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Deuterium NMR Investigation of a Discotic Mesogen Based on Hexasubstituted Truxene

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We report a ^2H nuclear magnetic resonance (NMR) investigation of 2,3,7,8,12,13-hexakis(octadecanoyloxy)-truxene (TxHA17) specifically labeled in the α -position of the alkyl chain. Results from these measurements, together with polarizing microscopy, show that the substance is in a crystalline state up to 90 °C. At this temperature the compound melts and a uniaxial discotic mesophase appears. The liquid crystalline phase persists until the clearing point at 191 °C. The differential scanning calorimetry thermograms confirmed these transitions but exhibited additional peaks below 90 °C. The phase behavior at low temperatures (<90 °C) differs significantly from previous reports by Warmerdam *et al.* (*Liq. Cryst.* **1988**, *3*, 149 and 1087). Solid-state deuterium line shape simulations were used to examine the motions of the labeled methylene site. A Gaussian libration model gave excellent agreement between experimental and calculated ^2H NMR spectra. A pronounced spatial inhomogeneity of the motion was found in the high-temperature region of the solid phases. By combining line shape simulations with nuclear spin relaxation measurements, mean correlation times for the α -site could be estimated. It was shown that there exist, even at -100 °C, fast motions of the α -deuterons with rates relatively close to the Larmor frequency. Deuterium NMR spectra of benzene- d_6 dissolved in protonated TxHA17 are also reported. These spectra were interpreted using a model in which the benzene molecules occupy two solvation sites: (i) intercalated within the columns of TxHA17 and (ii) dissolved in the aliphatic chains. The exchange of C_6D_6 between the two sites is slow on the NMR time scale in the crystalline phase whereas it is fast in the mesophase.

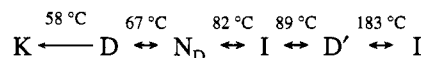
Introduction

Nuclear magnetic resonance (NMR) spectroscopy is a powerful experimental tool for studies of solid and liquid crystalline phases. In particular, deuterium NMR has extensively been used for investigations of the nature and degree of macroscopic order. A careful analysis of ^2H NMR line shapes can, under favorable conditions, provide detailed information about the rate and geometry of molecular motions. If, however, the dynamic processes occur on a time scale which is short compared to the inverse of the quadrupole coupling constant, the dynamical information is lost and the ^2H line shape only provides spatial information of the motion. In this fast exchange regime, nuclear spin relaxation can be used for investigations of various motional processes and of their characteristic rates.

Several investigations of discotic liquid crystals using ^2H NMR can be found in the literature.^{3–6} Discotic molecules usually consist of a rigid aromatic core with symmetrically attached aliphatic chains. Most of the mesophases formed by these molecules show an architecture where the molecules are stacked into columns which in turn form two-dimensional arrays with various symmetries. Nematic phases have also been observed for some of the discotic compounds.^{7–9} The mesomorphic properties of these systems are strongly dependent on the molecular structure. Accordingly, both the size of the aromatic core and the length of the alkyl chains are crucial for the temperature range of the liquid crystalline phases. In addition, the type of linkage between these two molecular fragments is of significant importance.

In this article we report a ^2H NMR investigation of the solid and liquid crystalline phases of 2,3,7,8,12,13-hexakis(octadecanoyloxy)truxene (TxHA17), see Figure 1. It has been observed⁹ that the temperature range of the mesomorphic region in discotic systems usually increases with increasing size of the aromatic core. The truxene core is relatively large, and therefore the homologous series of truxenealkanoates exhibits rich polymorphism which includes normal, inverted, and re-entrant sequences of nematic and columnar phases. This polymorphism has been investigated by X-ray, optical, and thermodynamical methods.^{9–12} A ^2H NMR study of the polymorphic behavior was previously performed¹³ using a probe molecule (benzene- d_6) dissolved in the mesophases of TxHA11–14.

The present work was motivated by the unusual phase behavior of TxHA17 reported by Warmerdam *et al.*¹ The phase diagram of TxHA17 was determined using polarizing microscopy and refractive index measurements, and the following phase transitions were observed:



where K denotes a solid phase, D and D' are two columnar phases, N_D is a nematic discotic phase, and I denotes isotropic phases. The mesogen was further studied in an extended investigation² where small-angle X-ray scattering, calorimetric, and elastic constant measurements were performed. The latter examination showed that the phase diagram was somewhat more complicated than initially believed, leading to difficulties in establishing an unambiguous phase sequence. To our knowledge this is the first example of a one-component system which is claimed to exhibit a re-entrant isotropic phase. Such anomalous behavior has previously been reported for a mixture of two discotic compounds.¹² Several observations¹

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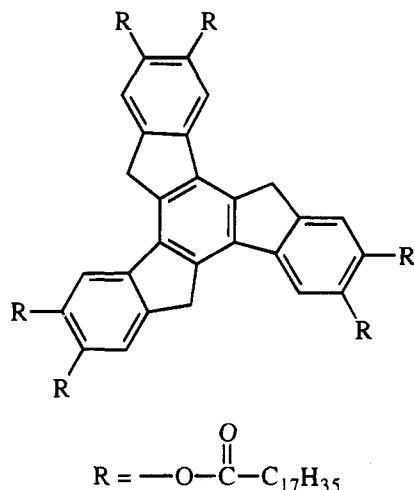


Figure 1. Chemical structure of 2,3,7,8,12,13-hexakis(octadecanoyloxy)truxene (TxHA17).

indicated that the re-entrant isotropic phase indeed was a normal isotropic liquid; a cubic structure could however not be completely ruled out. In addition to the unusual re-entrant isotropic phase in TxHA17, the columnar-nematic sequence is inverted. That is, a nematic phase exists at temperatures below those for the columnar phase.

