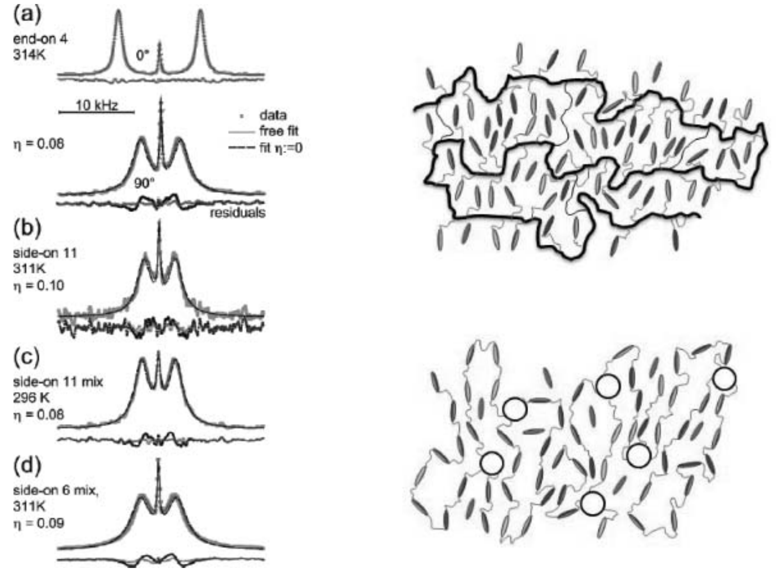


Figure 1. On the left: (a) ^{2}H NMR spectrum of a LCE recorded at $\theta = 0°$; (b)–(d) several ^{2}H NMR spectra of various LCEs recorded at $\theta = 90°$. Data and fitted spectra with and without taking into account the phase biaxiality are reported. Reprinted with permission from [7]. Copyright 2011 by American Society of Chemistry. On the right: schematic representation of side-chain and main-chain liquid crystal elastomers doped with deuterium labelled probes (red rods).

and

$$\frac{2\left|\Delta\nu_q(90°, 90°)\right|}{\left|\Delta\nu_q(0°, 90°)\right|} = 1 + \eta. \tag{10}$$

In uniaxial phases, namely $\eta = 0$, the two equations are identical and the quadrupolar splitting at $\theta = 90°$ is simply half of that at $\theta = 0°$. Different is the case of biaxial nematics: in several LSCEs, for instance, $2|\Delta\nu_q(90°)| < |\Delta\nu_q(0°)|$ leading to a value of η in the range $0.05 \div 0.26$.

Except for the LSCEs, in general, the value of ϕ in a macroscopic LC sample is unknown and the second main director $\mathbf{n}_x$ (or $\mathbf{n}_y$) is distributed in a plane perpendicular to $\mathbf{n}_z$. When angular measurements are performed, several scenarios may occur:

1) The main director $\mathbf{n}_z$ fast reorients parallel to the magnetic field;
2) The main director $\mathbf{n}_z$ does not reorient, while the second director align with the magnetic field;
3) All directors are partially distributed and not homogeneously aligned with respect to the field.

The first situation was observed in 2004 by Madsen et al. [5] studying a bent-core LC having a nematic phase stable at high temperatures (see Fig. 2). The fast reorientation of the main phase director $\mathbf{n}_z$ prevented the authors from biaxiality observation; however, the continuous fast rotation approach (see Scheme 3b) could be adopted. ^{2}H NMR spectra were acquired by rotating the sample at about 250 Hz around an axis perpendicular to the external magnetic field in order to get a planar distribution of both $\mathbf{n}_1$ ($\mathbf{n}_z$) and $\mathbf{n}_2$ ($\mathbf{n}_x$) as

