

Carbon-13 NMR Investigations of the Orientational Order in a Columnar Liquid Crystal

Zhi Huang,[†] Dick Sandström,[†] Ulf Henriksson,[‡] and Arnold Maliniak^{*,†}*Division of Physical Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden, and Department of Physical Chemistry, The Royal Institute of Technology, S-100 44 Stockholm, Sweden**Received: April 15, 1998*

We report a natural abundance carbon-13 nuclear magnetic resonance (NMR) investigation of benzene dissolved in a columnar liquid crystal formed by the carbohydrate mesogen octa-*O*-decanoyl- β -cellobiose (Cel-II-10). The alignment of the mesophase in the magnetic field is sensitive to the field strength and to the thermal history of the sample. From carbon-13 line shapes, the director distribution functions and the molecular order parameter of the solute were estimated. In contrast to most columnar phases, Cel-II-10 aligns parallel to the magnetic field. The orientational order parameter of benzene is positive, which is expected for a columnar liquid crystal where the symmetry axis of the disk is aligned parallel to the column axis. However, an unexpected increase of the order parameter with increased temperature was observed. This behavior is probably a consequence of an exchange process between different solvation sites in the columnar mesophase and indicates that the population in the environment with higher order parameter increases when the sample is heated.

Introduction

The investigation of molecular organization in liquid crystals and in biological membranes is a challenging research area. Liquid crystals are systems which are intermediate between solids and isotropic fluids. They usually flow like liquids while retaining some of the anisotropic properties of crystals. These properties, in particular the long-range orientational order, originate from the anisotropic intermolecular interactions. The tendency of orienting along a particular direction in space is characteristic to all mesophases, but other physical and chemical properties may vary substantially. For example, nematic liquid crystals are usually low viscous (similar to isotropic liquids), while columnar phases often show highly ordered structures. During the last decade carbohydrates have been recognized as mesogenic compounds. In contrast to conventional discotic mesogens, the carbohydrates show an enormous isomeric variety.¹ Carbohydrate-based liquid crystals are able to form both lyotropic and thermotropic phases. Furthermore, columnar phases and bilayered structures can be formed.^{2,3}

The molecular organization of liquid crystals has been studied by a variety of techniques. Among these, nuclear magnetic resonance (NMR) plays probably the most important role. Information about molecular order, structure, and dynamics can be obtained from various NMR experiments.^{4,5} In particular, deuterium NMR has proven to be a powerful tool for studies of liquid crystalline systems. A major disadvantage of this method is the necessity of specific deuterium labeling which may be difficult and expensive. In addition, the sign of the quadrupolar interaction cannot be determined from a deuterium experiment.⁵ Natural abundance carbon-13 NMR studies constitute, therefore, an attractive alternative method for determination of molecular order.^{6–9}

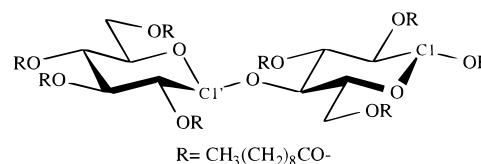


Figure 1. Chemical structure of octa-*O*-decanoyl- β -cellobiose (Cel-II-10).

Investigations of probe molecules dissolved in liquid crystals is a common method to monitor phase transitions, symmetries of mesophases, and magnetic field alignment. In addition, these studies provide information about molecular interactions responsible for solute orientation in liquid crystalline solvents. These interactions also determine the equilibrium between different solvation sites in the mesophase.

A characteristic property of liquid crystals is the tendency of the director to orient in electric and magnetic fields. For alignment in magnetic fields, two situations may occur depending on the sign of the diamagnetic anisotropy, $\Delta\chi$. A negative $\Delta\chi$ results in a perpendicular orientation of the director with respect to the magnetic field, while a positive sign forces the director to align parallel to the field. Columnar phases based on conventional discotics containing an aromatic core often orient perpendicular to the field, and some of them do not align at all.^{10,11} The reason for this is that the negative contribution to the anisotropic magnetic susceptibility originating from the aromatic cores either dominates or is essentially canceled by a positive contribution from the aliphatic chains in the molecules.