The TxHA17 compound used in the present investigation was specifically deuterium labeled in the α -position of the alkyl chain. In general, the ^2H NMR line shape of a methylene segment in a discotic liquid crystal is affected by several types of molecular motions and sometimes becomes quite complex. In particular, these dynamic processes may involve fast internal motions in the aliphatic chain, relatively slow overall reorientation of the molecule, and possibly an intermediate process connected with the flexibility of the linkage group.¹⁴ The onset of these motions is usually correlated with macroscopic phase transitions. We can therefore monitor the effects of various dynamic processes (and phase transitions) on the ^2H line shape and *via* the nuclear spin relaxation times. The measurements were performed over a wide temperature range (-100 to 140 $^{\circ}\text{C}$), covering all phases according to the sequence shown above, except for the high-temperature isotropic phase. Similar analyses of the segmental dynamics in the solid-state of Nylon 66¹⁵ and in polymeric discotic mesophases⁵ have been reported recently.

Another possibility to examine the phase transitions is to study their effect on a probe molecule dissolved in the liquid crystal. Investigations of probe molecules also provide information about molecular ordering and possible solvation sites. The environment of the solute molecule is clearly different (and hence the NMR spectrum) when intercalated within the columnar structure as compared to when dissolved in the aliphatic part of mesogens, i.e. between the columns. In this investigation we have dissolved C_6D_6 in TxHA17 in order to examine the phase sequence, solvation sites, and macroscopic orientational order.

In section A we present the line shape simulations and the obtained differential scanning calorimetry (DSC) thermograms. In section B we analyze ^2H spin relaxation measurements and calculate correlation times. Section C deals with probe molecule studies, and the last part, section D, is devoted to a more detailed discussion of phase transitions and of the DSC results.

Experimental Section

Synthesis. The fully protonated and specifically deuterated compounds (TxHA17 and TxHA17- α - d_2) were prepared according to previously published procedures.^{16,17}

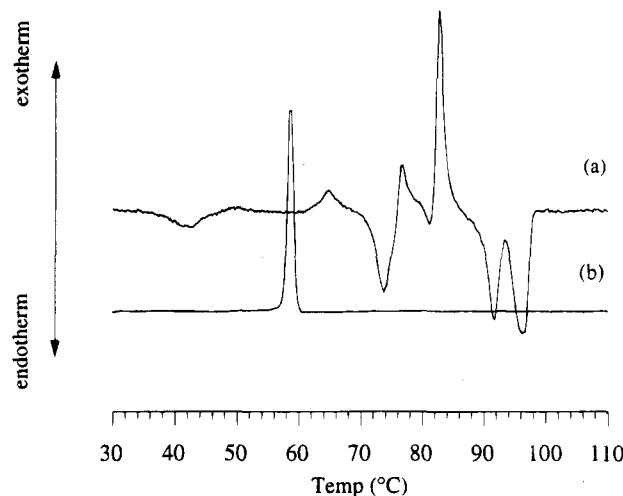


Figure 2. Differential scanning calorimetry thermograms of TxHA17- α - d_2 recorded upon (a) heating and (b) cooling. The high-temperature transition peak at 191 $^{\circ}\text{C}$ observed when heating the sample is not shown. The sample was heated to 250 $^{\circ}\text{C}$ and then cooled to -25 $^{\circ}\text{C}$ before the curves in the figure were recorded. The heating and cooling rates were 1.25 and 2.5 K/min , respectively.

Thermal Analysis. Transition temperatures were determined by differential scanning calorimetry, using a Perkin-Elmer DSC-2C instrument.

^2H NMR Measurements of TxHA17- α - d_2 . All NMR experiments were performed on a Bruker MSL200 spectrometer operating at a magnetic field strength of 4.7 T. A high-power probe was used with a 5 mm horizontal solenoid coil. The ^2H NMR spectra were obtained by the quadrupole echo sequence $90_x^\circ - t_1 - 90_{\pm y}^\circ - t_2 - \text{acq}$ with a 90° pulse length of 2.2 μs and a recycle delay of at least five times the spin-lattice relaxation time. The echo delay, t_1 , was set to 20 μs , and t_2 was carefully chosen such that the first point of the free induction decay (FID) was digitized at the spin echo maximum. Typically, $10\,000$ transients were accumulated for the full width (~ 250 kHz) ^2H spectra. The ^2H spin-lattice relaxation rates, T_1^{-1} , were measured by the standard inversion recovery technique using quadrupole echo for signal detection. The ^2H spin-spin relaxation rates, T_2^{-1} , were determined by measuring the signal intensity as a function of t_1 in the quadrupole echo. Reported nuclear spin relaxation times are averages of at least two measurements. On the basis of reproducibility, the random error in this experimental data set is estimated to be on the order of 10% . The temperature was controlled with a Bruker B-VT 1000E unit and was calibrated with a Testo Term 9000 digital thermometer (estimated accuracy ± 1 $^{\circ}\text{C}$).

^2H NMR Measurements of C_6D_6 Dissolved in TxHA17.

A solution of benzene- d_6 in fully protonated TxHA17 was prepared by adding a weighted amount of C_6D_6 into a known quantity of the mesogen, which resulted in a concentration of 5.1 wt %. The deuterated solute molecule was purchased from Merck and used without further purification. The ^2H NMR spectra were recorded using a high-resolution probe in order to increase the sensitivity. The quadrupole echo was employed with a 90° pulse width of 6.7 μs .

Results and Discussion

A. DSC Thermograms and Analysis of Deuterium NMR Line Shapes in TxHA17- α - d_2 . The DSC curves of TxHA17- α - d_2 are displayed in Figure 2. A detailed discussion of these calorimetric results will be presented at the end of the paper. However, some immediate remarks can be made. First, the heating curve, Figure 2a, shows very complex behavior with a

number of phase transitions, in contrast to the cooling diagram, Figure 2b, which only exhibits one transition. Second, the DSC measurements of the fully protonated sample gave the same results (within ± 1 °C) as the TxHA17- α - d_2 compound did. Small variations in transition temperatures between protonated and deuterated molecules may be ascribed to isotope effects.