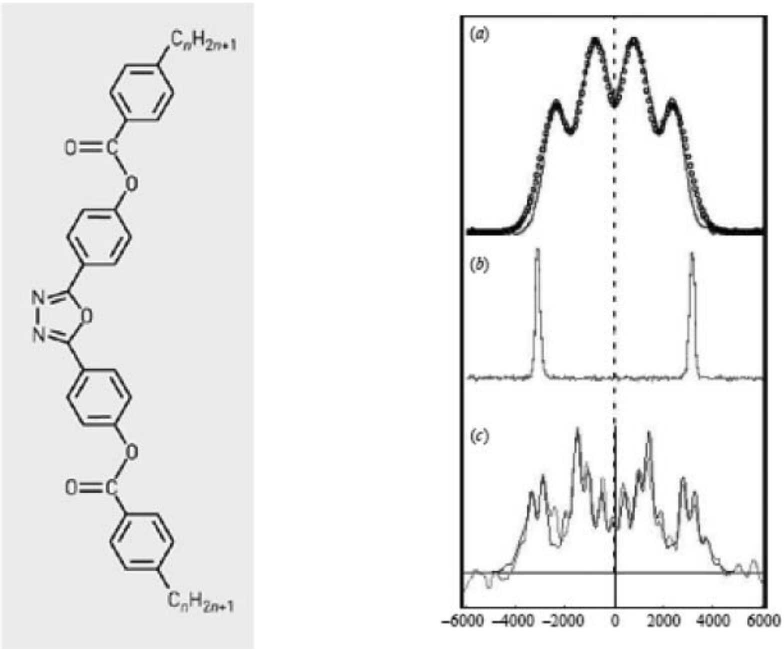


Figure 2. On the left: molecular structure of the biaxial nematogen based on the 2,5 oxadiaziol biphenol core (ODBP-Ph-C$_7$) investigated by Madsen et al. [5]. On the right: (a) ^{2}H NMR spectrum of ODBP-Ph-C$_7$ obtained by fast continuous rotation. Data and fitted spectrum with a phase biaxiality $\eta = 0.11$ are reported. (b) Static ^{2}H NMR spectrum of ODBP-Ph-C$_7$. (c) ^{2}H NMR spectrum of a uniaxial nematogen (TBBA) obtained by fast continuous rotation similarly to (a). Data and fitted spectrum with a phase biaxiality $\eta = 0$ are reported. Reprinted figure with permission from [4]. Copyright (2011), by the American Physical Society.

shown in Scheme 3b. The simulation of the ^{2}H NMR spectra allowed Madsen et al. [5] the determination of a value of the biaxial order parameter η equal to 0.11.

The effect of φ distribution on the spectra measured by the continuous rotation method was nicely explained by Cruz et al. [21] commenting the ^{2}H NMR study of a polydomain sample of an organo-siloxane tetrapode showing a biaxial nematic phase. A selection of these spectra are reported in Fig. 3, showing that the distribution of the second main director $\mathbf{n}_x$ (or $\mathbf{n}_y$) perpendicularly to $\mathbf{n}_z$ produces a 2D powder pattern with characteristic spectral features which strongly depend also on the motions affecting the deuterated probes. The correct determination of the phase biaxiality η is clearly related to the quality of the simulation of the experimental spectra, as pointed in ref. [21].

4. Discussion and Conclusions

Several considerations concerning the methodology used to determine the phase biaxiality in nematic phases by means of ^{2}H NMR spectroscopy are here summarized:

1. Monodomain nematic elastomers, usually referred as LSCEs, form a biaxial nematic phase [22] with orthorhombic symmetry (D_{2h}). The macroscopic geometry of these samples allows in principle to know the orientation of the three directors $\mathbf{n}_z$, $\mathbf{n}_x$ and $\mathbf{n}_y$. Moreover, due to the high viscosity of these samples, the reorientation of