Benzene dissolved in a columnar phase formed by octa-*O*-decanoyl- β -cellobiose (Cel-II-10), see Figure 1, was previously investigated using deuterium NMR.¹² In that work we investigated molecular order and the alignment of the liquid crystal in magnetic fields. We were able to simulate deuterium line shapes using two different approaches. In the first method an analytical function for director distributions in the sample was used. The second approach was based on the assumption that the experimental spectrum consists of weighted fractions of

* Author for correspondence. E-mail: arnold@phycs.se. Fax: + 46 8 15 21 87.

[†] Stockholm University.

[‡] The Royal Institute of Technology.

aligned and unaligned domains. Both analyses produced spectra that were consistent with the experimental line shapes. However, as we already pointed out, from a ^2H NMR spectrum it is not possible to obtain the sign of the molecular order parameter.

Carbon-13 NMR in Ordered Media

Proton-decoupled carbon-13 spectra are determined by isotropic ^{13}C chemical shifts and averages of the carbon-13 chemical shift anisotropies (CSA)

$$\langle\omega\rangle = \omega_0(1 - \sigma_{\text{iso}} - \langle\sigma_{\text{aniso}}\rangle) \quad (1)$$

where the angular brackets denote an average over the rapid anisotropic molecular motion in the ordered phase, $\omega_0 = -\gamma B_0$ is the Larmor frequency, γ is the magnetogyric ratio, and B_0 is the magnetic field. In this equation, $\sigma_{\text{iso}} = 1/3(\sigma_{xx}^{\text{P}} + \sigma_{yy}^{\text{P}} + \sigma_{zz}^{\text{P}})$ is the isotropic average of the chemical shift and the superscript P indicates the principal values. In the present work, we investigate the orientational order of benzene in a uniaxial liquid crystal. We consider, therefore, only the simple situation of a uniaxial molecule in a uniaxial phase. Noting that the z component of the CSA tensor is parallel with the molecular C_6 axis,¹³ the orientationally averaged contribution to the chemical shift may be written as

$$\langle\sigma_{\text{aniso}}\rangle = S\sigma_{\text{aniso}}^{\text{P}} \frac{1}{2}(3\cos^2\theta_0 - 1) \frac{1}{2}[(3\cos^2\theta - 1)] \quad (2a)$$

with

$$\sigma_{\text{aniso}}^{\text{P}} = \sigma_{zz}^{\text{P}} - \sigma_{\text{iso}} \quad (2b)$$

In eq 2a, the transformation between the laboratory frame (defined by the magnetic field) and the principal axis system is performed using three successive rotations. Transformation from the laboratory space to the director frame is defined by the angle θ_0 . The averaged transformation from the director frame to the molecular coordinate system is characterized by the second-rank order parameter S . Finally, the angle θ is used to describe the rotation from the molecular frame to the principal axis system of the CSA interaction. The principal values of the carbon-13 CSA tensor in benzene are taken from the literature ($\sigma_{xx}^{\text{P}} = -97$, $\sigma_{yy}^{\text{P}} = -21$, and $\sigma_{zz}^{\text{P}} = 118$ ppm).¹³ The anisotropic contribution, $\langle\sigma_{\text{aniso}}\rangle$, vanishes in isotropic liquids ($S = 0$), and the NMR frequency is completely determined by σ_{iso} .

Experimental Section

The solute (benzene) was purchased from Merck and used without further purification. Octa-*O*-decanoyl- β -cellobiose was synthesized according to a previously described procedure.¹⁴ The liquid crystalline properties of this compound were characterized in our earlier communication.¹²

The solution was prepared by adding weighed amount of benzene into known quantity of mesogen and resulted in a concentration of 5.8 wt %. The samples were sealed in 5 mm NMR tubes. The mesomorphic region for Cel-II-10 was significantly shifted and reduced compared with the pure columnar phase. The two phase transitions of the neat compound determined in a cooling process were¹² 90 and 51 $^{\circ}\text{C}$, while the corresponding temperatures for the mixture were 75 and 33 $^{\circ}\text{C}$.