In the left column of Figure 3 we show experimental ^2H NMR spectra of the α -deuterated mesogen as a function of temperature. At the lowest temperature (-102 °C) the spectrum resembles a powder pattern of a solid with a splitting of 120 kHz, which is typical for rigid, or at least motionally very restricted, deuterons in aliphatic chains. Already at -80 °C spectral narrowing of the line shape takes place. With increasing temperature, further motional narrowing is observed together with a pronounced intensity enhancement at the center of the spectra. Above 90 °C, the line shapes exhibit dramatic spectral narrowing, see Figure 4, with a quadrupolar splitting of only 13 kHz. It should be noted that the change in line shapes when going from -100 to 90 °C is *continuous*. No discontinuous behavior in either line shape nor line width could be detected (we recorded spectra at intervals of 3 °C between 60 and 90 °C). This is even more obvious if the total line width is plotted as a function of the temperature; see Figure 5. The main feature in this figure is the conspicuous drop in line width at 90 °C. This is indeed a rather remarkable result; none of the phase transitions observed in the DSC measurements (cf. Figure 2) are visible in the ^2H NMR spectra except the one at 90 °C. It must however be remembered that motions with rates much slower than the quadrupolar coupling constant ($\nu_{\text{motion}} \ll \nu_Q = e^2qQ/h \approx 10^5 \text{ s}^{-1}$) do not lead to motional narrowing.

The previously reported phase diagram^{1,2} contains two columnar phases, one nematic phase, and one re-entrant isotropic phase below the clearing point at 183 °C. A very characteristic motional process observed in discotic liquid crystalline phases (both columnar and nematic) is fast rotation of mesogens around the molecular symmetry axis.¹⁸ This semiplanar motion leads to substantial line width reduction of α -deuterons.^{19,20} No such reduction in line width could be observed in our case except at 90 °C. The line shape of an isotropic liquid is even more characteristic, since it only consists of a narrow peak due to complete averaging of the quadrupolar interaction. Consequently, we cannot, on the NMR time scale, observe any core rotation below 90 °C. Above this temperature, the line shapes exhibit dramatic spectral narrowing, which we interpret as an onset of fast reorientation of the molecule around the core symmetry axis. These results rule out mesophases and isotropic phases below 90 °C and indicate a liquid crystalline phase above the transition temperature. The deuterium NMR spectra in Figure 4 are typical for a uniaxial mesophase. This is consistent with preliminary X-ray diffraction studies,² where the liquid crystalline phase was reported to be a hexagonal, disordered (D_{hd}) phase which indeed has uniaxial symmetry. The only transitions below 90 °C that are consistent with our ^2H NMR data are solid–solid transitions which do not affect the α -site. Such solid–state polymorphism has been interpreted as a gradual melting of the side chains.^{19,21}

Note that the mesophase of TxHA17 is not aligned by the magnetic field and a partially averaged powder pattern is therefore observed (cf. Figure 4). Columnar phases of truxene and triphenylene derivatives with shorter chains are usually oriented by the field of the NMR spectrometer.⁶ The liquid crystalline directors are then distributed in a plane perpendicular to the field direction. Such a distribution is due to the fact that the net anisotropic magnetic susceptibility of discotic phases is negative, which in turn is an effect of the strongly negative

contribution of the aromatic core. When the chain length is increased, the positive contribution from the aliphatic part may result in a very small net magnetic susceptibility of the phase and therefore no orientation in the field. There is probably also another explanation of the isotropic distribution of the TxHA17 domains. The alignment of columnar mesophases in the magnetic field usually takes place when the sample is slowly cooled from a nonviscous phase (isotropic or nematic). Due to probehead material limitations, we were not able to heat the sample into the isotropic phase within the spectrometer and could consequently not test whether or not the liquid crystalline phase orients by a slow cooling procedure.

After heating the sample to 140 °C, we recorded ^2H NMR spectra as a function of temperature upon cooling. The results were in agreement with the DSC thermogram in Figure 2b. Above 60 °C the line width remained close to 14 kHz (cf. Figure 5). A phase transition occurred around 60 °C which resulted in a spectral broadening to 115 kHz. The spectra obtained when cooling the compound were identical to those observed upon heating.

In order to extract quantitative information about the dynamic process of the specifically labeled methylene segment, line shape simulations have been performed in the temperature range -100 to 90 °C. From now on, phases occurring in this interval will be referred to as solids. General procedures for ^2H NMR line shape calculations have been described by others²² and will only briefly be commented on here.

No significant T_2 anisotropy²³ could be observed when t_1 in the quadrupole echo was varied. The absence of T_2 distortion in the entire temperature range indicates that the motion is rapid compared to the quadrupolar coupling constant ($\nu_{\text{motion}} > 10^7 \text{ s}^{-1}$). This will later be confirmed by the measured spin–lattice relaxation rates discussed in section B. The spectral line shape problem is particularly simple in this fast motion limit; the calculated powder spectrum depends only on the partially averaged quadrupolar coupling constant $\bar{\nu}_Q$ and the asymmetry parameter $\bar{\eta}$. The ^2H NMR frequency is then given by

$$\nu = \nu_0 \pm \frac{3}{8} \bar{\nu}_Q (3 \cos^2 \Theta - 1 + \bar{\eta} \sin^2 \Theta \cos 2\Phi) \quad (1)$$

where the Euler angles Θ and Φ specify the orientation of the averaged electric field gradient (EFG) tensor with respect to the laboratory frame. If the dynamic process can be described by a single trajectory of motion, the line shape contains well-defined singularities²⁴ and $\bar{\nu}_Q$ and $\bar{\eta}$ can immediately be extracted from the experimental powder spectrum. However, when the NMR spectrum does not exhibit these characteristic singularities, an inhomogeneous distribution of motional amplitudes must be invoked.²⁵

