Deuterium NMR Investigation of the Biaxial Nematic Phase in an Organosiloxane Tetrapode

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Deuterium NMR is used to examine the molecular order exhibited by an organosiloxane tetrapode giving the first experimental evidence, using a bulk sample, for the existence of a biaxial nematic phase in this type of compounds. The temperature dependence of the averaged quadrupolar coupling constant and asymmetry parameter was determined in the compound's nematic phase. Two distinct regimes could be identified, one with a vanishing asymmetry parameter corresponding to a uniaxial nematic phase and another with a significant temperature dependent asymmetry parameter, corresponding to a biaxial nematic phase. The high values obtained for the asymmetry parameter at the lower end of the nematic range are well above experimental error and constitute a definite proof of the biaxial nature of the nematic phase exhibited by the studied compound for those temperatures.

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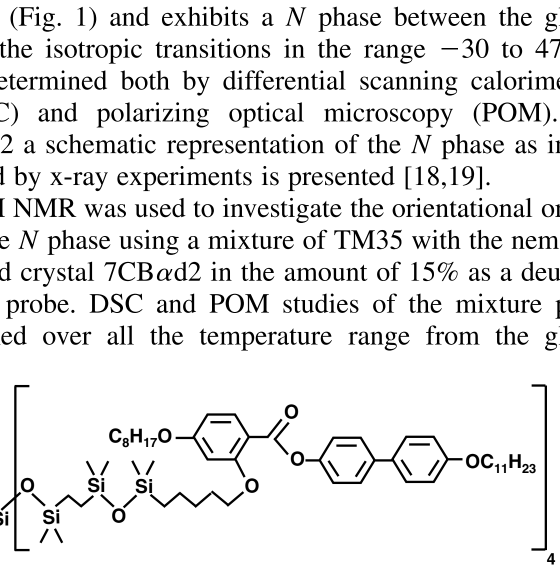
The biaxial nematic (N_b) phase, theoretically predicted by Freiser in 1970 [1], was first observed by Yu and Saupe [2] in a lyotropic system. Despite the interest in obtaining experimental evidence for this phase in thermotropic liquid crystals over the years, this topic has remained difficult. Several synthetic projects were undertaken in order to investigate molecules with structures clearly deviating from the quasicylindrical shape, aiming to achieve the elusive N_b phase [3–6]. It was expected that the increased molecular biaxiality would give rise to N_b phases. The question of nematic (N) phase biaxiality has since then been discussed controversially as different methods yielded contradictory results [7].

The determination of second rank tensorial physical properties in a bulk sample is an unambiguous method for the verification of the N phase biaxiality. For a biaxial phase, all three principal values of the tensorial quantity are distinct as opposed to the uniaxial case where two of them are equal. The asymmetry parameter defined as $\eta = (Q_{xx} - Q_{yy})/Q_{zz}$, where Q is a symmetric and traceless second rank tensorial quantity and Q_{ii} are its principal values labeled to fulfil $|Q_{zz}| > |Q_{yy}| \geq |Q_{xx}|$, will be finite in the biaxial phase and zero in the uniaxial one. The z axis of the principal frame defines the main director of the phase, $\boldsymbol{n}_1$. In addition, in the biaxial phase, the x and y axes define the secondary directors $\boldsymbol{n}_2$ and $\boldsymbol{n}_3$ which are degenerate in the uniaxial case. ^{2}H NMR, where the electric field gradient tensor associated with a C—D bond in a molecule is detected, is an appropriate technique for the study of the N_b order. This method clarified the question of phase biaxiality for a number of systems [7–9].

Very recently, the possibility of the appearance of the N_b phase has been reported in different kinds of low molecular weight thermotropic systems, namely, bent-core mesogens [10], confirmed by NMR studies, bent-core dimmers [11], and mixtures of calamitic and/or discotic molecules with linked rod-plate amphiphiles [12,13]], systems for which biaxiality had been predicted [14–16]. In particular, for tetrapode systems, the N_b phase was also predicted in the form of a cubatic phase [17].

In this Letter we report an investigation of the N_b phase in a organosiloxane tetrapode compound (TM35) where the biaxiality of the phase could be expected due to the lateral attachment of the mesogens to the central siloxane core, as indicated for related systems [18–21]. TM35 contains a siloxane core and four laterally connected mesogens (Fig. 1) and exhibits a N phase between the glass and the isotropic transitions in the range −30 to 47 °C as determined both by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). In Fig. 2 a schematic representation of the N phase as indicated by x-ray experiments is presented [18,19].