Carbon-13 NMR spectra were recorded at two different magnetic field strengths, 4.7 and 9.4 T, using Chemagnetic CMX spectrometers. The spectra were acquired using a single 90 $^{\circ}$

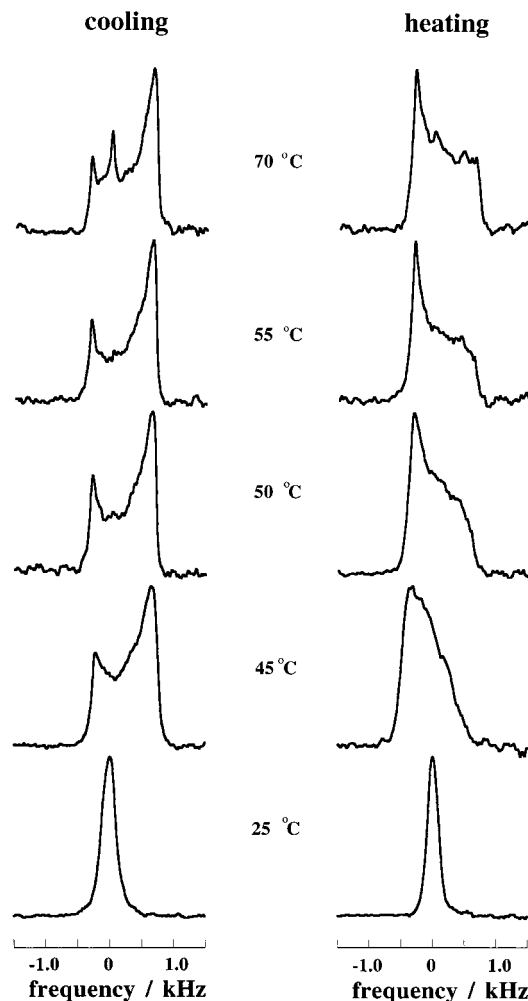


Figure 2. Experimental carbon-13 NMR spectra of benzene dissolved in Cel-II-10 recorded at 9.4 T. Cooling and heating refer to the procedures described in the text.

pulse experiment with WALTZ-16 broad-band proton decoupling.¹⁵ The decoupler power and frequency were carefully adjusted in order to limit heating effects and to obtain a reasonable resolution. The carbon-13 pulse length was 8 μs , and the delay between pulses was always at least five times the spin-lattice relaxation time. For a typical spectrum in the columnar phase, 2000 transients were required. The temperature was calibrated by measuring the proton shift difference in ethylene glycol.¹⁶

Results and Discussion

In Figure 2 we show carbon-13 NMR spectra of benzene dissolved in Cel-II-10 as a function of temperature. The spectra were collected at 9.4 T. The line shapes shown in the left column were acquired by slowly cooling the solution from the isotropic phase within the magnetic field of the spectrometer. The spectra to the right were acquired in a heating procedure. Here, the sample was heated to the isotropic liquid and cooled to the solid outside the magnet. Subsequently, the mixture was placed in the magnet where it was heated, and the spectra were recorded.

The carbon-13 line shapes are wide and powder-like, indicating only partial alignment of the liquid crystal in the magnetic field. Furthermore, the spectra recorded in cooling and heating procedures exhibit very different features. In particular, the traces in the right column have a shape that is characteristic for

an essentially disordered uniaxial sample. The line shapes in the left column exhibit features that correspond neither to an aligned sample nor to an isotropic powder. Therefore, we conclude that the columnar liquid crystal prepared by cooling in the magnetic field of the spectrometer is partially aligned in the static magnetic field of the spectrometer. The central peak in the top cooling spectrum is due to isotropic benzene. We note that the top four traces in both columns of Figure 2 show only minor temperature dependence which is in agreement with our previous deuterium investigation.¹² The spectra at 25 °C were acquired in the solid phase and consist of a single, nearly Lorentzian line shape. A possible explanation may be that the benzene molecules are collected in sites or domains which are essentially isotropic. Similar behavior was observed in the deuterium spectra of the solid phase.¹²