The line shapes shown in Figure 3 do not correspond to well-defined values of $\bar{\nu}_Q$ and $\bar{\eta}$. This is most obvious for the spectra recorded above 0 °C. Similar line shapes have been observed in various polymeric phases.^{5,15} In these investigations a Gaussian libration model was applied, and we will use the same model here. Specifically, the α -deuterons are assumed to execute fast torsional oscillations about the bond connecting the carboxyl carbon and the α -carbon. As mentioned above, these oscillations will be described by a Gaussian of standard deviation $\Delta\theta$. Moreover, in order to account for the smeared-out singularities in the observed line shapes, an inhomogeneous distribution of librational amplitudes $P(\Delta\theta)$ was considered. Following English and colleagues,^{15,26} we describe $P(\Delta\theta)$ as a Gaussian distribution of standard deviation $\Delta(\Delta\theta)$ with a low-angle cutoff.

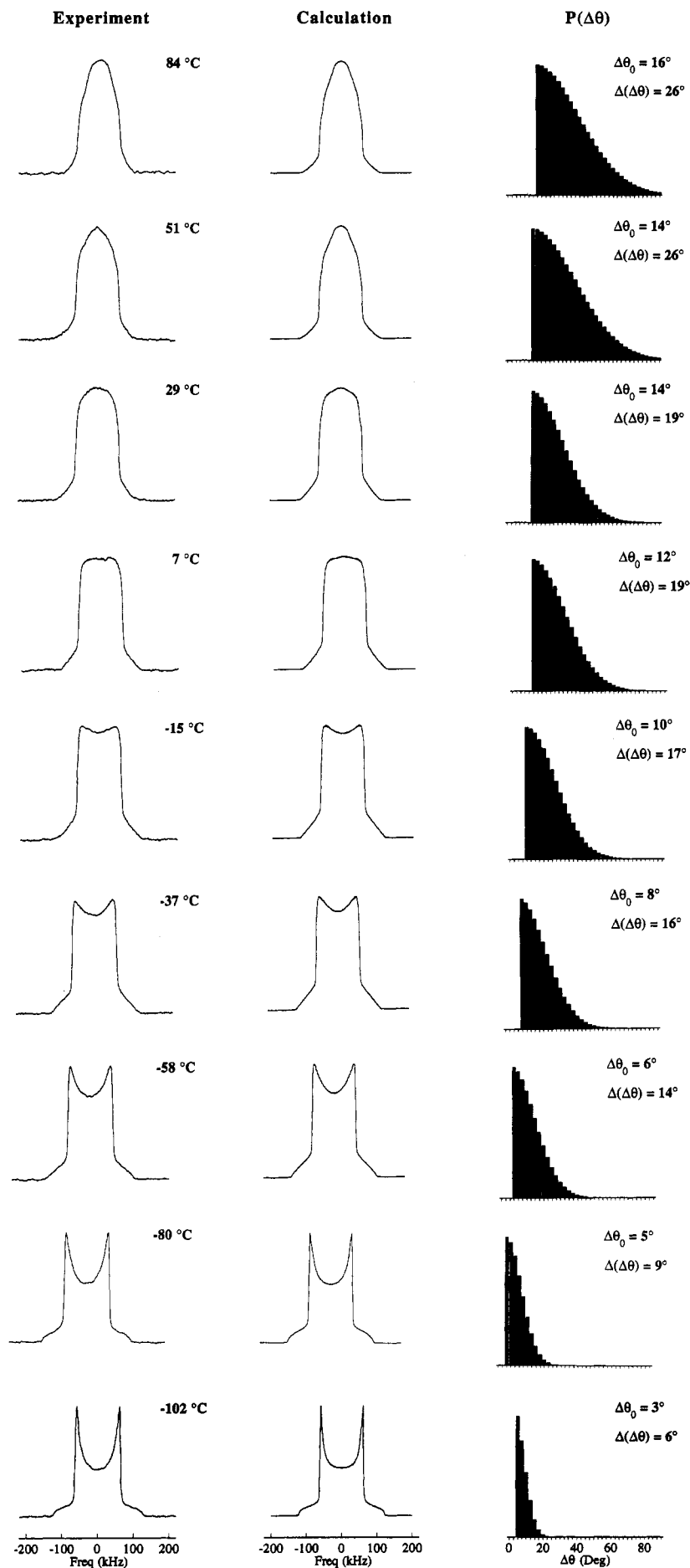


Figure 3. Experimental and calculated ^2H NMR line shapes of TxHA17- α - d_2 . The distributions of standard deviations together with the corresponding parameters are shown in the right column. All experimental ^2H NMR spectra in the figure were recorded upon heating.

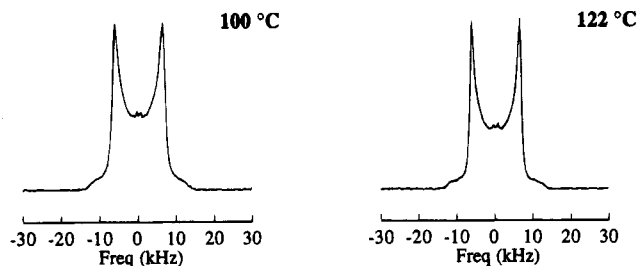


Figure 4. Experimental high-temperature ^2H NMR spectra of TxHA17- α - d_2 obtained when the compound was heated. Notice the difference in frequency scale between this figure and Figure 3.