^{2}H NMR was used to investigate the orientational order in the N phase using a mixture of TM35 with the nematic liquid crystal 7CBαd2 in the amount of 15% as a deuterated probe. DSC and POM studies of the mixture performed over all the temperature range from the glass



$$T_g \xrightarrow{-30°C} N \xrightarrow{47°C} I$$

FIG. 1. Molecular structure and phase sequence of the organosiloxane tetrapode which exhibits the N_b phase.

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transition to the isotropic phase assure the miscibility of the probe and the preservation of the N phase. Those measurements give evidence for a N phase between -40 and 37 °C in the mixture.

The ^{2}H NMR spectra, $G(\nu)$, result from the sum of contributions [corresponding to different nematic domains with a distribution of orientations $P(\Omega)$ relative to the static magnetic field $\boldsymbol{B}_0$] of pairs of Lorentzian absorption lines $L(\nu)$

$$G(\nu) = \int_\Omega [L(\nu - \delta\nu/2) + L(\nu + \delta\nu/2)]P(\Omega)d\Omega \quad (1)$$

with frequency splitting given by

$$\delta\nu = \frac{3}{2}\nu_Q\left[\frac{1}{2}(3\cos^2\theta - 1) + \frac{\eta}{2}\sin^2\theta\cos2\varphi\right],$$

where ν_Q is the averaged quadrupolar coupling constant and θ and φ [$\Omega \equiv (\theta, \varphi)$] are the Euler angles giving the orientation of the magnetic field B_0 in the principal frame of the averaged field gradient (AFG) tensor associated with each domain. As defined earlier for a general second rank tensorial quantity, the asymmetry parameter is given in this case by

$$\eta = (\bar{V}_{xx} - \bar{V}_{yy})/\bar{V}_{zz}, \quad (3)$$

where $\bar{V}^{ii}$ are the principal values of the AFG tensor.

In this work, measurements of ν_Q and asymmetry parameter were obtained from partial powder patterns (obtained after a 90° sample rotation about one axis perpendicular to the static magnetic field, $\boldsymbol{B}_0$) corresponding to distributions of the secondary directors $\boldsymbol{n}_2$ and $\boldsymbol{n}_3$ in the sample. As a reference, the spectra from the aligned sample (where the main directors, $\boldsymbol{n}_1$, of the different domains are aligned with $\boldsymbol{B}_0$ and the secondary directors $\boldsymbol{n}_2$ and $\boldsymbol{n}_3$ are uniformly distributed by symmetry reasons in the plane perpendicular to $\boldsymbol{B}_0$) were also recorded after the sample had been slowly cooled from the isotropic phase to the measuring temperature and prior to the sample rotation and are shown in Fig. 3.

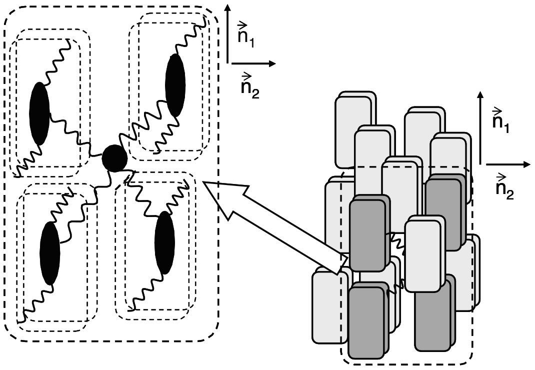

FIG. 2. Schematic representation of the structure of the nematic phase formed by the tetrapodes.

The 90° rotated sample spectra were obtained by averaging several sets of scans registered while the sample is kept at 90° for short time periods up to 30 s and after brought back to 0° orientation for periods of 150 s. With this scheme, the spectra recorded at 90° did not suffer from principal director realignment as the highest temperature spectra clearly show.

Spectra recorded for the sample rotated by 90° from the initial orientation, around an axis perpendicular to the magnetic field, reflect the distribution of the $\boldsymbol{n}_2$ and $\boldsymbol{n}_3$ directors corresponding to the different domains in the sample. If biaxiality is present, a finite η can give rise to a linewidth increase or to a partial powder pattern. To fit the spectra from the rotated sample, a nonuniform distribution of the secondary directors around the main director had to be considered, which is compatible with a partial reorientation of the secondary directors induced by $\boldsymbol{B}_0$ in this sample orientation.