In order to extract more information about the molecular organization in the columnar phase, carbon-13 line shape analysis has been performed. If homogeneous broadening is neglected, the NMR spectrum is given by

$$I(\omega) = \int_0^{\pi/2} \delta[\omega - \langle\omega\rangle] P(\theta_0) \sin \theta_0 d\theta_0 \quad (3)$$

where $\langle\omega\rangle$ is defined in eq 1, $P(\theta_0)$ is the uniaxial director distribution function, and the absorption signal is represented by a delta function, δ . Our main objective is to find a director distribution, $P(\theta_0)$, that corresponds to the experimental line shape. To that end, two procedures were employed: (i) $P(\theta_0)$ was extracted directly from the experimental spectra and (ii) line shape simulations were performed using an analytical distribution function.

In the first approach we consider the anisotropic contribution to the chemical shift which, using eqs 1 and 2, gives the transition frequency as

$$\omega = a \cos^2 \theta_0 + b \quad (4)$$

with $a = \frac{3}{2}\omega_0\sigma_{\text{aniso}}^P S$ and $b = -\frac{1}{2}\omega_0\sigma_{\text{aniso}}^P S$. The order parameter, S , is determined as a scaling factor from the overall width of the line shape. Equation 3 provides a direct relation between the signal intensity (in the frequency domain) and the distribution function

$$I(\omega) = P(\theta_0) |\sin \theta_0 d\theta_0/d\omega| \quad (5)$$

From eq 4 we find

$$|d\theta_0/d\omega| = \frac{1}{2}|a \sin \theta_0 \cos \theta_0| \quad (6)$$

and

$$\cos \theta_0 = \pm \sqrt{(\omega - b)/a} \quad (7)$$

which inserted in eq 5 gives the final expression for the signal intensity

$$I(\omega) = \frac{P(\theta_0)}{2\sqrt{a(\omega - b)}} \quad (8)$$

Using eq 8, $P(\theta_0)$ can be determined directly from the experimental spectra without any assumptions about the physical model. The distribution functions shown in Figure 3 correspond to the two traces collected at 60 °C and shown in the top row of Figure 4. We note that the distribution derived from the spectrum obtained upon cooling has a maximum close to $\theta_0 \approx$

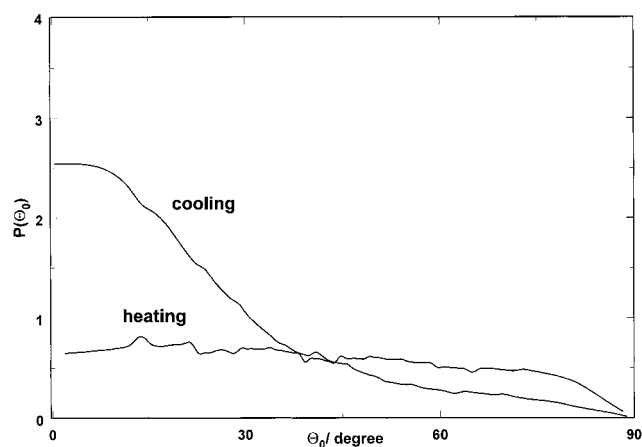


Figure 3. Director distribution functions determined from the experimental line shapes at 60 °C shown in Figure 2. The order parameter $S = 0.058$ was used.