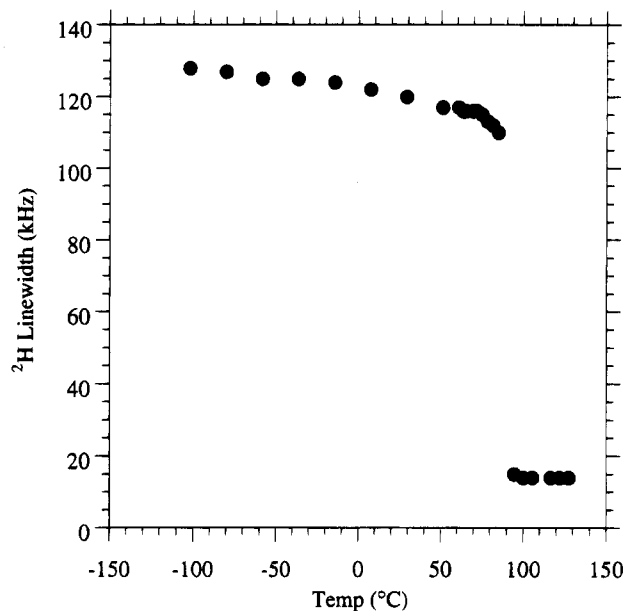


Figure 5. Line width at half-height of ^2H NMR spectra as a function of temperature for TxHA17- α - d_2 . The measurements were performed upon heating.

In the middle and right columns of Figure 3 we show calculated ^2H NMR line shapes and the corresponding $P(\Delta\theta)$ distributions. The following parameters were used in the simulations: $\nu_Q = 165$ kHz, $T_2^{-1} = 1$ kHz, $\beta = 109.5^\circ$, and $\eta = 0$ where β is the tetrahedral angle between the $\text{C}_{\text{carboxyl}}-\text{C}_\alpha$ axis and the C-D vector and η is the asymmetry parameter of the static EFG tensor. All calculated spectra were corrected for finite pulse length.²⁷ The inhomogeneous distribution of librational amplitudes was truncated at $\Delta\theta_0$, producing a half-Gaussian. Both $\Delta\theta_0$ and the standard deviation of $P(\Delta\theta)$ are given in Figure 3. At the lowest temperature $P(\Delta\theta)$ is narrow and $\Delta\theta_0$ is small, indicating highly restricted motions of the α -deuterons. With increasing temperature the width of $P(\Delta\theta)$ grows and $\Delta\theta_0$ increases due to enhanced mobility of the C-D vectors. Above 50 $^\circ\text{C}$, a substantial fraction of the labeled methylene segments undergo large angle librations with amplitudes exceeding $\pm 45^\circ$. The $P(\Delta\theta)$ distributions clearly demonstrate that different α -sites have very different mobility. It is this spatial inhomogeneity of the motion which is responsible for the lack of singularities in the ^2H NMR line shapes. The agreement between experimental and calculated spectra is excellent. It should however be noted that the inhomogeneous distributions shown in Figure 3 are not completely unique. Different combinations of $\Delta(\Delta\theta)$ and $\Delta\theta_0$ were sometimes found to produce essentially identical line shapes. We estimate the accuracy of both parameters to be $\pm 2^\circ$.

Our model describing the reorientation of the α -methylene sites assumes a rigid carboxyl linkage. It has been shown in similar compounds¹⁹ that the carboxyl group is fixed in solid

phases. On the other hand, this is not necessarily true in mesophases of discotic molecules.¹⁴

B. Deuterium Nuclear Spin Relaxation in TxHA17- α - d_2 .

The line shape simulations presented in the previous section were performed assuming that the fast exchange limit was reached. This assumption was based on the absence of T_2 anisotropy when the quadrupole echo delay, t_1 , was varied. The ^2H NMR spectra in this motional regime are insensitive to the time scale of the reorientation, and we can only obtain geometrical information, i.e. amplitudes of the motion. However, by measuring nuclear spin relaxation rates, dynamical information is recovered and correlation times can be calculated. The relaxation times are sensitive to both the rate ν_{motion} and amplitude of the motion. Hence, relaxation measurements must be combined with line shape simulations in order to determine ν_{motion} .

The ^2H spin-lattice relaxation rate is given by²⁸

$$T_1^{-1} = \frac{3\pi^2}{4} \nu_Q^2 [J_1(\omega) + 4J_2(2\omega)] \quad (2)$$

The spectral density functions in eq 2 are defined as

$$J_m(\omega) = 2 \int_0^\infty C_m(t) \cos(\omega t) dt \quad (3)$$

where $C_m(t)$ is the time correlation function. In general, $C_m(t)$ for solids varies as a function of crystal orientation, which results in anisotropic T_1 relaxation.^{28,29} However, since T_1^{-1} is a linear combination of $J_1(\omega)$ and $J_2(2\omega)$, which have different orientation dependencies, the anisotropy of T_1 is often weak. Only minor effects of orientation dependence in the inversion recovery experiment were observed. We will therefore perform an angular independent analysis of the spin-lattice relaxation by calculating the powder average of the time correlation function. This is done by integrating $C_m(t)$ over all possible crystallite orientations. If the time dependence of $C_m(t)$ is approximated by a single exponential term $\exp(-t/\tau)$, it can be shown¹⁵ that the powder-averaged time correlation function, $C_m^*(t)$, for a Gaussian libration follows the relation

$$C_m^*(t) = \frac{3}{20} [\sin^4 \beta (1 - \exp(-4\Delta\theta^2)) + 4 \cos^2 \beta \sin^2 \beta (1 - \exp(-\Delta\theta^2))] \exp(-t/\tau) \quad (4)$$

where β is a fixed angle between the reorientation axis and the C-D vector, $\Delta\theta$ is the standard deviation of the Gaussian libration, and τ is the correlation time. An axially symmetric electric field gradient tensor ($\eta = 0$) was assumed in the derivation of eq 4. Note that the maximum of the geometrical part of eq 4 is equal to $1/5$. By inserting this maximum value of the averaged time correlation function ($C_m^*(t) = 1/5 \exp(-t/\tau)$) in eq 3, the spectral density function for an isotropic rotational small-step diffusion process³⁰ is obtained.