Following these hypotheses, for each temperature, the 90° rotated sample spectrum was fitted together with the corresponding aligned one, using expression (1). The distribution $P(\Omega)$ for the aligned sample is proportional to $\delta(\cos\theta - 1)$ (Dirac δ) expressing the alignment of the main directors with $\boldsymbol{B}_0$ and the uniform distribution of the secondary directors. In the rotated sample the main

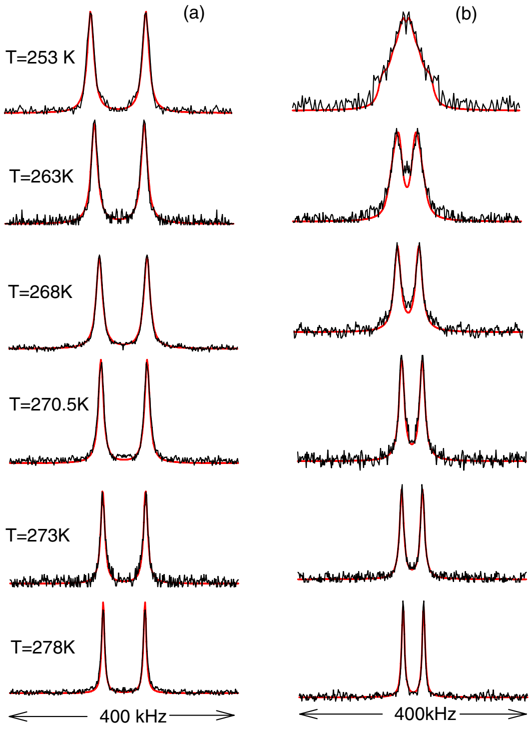

FIG. 3 (color online). Deuterium NMR spectra obtained at different temperatures for (a) aligned samples; (b) samples rotated 90° around an axis perpendicular to the static magnetic field $\boldsymbol{B}_0$ and fits of expression (1) to the spectra registered from aligned (a) and 90° rotated spectra (b). Experimental data: thin line; fits: thick line.

director is orthogonal to $\boldsymbol{B}_0$ and the secondary directors are nonuniformly distributed in the plane perpendicular to $\boldsymbol{n}_1$ giving rise to a $P(\Omega)$ proportional to $\delta(\cos\theta)h(\phi)$ where $h(\phi)$ is parametrized using the two lowest order terms of a Fourier series in ϕ compatible with the symmetry of the magnetic contribution to the free energy of a nematic domain [22]. Further details will appear elsewhere [23].

From the fits presented in Fig. 3 (thick line), the temperature dependence of ν_Q and η, presented in Fig. 4, was obtained. The fitting parameters are ν_Q, η, the Lorentzian linewidth λ and the two Fourier coefficients.

Within experimental error, the asymmetry parameter (measured in a bulk sample) is zero at 273 K and above (corresponding to a uniaxial N phase) and is finite below that temperature (corresponding to the N_b phase). These results are in agreement with polarized IR spectroscopy and optical investigations (in confined samples) where biaxiality is observed for the tetrapode studied in this work [20]. The difference between the uniaxial-biaxial transition temperatures found in the two studies may be attributed to a set of factors that includes the confinement of the IR tested sample, the presence of the probe in the NMR sample and the experimental error in the NMR determined asymmetry parameter.

The results obtained for the biaxial ordering in the investigated system can be discussed in terms of the molecular architecture and the structure of the nematic phase formed by the tetrapodes.

In TM35, the N phase is formed with interdigitation of laterally attached mesogenic units belonging to different tetrapodes (Fig. 2). This effect is easily understood considering basic steric and entropic reasons and is confirmed by the analysis of x-ray diffraction and polarized IR spectroscopy results [18–20].

Because of the local packing resulting from the interdigitation, the rotational movements of the mesogenic units are clearly hindered as a consequence of their lateral attachment to the silicon core of TM35, giving rise to the biaxiality of the phase.

The effect that explains the biaxiality in this monodispersed dendritic system (generation 0) has some similarities to that observed in the side-on nematic polymer discussed in [21] where the biaxiality results from the lateral attachment of the mesogenic units to the polymeric chain. However, the system investigated here is a monodisperse supermolecular system, with a clear overall geometry that gives NMR patterns where biaxiality is immediately observed.

The results of Monte Carlo simulations, where biaxiality of the molecules and of the interactions is considered [24], are useful to the discussion of the origin of biaxiality in supermolecular systems. Simulations show that the biaxiality of the molecules and of the interactions which contribute to the onset of a N_b phase also favor the formation of smectic phases. These theoretical results are in line with the physical experimental evidence as discussed in [7]. The reason the N_b phase does not appear frequently is because the other phase intervenes at lower temperatures (normally a smectic phase) as a consequence of the molecular biaxiality. Therefore, it could be expected that the N_b phase would be observed if the onset of a smectic phase could be prevented. That is precisely what happens in the system formed by supermolecular tetrapodes discussed here, where the lateral attachment of the mesogenic units to the siloxane cores avoids the formation of a lamellar phase due to basic steric and entropic reasons [18,19]. The origin of the biaxiality in the system studied here can thus be explained by the molecular geometry and characteristics of the local arrangement in the N mesophase. Nevertheless, the question of the relative values of η, which are considerably higher than those reported previously for other systems [10,21] has to be considered. The most likely explanation for this is that all the systems in question were investigated at very different temperature ranges. For the bent-core mesogen presented in [10] the temperatures are very high (>170 °C), and in the case of the polymer [21] they are above room temperature. For TM35 the N_b range was observed between -30 and 0 °C. For these low temperatures it may be expected that the hindering of the rotational movements of the mesogenic units, which is associated with the biaxiality, will be much more effective and therefore produce a considerably higher value of η.