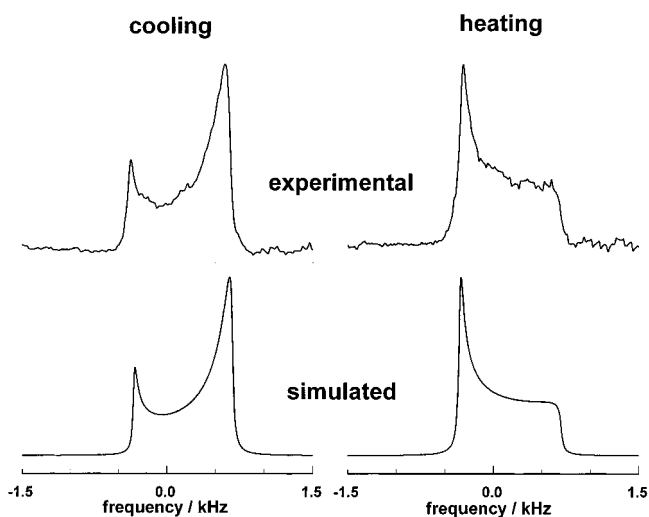


Figure 4. Carbon-13 NMR (9.4 T) line shapes of benzene dissolved in Cel-II-10 ($T = 60$ °C). The distribution functions used in the simulations are depicted in Figure 5. The cooling spectrum was calculated using the parameters $(\pi T_2)^{-1} = 33$ Hz and $c = 1.013$, while for the heating line shape, $(\pi T_2)^{-1} = 38$ Hz and $c = 0.21$ were used.

0°, which indicates that alignments parallel to the magnetic field are overrepresented. The orientation of the director parallel to the magnetic field is unusual for columnar phases and reflects the positive value of the net magnetic susceptibility of Cel-II-10. The positive magnetic susceptibility originates from the absence of an aromatic core in the mesogenic molecules. The distribution derived from the line shape in the heating procedure is considerably flatter, which is reflected in the powder-like shape of the spectrum.

In the following, the carbon-13 line shape simulations will be discussed. If the sample consists of a distribution of liquid crystalline domains, the NMR spectrum reflects a weighted sum of spectra for all possible orientations. Assuming a Lorentzian form for each orientation, the overall line shape is given by

$$I(\omega) = \int_0^{\pi/2} \frac{T_2}{1 + T_2^2(\omega - \langle\omega\rangle)^2} P(\theta_0) \sin \theta_0 d\theta_0 \quad (9)$$

where the half-height width of the individual signals, $(\pi T_2)^{-1}$, is assumed to be orientation-independent. In our previous investigation of this system, we simulated deuterium NMR spectra using different functional forms of the director distribu-

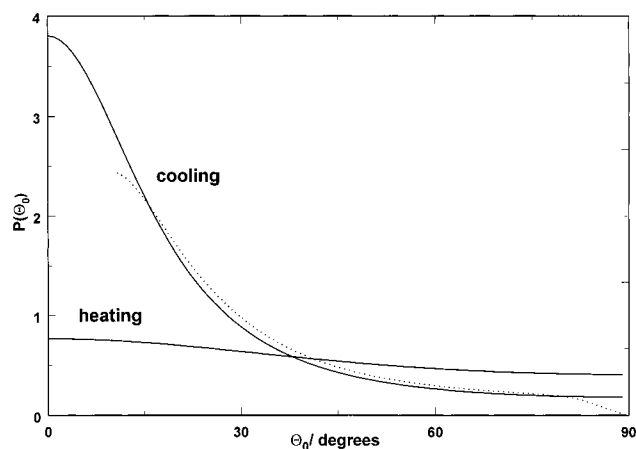


Figure 5. Director distribution functions used in the simulations of line shapes shown in Figure 4. The dotted line corresponds to the distribution recovered from the simulated line shape using the model-independent approach (see the text).

tion and found an agreement with experimental ^2H line shapes using $P(\theta_0)$ defined by

$$P(\theta_0) = \frac{\exp(2c) \cos^3 \{\tan^{-1}[\tan \theta_0 \exp(c)]\}}{2 \cos^3 \theta_0} \quad (10)$$