The experimental T_1 values are displayed in Figure 6. In the temperature range -100 to 90 $^\circ\text{C}$ the longitudinal relaxation times follow a continuous curve with a minimum close to -25 $^\circ\text{C}$. Above 90 $^\circ\text{C}$ the T_1 values suddenly drop to 15 ms and stay essentially constant up to 140 $^\circ\text{C}$. This further strengthens the proposed phase behavior of TxHA17 discussed in section A. Below 90 $^\circ\text{C}$ we have a continuous change in both line shapes and spin-lattice relaxation times, indicating a simple thermally activated process. At 90 $^\circ\text{C}$ a drastic line width reduction takes place (see Figure 5) together with a sudden shortening of T_1 . We believe that this discontinuous behavior is due to a phase transition from a solid to a liquid crystalline phase, accompanied by the onset of rapid rotation of the

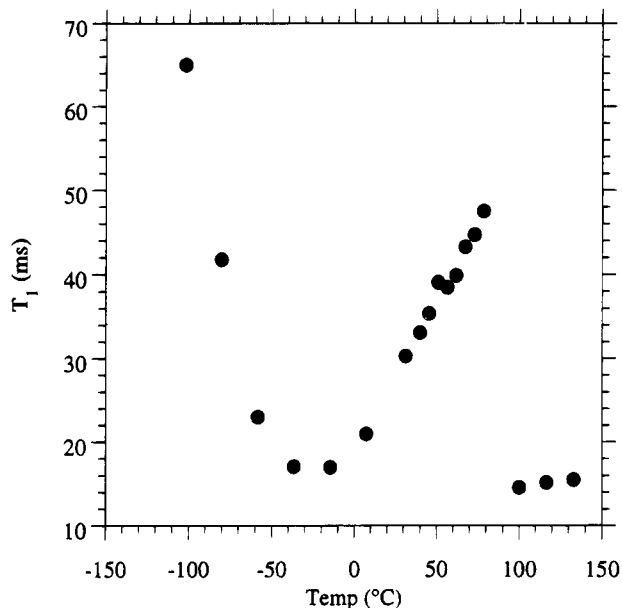


Figure 6. Temperature dependence of the α -deuteron spin-lattice relaxation times of TxHA17- α - d_2 recorded upon heating.

mesogenic core. For this reason we will restrict the relaxation data analysis to temperatures below 90 °C, where only one type of motion (torsional oscillations) is assumed to be present. In order to quantitatively interpret the spin-lattice relaxation above 90 °C, a much more complicated time correlation function than $C_m^*(t)$ given in eq 4 must be employed.

The very short T_1 relaxation times ($T_1 < 70$ ms) in Figure 6 show that there exists, even at the lowest temperatures, a rapid motion with a rate relatively close to the Larmor frequency.^{5,26} By combining the line shape calculations (i.e. the $P(\Delta\theta)$ distributions in Figure 3) with the T_1 measurements, it is possible to extract a mean correlation time τ for the local librational process. It must be realized that this τ is rather approximate due to the pronounced spatial inhomogeneity of the motion. In addition, the experimental error in T_1 and the nonunique nature of $P(\Delta\theta)$ both contribute to the uncertainty in τ . The calculated correlation times give nevertheless information about the time scale of the methylene oscillations. In Figure 7 we show the mean correlation times obtained from the ^2H spin-lattice relaxation rates. At the lowest temperature τ is close to 660 ps and decreases to 100 ps near the phase transition at 90 °C. This clearly demonstrates that $\nu_{\text{motion}} \gg \nu_Q$ in the entire investigated interval and hence that the fast motion limit treatment in section A was correct. Similar values of τ , describing the fast isomerization process of α -deuterons in benzene-hexa-*n*-hexanoate (BHA6), were found in a previous solid-state ^2H NMR investigation.¹⁹ It is also worth comparing our data obtained in the *solid* phase of TxHA17 with correlation times calculated from ^{13}C relaxation measurements¹⁴ in the *isotropic* phase of benzene-hexa-*n*-heptanoate (BHA7). There, τ for the local motion of the α -protons was estimated to be 100 ps at 95 °C. Accidentally, this happens to be the same value as we obtained at 85 °C (cf. Figure 7). We note that the isomerization of the α -segment is virtually independent of the aggregation state. Hence, this dynamical process can roughly be considered as an intramolecular property.

^2H spin-spin relaxation measurements have also been performed. In Figure 8 T_2 relaxation times are plotted as a function of temperature. Below 90 °C the transverse relaxation times are smaller than 400 μs , showing that the T_2 relaxation is completely dominated by dipole-dipole interactions with neighboring spins³¹ (both protons and deuterons). The T_2 values

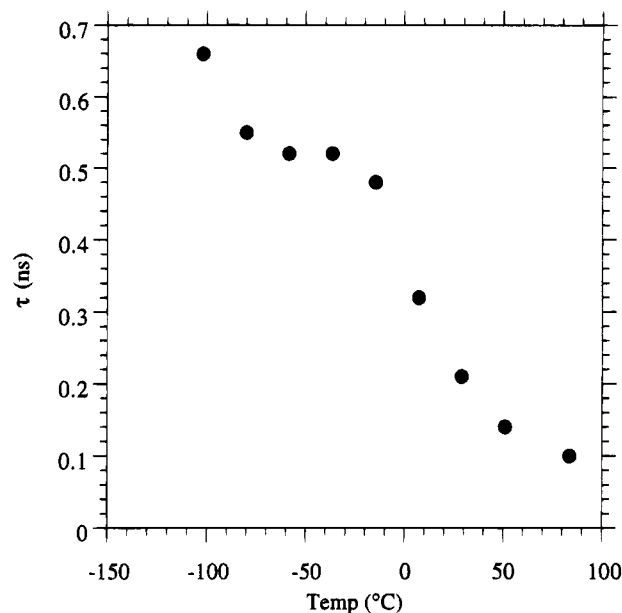


Figure 7. Temperature dependence of the mean correlation times for the librational process of the α -methylene segments of TxHA17- α - d_2 .