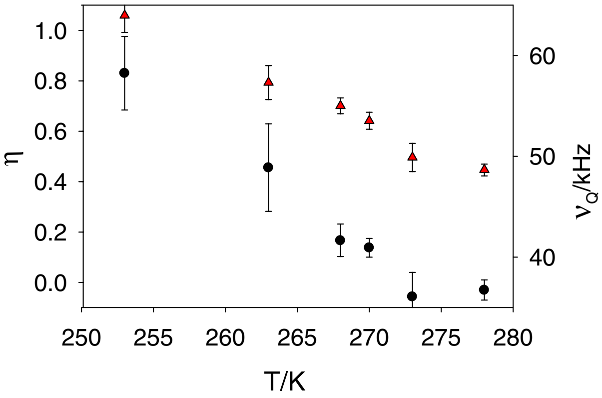

FIG. 4 (color online). Averaged quadrupolar coupling constant, ν_Q (triangles) and asymmetry parameter, η (circles) as a function of temperature as obtained from the fits of expression (1), presented in Fig. 3.

Actually, this hypothesis can be examined, in a first approximation, considering a simplified model where the biaxiality is originated by hindered rotational movements in a highly ordered system. Following the approach described in [25] the AFG tensor from the C—D bond from the α position of the probe is calculated by using an effective potential $U(T, \gamma)$ that reflects the asymmetry imposed by the local molecular arrangement on the reorientational movements around the long molecular axis. The effective potential considered here is given by

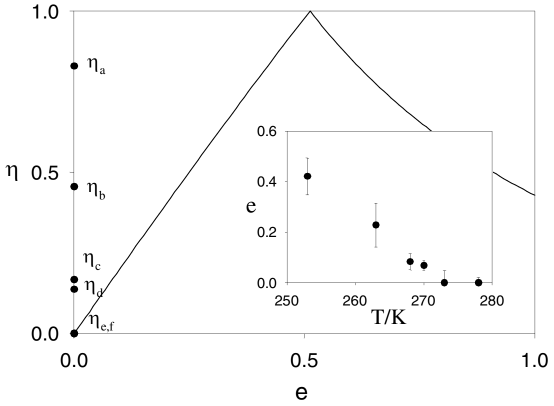

FIG. 5. Estimated values for the asymmetry parameter, η, as a function of $e = U_0(T)/2kT$ considering a simplified model where the averaged field gradient tensor from the C—D bond corresponding to the α position of the probe molecule is calculated using an effective potential for rotations around the long molecular core axis [expression (4)]. The experimental values η (Fig. 4) were used to estimate the dependence of the parameter e with the temperature, T, for the system studied, as presented in the inset plot. Points η_a, η_b, η_c, η_d, and $\eta_{e,f}$ on the η axis correspond to $T = 253$, 263, 268, 270, and >273 K, respectively.

$$U(T, \gamma) = U_0(T)\cos^2\gamma + U_1(T), \tag{4}$$

where $U_0(T)$ is the temperature dependent potential barrier height for rotations around the long molecular axis, γ is the rotation angle, and $U_1(T)$ is the γ independent part of U. Following [25] the orientational distribution function is given by

$$f(\gamma) = \frac{\exp\{-\frac{U(T,\gamma)}{KT}\}}{\int d\gamma \exp\{-\frac{U(T,\gamma)}{KT}\}}. \tag{5}$$

The components of the AFG tensor are given by

$$\overline{V}_{ij}(\gamma) = \int d\gamma f(\gamma) V_{ij}(\gamma), \tag{6}$$

where V_{ij} are the components of the field gradient tensor from the C—D bond expressed in a molecular frame with the z axis aligned with the molecular core long axis. η is estimated from the values of $\overline{V}_{ij}$ given by (6), using (3), and plotted in Fig. 5 as a function of the ratio $e = U_0(T)/(2KT)$. As shown in that plot, large values of η occur for $e \cong \frac{1}{2}$, just reflecting the fact that, at lower temperatures, in the biaxial phase [$U_0(T) \neq 0$], the potential barrier associated with the hindering of the rotations becomes important compared to the available thermal energy. The values of η obtained experimentally from the fits and presented in Fig. 4 can be used as inputs to this model in order to estimate the temperature dependence of the parameter "e," as plotted in the inset of Fig. 5.

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