This relation was originally derived for describing the kinetics of director reorientation in polymeric liquid crystals.¹⁷ There, parameter c was time-dependent and characteristic to the director dynamics. In our studies no time dependence of the director was observed, and we treat c as an adjustable parameter, which depends on the field strength, anisotropic magnetic susceptibility, and the thermal history of the sample. Experimental and simulated carbon-13 spectra at 60 °C are shown in Figure 4. The line shapes were simulated using two parameters, T_2 and c , while the order parameters, S , were derived from the experimental spectra. The director distribution functions used in the simulations are depicted in Figure 5. The distribution function corresponding to the cooling procedure is clearly peaked at $\theta_0 = 0^\circ$, while an essentially isotropic distribution was used in the simulation of the heating trace. The shapes of the distribution functions are similar to those derived directly from the line shapes and plotted in Figure 3. The parameters used for the simulation of the carbon-13 line shapes corresponding to the cooling process are in close agreement with those derived from the deuterium spectra.¹² We performed a test of the assumption about the δ function line shape introduced in eq 3. To that end, the simulated spectrum in Figure 4 was analyzed using the model-independent approach, i.e., eq 8. This procedure should recover the distribution function used in the simulation. In Figure 5, such a recovered function is included and compared with the director distribution (corresponding to the cooling procedure spectrum) calculated using eq 10. The agreement between the distribution functions is good, apart from the regions close to $\theta_0 = 0^\circ$ and $\theta_0 = 90^\circ$. We conclude, therefore, that the δ function line shape is a reasonably accurate approximation for this system.

The line shape analysis provides information about the director distribution functions as well as about the molecular order parameter. In Figure 6 we show the temperature dependence of benzene order parameter in the columnar phase derived from the carbon-13 NMR spectra. Note that identical values of the order parameter were obtained for cooling and heating spectra, which is reflected in identical widths of the

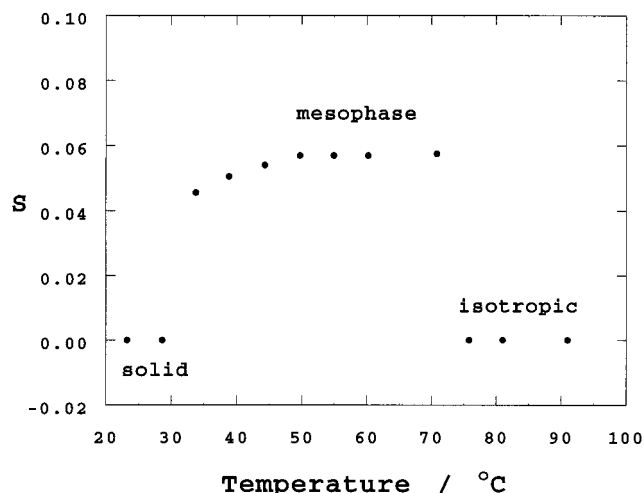


Figure 6. Temperature dependence of the order parameter, S , for benzene dissolved in Cel-II-10.

line shapes. The temperature dependence of the order parameter in the mesophase is weak which is expected from the spectra in Figure 2. The positive orientational order parameter that increases with increased temperature is not what we normally would expect. The observation of $S > 0$ in a columnar phase, where solute molecules are intercalated within mesogenic cores, is clearly expected, since the symmetry axis of the disk is, on average, aligned parallel to the column axis and hence to the director. The increase of the order parameter upon heating cannot reflect the behavior of the mesophase, and therefore a physical model for interpretation of such a trend is required. In several investigations of columnar phases, deuterated benzene has been used as a probe molecule.^{10,12,18,19} In all these studies, an increase of the quadrupolar splitting was observed. This increase was explained using a simple two-site exchange model. Benzene molecules were assumed to undergo a fast (on the NMR time scale) exchange process between two inequivalent sites: one where the molecules are intercalated within the columnar cores (site 1) and the other where they reside in the disordered region of the aliphatic chains (site 2). In this model, the averaged (observed) order parameter is given by