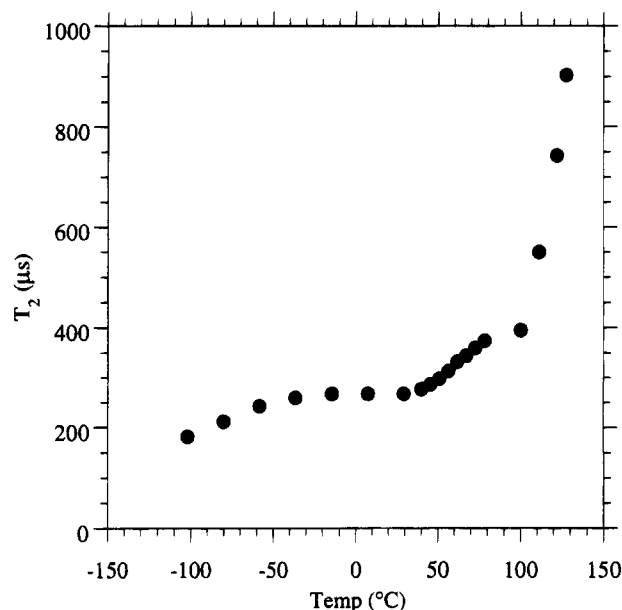


Figure 8. Temperature dependence of the α -deuteron spin-spin relaxation times of TxHA17- α - d_2 recorded upon heating.

do not exhibit any discontinuous jumps below 90 °C. Only a tiny hump around 40 °C is observed. It is tempting to correlate this hump with the broad peak at 43 °C in the DSC heating thermogram (see Figure 2a). Above the phase transition at 90 °C the T_2 curve raises very steeply, which we once again interpret as the onset of rapid core rotation.

C. Benzene- d_6 Dissolved in TxHA17. The temperature dependence of the ^2H NMR spectra of benzene- d_6 dissolved in fully protonated TxHA17 is shown in Figure 9. The line shape undergoes a clear change as a function of temperature, and three different types of spectra can be observed within the investigated interval.

At low temperatures (approximately below -5 °C) in the solid phase, a common feature for all spectra is that two components are observed: one narrow, nearly Lorentzian line shape (5–10 kHz) and one broad (~ 70 kHz) with a Pake doublet appearance. The first conclusion must therefore be that benzene molecules occupy two sites with clearly different environments. A two-

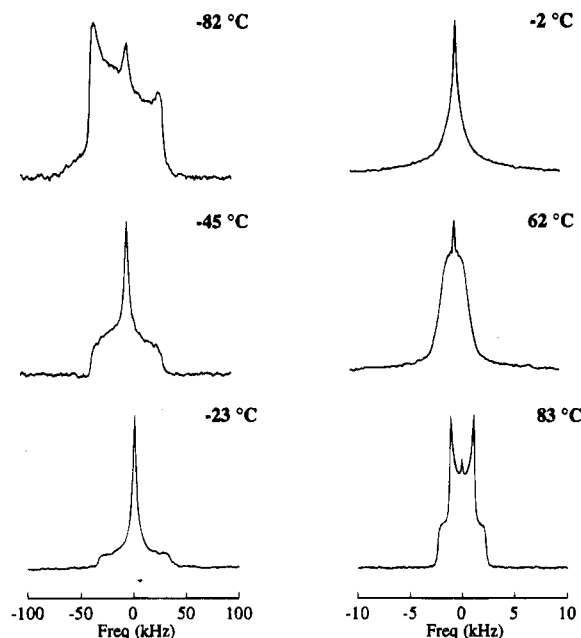


Figure 9. Experimental ^2H NMR spectra of C_6D_6 dissolved in TxHA17. Notice the difference in frequency scale between the two columns. The apparent spectral distortion in the -82°C trace is due to probe tuning problems at low temperatures. The sample was heated between subsequent measurements.

site model has previously been proposed for benzene dissolved in mesophases of other columnar discotic liquid crystals.^{32,33} However, in those investigations only the population-averaged signal was recorded. The fact that two subspectra can be observed shows that the exchange between the two sites is slow on the NMR time scale. The quadrupolar splitting, characteristic for ordered systems, is absent or very strongly reduced (smaller than the line width) in the narrow spectrum. This indicates a nearly isotropic environment with low ordering of benzene molecules which may correspond to solvation in the disordered aliphatic chains of the TxHA17 compound. The presence of isotropic liquid domains of C_6D_6 can be ruled out, since the melting point of benzene is 5°C . The quadrupolar splitting of the broad component is approximately 70 kHz, which is the expected value for an oriented benzene molecule undergoing fast reorientation about its C_6 -axis. The expression for this splitting is given by

$$\bar{\nu}_Q = \frac{3}{8} \nu_Q S_{ZZ} \quad (5)$$

where ν_Q is the static quadrupolar coupling constant ($\nu_Q \approx 183$ kHz for C_6D_6) and S_{ZZ} is the orientational order parameter related to the C_6 symmetry-axis. We may therefore conclude that the broad subspectrum is due to benzene molecules intercalated in the columns. Rotation around the C_6 -axis is relatively unrestricted in this site, whereas all other motions are strongly hindered. The width of the broad component is essentially constant up to 0°C , indicating that the benzene molecules are very well ordered within the columns with a molecular order parameter close to unity. Note that the outer wings are missing in the broad subspectrum. This is an effect of the relatively long 90° pulse used in the high-resolution probe (see the Experimental Section). The ratio between integrals of the narrow and broad components increases with increasing temperature. This behavior is expected in the two-site interpretation, since the entropy effect promotes the solvation of benzene molecules in the aliphatic region.