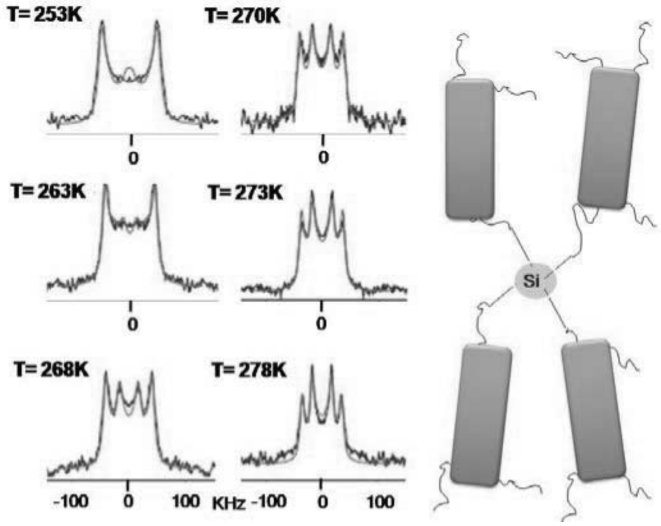


Figure 3. On the left: ^{2}H NMR spectra recorded at different temperatures in the nematic phase of an organo-siloxane tetrapode doped with a deuterated probe. All experimental spectra (blue) are recorded by using the fast continuous rotation approach. The fitted spectra are obtained taking into account the phase biaxiality, the director distribution and the presence of slow motions. Reprinted figure with permission from [21]. Copyright (2011), by the American Physical Society. On the right: schematic representation of the organo-siloxane tetrapode investigated by Cruz et al. [21].

the directors with respect to the field when the sample is flip of 90° is rather slow and the angular NMR measurements can be performed by means of the standard method or by the fast jump rotation one [6–9]. All investigations performed so far on doped LCEs or on selectively labelled LCEs report $2|\Delta\nu_q(90^\circ)| < |\Delta\nu_q(0^\circ)|$ independently from the initial value of φ: the direct consequence is that the observed phase biaxiality in all these works [6–9] is *induced* by the external magnetic field. In other words, when the sample is flipped from $\theta = 0^\circ$ to $\theta = 90^\circ$, the magnetic field induces (via a magnetic torque) the second director, $\mathbf{n}_2$, to align parallel to it, independently from the initial value of φ.

2. The use of deuterated molecular probes to check phase biaxiality has to be considered a good qualitative (but not quantitative) method. In fact, deuterated probes allow one to get only ‘scaled’ values of the order parameters of the LC environment, and the scaling factor depends on the probe (i.e. on its mobility through the sample). Small probes are expected to rotate freely and the assumption of molecular uniaxiality in these studies [4–10] is safe. However, the self-diffusion of the small probes through the LC systems is much more critical than the rotational diffusion. In fact, especially at low temperatures, the self diffusion is slow compared with the NMR time-scale and the probe is much more sensitive to eventual heterogeneities in the sample and to different orientations of the local phase director. This aspect is probably at the basis of the ‘apparent’ transition between the uniaxial and biaxial nematic phases in LCEs and LCPs recently reported, based on ^{2}H NMR measurements [6]. Due to similar considerations, the value of η determined by using probe molecules may be overestimated [22].

3. The quantitative determination of the phase biaxiality parameter η from the fitting of the experimental ^{2}H NMR spectra of bent-core LCs [1,5] or tetrapode LCs [10,21] obtained with the continuous rotation approach, can be done by taking into account both director distributions and molecular motions, which strongly affect both the spectral width and shape [21]. For the amount of parameters to be known in these fittings, the analysis of ^{2}H NMR spectral features should be supported by independent measurements (self diffusion coefficients, relaxation times and characteristic director reorientation times, evidence of director inhomogeneities, molecular biaxiality of the deuterated probes, . . .). However, since the continuous rotation approach alters the directors' distribution and alignment, this method cannot be used to establish the symmetry of the mesophase (if triclinic, monoclinic or orthorhombic) unless with the support of additional experiments.

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