$$S = p_1 S_1 + p_2 S_2 \quad (11)$$

where p_i and S_i are the fractional populations and the order parameters of the two sites, respectively. We use the two-site model with two additional assumptions: (i) intercalated molecules are assumed to orient parallel to mesogen molecules within the columns ($S_1 > 0$) and (ii) the order parameters S_1 and S_2 are essentially constant within the investigated temperature interval. Thus, the temperature dependence of S is mainly determined by the population ratio, p_1/p_2 . Since the order parameter increases with increased temperature we conclude that the most ordered site (p_1) becomes more populated. Defining the equilibrium constant as $K = p_1/p_2$, the temperature dependence of the exchange process is governed by $d \ln K/dT = \Delta H^\circ/RT^2$, where ΔH° is the enthalpy difference ($H_1^\circ - H_2^\circ$) referring to the two sites. Obviously, ΔH° is positive which in turn indicates that intercalation of benzene molecules within the columns is an energetically less favored process. A possible explanation is that benzene interacts more favorably with the aliphatic chains compared to the polar carbohydrate core of the mesogen. Such a trend is in qualitative agreement with experimental solubility data²⁰ of benzene in dodecane and in dodecanol.

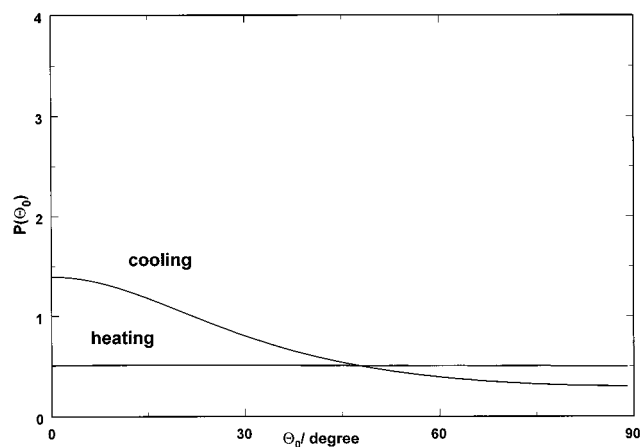


Figure 7. The director distribution functions derived from carbon-13 NMR spectra (not shown; $T = 55\text{ }^{\circ}\text{C}$) at 4.7 T. The following values of the c parameters were used: 0.51 for cooling and 0.0075 for heating.

We also note that the magnitude of the order parameter in the columnar phase is significantly smaller compared to the values in a nematic phase.²¹ This observation is surprising, since columnar phases usually show a much higher orientational order than nematic liquid crystals. It gives additional support to the exchange model where an averaging between sites with high- and low-order parameters, or perhaps with order parameters having different signs, results in a low observed order parameter.

Before closing this section we comment on the effect of magnetic field strength on the alignment of the liquid crystal. Carbon-13 NMR spectra were also recorded in a 4.7 T magnet (not shown). The overall width of these line shapes is only half of that observed in the higher field, which simply reflects the linear relationship between the Larmor frequency and B_0 in eq 1. But more importantly, the degree of director alignment is much lower at 4.7 T than at 9.4 T. The director distribution functions corresponding to experimental spectra are shown in Figure 7. The distribution corresponding to the cooling process shows a weak preference to align parallel to the field whereas no such alignment is observed in the heating process, resulting in a completely isotropic distribution. Note that the values of the c parameter (eq 10) used in the simulations deviate significantly from those used in the simulations of the 9.4 T line shapes (Figure 4). This is not surprising since the magnetic torque acting on a liquid crystal is proportional to the square of the magnetic field strength.²² The theoretical ratio between the c values at the two fields is 4, while the experimental value determined upon cooling is 2.0. In fact, a similar ratio (2.3) was obtained from deuterium spectra.¹² It was already pointed out that c depends on, in addition to the field strength, the thermal history of the sample. We do not, however, have any model to quantitatively account for the latter effect and refrain therefore from further analysis.

Conclusions

We have performed a natural abundance carbon-13 NMR study of benzene dissolved in a columnar liquid crystal formed by octa-*O*-decanoyl- β -cellobiose (Cel-II-10). The alignment of the columnar directors was studied as a function of thermal history and of the magnetic field strength. Both parameters have significant influence on the macroscopic orientation. In contrast

to most columnar phases formed by disc-like molecules, the columns of Cel-II-10 align parallel to the field, indicating a positive value of the anisotropic diamagnetic susceptibility.

The director distribution functions were determined from carbon-13 line shapes employing two different procedures: (i) directly from the spectra and (ii) performing line shape simulations. In the latter procedure a continuous function for the director distribution was used. The general features of distribution functions determined directly from the spectra were similar to those obtained in the simulation procedure.

A carbon-13 NMR spectrum provides both the sign and the magnitude of the molecular order parameter, S . An increase of S was observed when the sample was heated. Usually, we expect the orientational order of mesophases to decrease with increased temperature. A possible explanation for the anomalous trend for the solute is provided by invoking an exchange model between several sites. The observed trend would correspond to a situation where the more ordered site becomes more populated with increased temperature. The temperature dependence of the order parameter in Cel-II-10 is very weak, so we refrain from further speculations on solvation sites for benzene molecules and on possible exchange mechanisms. In the near future we plan to investigate solvation sites in a columnar liquid crystal where the order parameter of the solute shows a much stronger temperature dependence.

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References and Notes

- (1) Jeffrey, G. A. *Mol. Cryst. Liq. Cryst.* **1984**, *110*, 221.
- (2) Jeffrey, G. A. *Acc. Chem. Res.* **1986**, *19*, 168.
- (3) Jeffrey, G. A.; Wingert, L. M. *Liq. Cryst.* **1992**, *12*, 179.
- (4) Emsley, J. W., Ed. *Nuclear Magnetic Resonance of Liquid Crystals*; Reidel: Dordrecht, 1985.
- (5) Dong, R. Y. *Nuclear Magnetic Resonance of Liquid Crystals*; Charvolin, J., Lam, L., Eds.; Springer: New York, 1994.
- (6) Rutar, V.; Blinc, R.; Vilfan, M.; Zann, A.; Dubois, J. C. *J. Phys.* **1982**, *43*, 761.
- (7) Sandström, D.; Levitt, M. H. *J. Am. Chem. Soc.* **1996**, *118*, 6966.
- (8) Tarroni, R.; Zannoni, C. *J. Phys. Chem.* **1996**, *100*, 17157.
- (9) Henriksson, U.; Klason, T. *Finn. Chem. Lett.* **1982**, 139.
- (10) Sandström, D.; Nygren, M.; Zimmermann, H.; Maliniak, A. *J. Phys. Chem.* **1995**, *99*, 6661.
- (11) Maliniak, A.; Greenbaum, S.; Poupko, R.; Zimmermann, H.; Luz, Z. *J. Phys. Chem.* **1993**, *97*, 4832.
- (12) Sandström, D.; Stenutz, R.; Widmalm, G.; Maliniak, A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 111.
- (13) Mehring, M. *Principles of High Resolution NMR in Solids*; Springer-Verlag: Berlin, 1983.
- (14) Itoh, T.; Takada, A.; Fukuda, T.; Miyamoto, T.; Yakoh, Y.; Watanabe, J. *Liq. Cryst.* **1991**, *9*, 221.
- (15) Shaka, A. J.; Keeler, J.; Freeman, R. *J. Magn. Reson.* **1983**, *53*, 313.
- (16) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319.
- (17) Fan, S. M.; Luckhurst, G. R.; Picken, S. J. *J. Chem. Phys.* **1994**, *101*, 3255.
- (18) Goldfarb, D.; Luz, Z.; Zimmermann, H. *J. Phys.* **1982**, *43*, 421.
- (19) Goldfarb, D.; Luz, Z.; Zimmermann, H. *J. Phys.* **1982**, *43*, 1255.
- (20) *Landolt-Börnstein, Zahlenwerte und Funktionen*; Springer-Verlag: West Berlin, 1964.
- (21) Sandström, D.; Komolkin, A. V.; Maliniak, A. *J. Chem. Phys.* **1996**, *104*, 9620.
- (22) de Gennes, P. G.; Prost, J. *The Physics of Liquid Crystals*; Clarendon Press: Oxford, 1993.