The intermediate temperature range is approximately between -5 and 80°C . In the low-temperature part of this interval, the

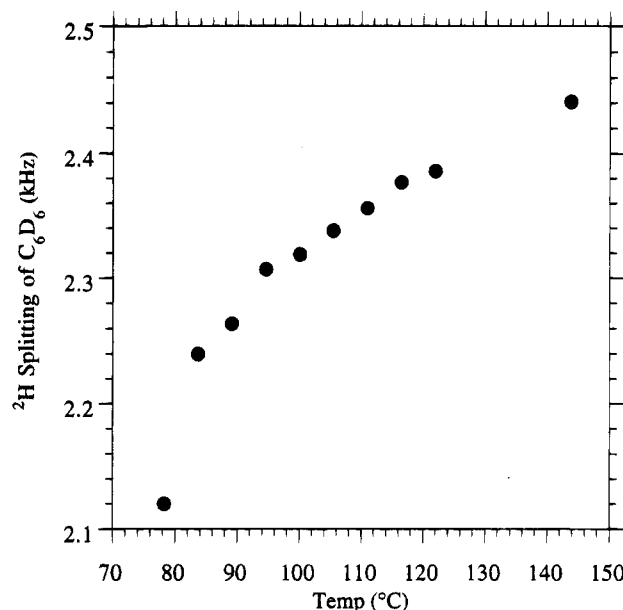


Figure 10. Temperature dependence of the ^2H quadrupolar splitting of C_6D_6 dissolved in TxHA17 recorded upon heating.

^2H NMR spectrum consists of a single, relatively sharp signal which essentially can be ascribed to isotropic domains (see the -2°C trace). This signal is broadened by the contribution from the benzene molecules in the aliphatic chains. At higher temperatures (cf. the 62°C trace) the signal from molecules dissolved in the aliphatic region dominates the spectrum. Furthermore, we observed that the change in the relative intensities of the two signals does not proceed smoothly as a function of temperature but occurs as a relatively sharp "transition" around 40°C . This "transition" may be related to the hump at 43°C in the DSC thermogram (Figure 2a) and the weak discontinuity in the spin-spin relaxation times (Figure 8). The broad component (~ 70 kHz, due to intercalated benzene molecules) is hidden in the baseline.

When the temperature is further increased (above 80°C), the liquid crystalline phase is entered and a typical motionally averaged Pake line shape of an unoriented, uniaxial liquid crystal is recorded. The sharp, small signal in the central part of the spectrum originates from isotropic domains. The transition to the liquid crystalline phase has been lowered some 10°C compared to that of pure TxHA17 (cf. previous sections). The temperature dependence of $\bar{\nu}_Q$ in the mesophase is displayed in Figure 10. In general, the quadrupolar splitting is expected to decrease with increasing temperature since $\bar{\nu}_Q$ is linearly related to the order parameter. However, in Figure 10 we note that the splitting increases with increasing temperature, indicating an exchange between two (or more) sites. In contrast to the low-temperature solid phase, the exchange is fast (on the NMR time scale) in the mesophase. Hence, only the population-averaged splitting is observed:^{32,33}

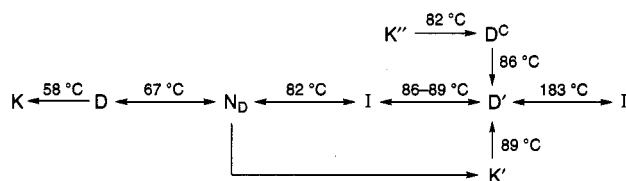
$$\bar{\nu}_Q = p_1 \bar{\nu}_Q^1 + p_2 \bar{\nu}_Q^2 \quad (6)$$

where p_i and $\bar{\nu}_Q^i$ are the fractional population and the averaged quadrupolar splitting of site i , respectively. Furthermore, the ratio p_1/p_2 is expected to be temperature dependent, which was clearly observed in the low-temperature phase. In analogy with that phase, we use the entropy argument and assume increasing population in the aliphatic region when the sample is heated. Since only the magnitude (and not the algebraic sign) of the splitting can be determined from the ^2H NMR spectrum, we may conclude that the splitting becomes more negative with

increased temperature and the order parameters in the two sites have opposite signs. This explanation requires the order parameter for C_6D_6 in the aliphatic region to be negative, implying that these benzene molecules are on average oriented perpendicularly to the truxene core. Such a conclusion is not obvious using molecular packing considerations, and it is difficult to provide a strong argument for this behavior. A similar increase of the quadrupolar splitting was reported³³ for benzene- d_6 dissolved in a hexagonal, ordered mesophase (D_{ho}). Because of the large number of parameters required for a meaningful physical picture and the weak temperature dependence, we are not able to perform any quantitative analysis of $\bar{\nu}_Q$ in the mesophase.

D. DSC Measurements and Phase Transitions. This section starts with a summary of previous studies of the TxHA17 phase diagram and then continues with a discussion of our results. Our aim is not to report a complete phase sequence but merely to compare results from various experimental methods and show the complexity of the problem.

We will start by discussing results presented in ref 2, where the following phase diagram was reported:



K, K', and K'' are crystalline phases, N_D is a nematic phase, D and D' are columnar phases, and I is isotropic liquid phases. D_c is an unidentified phase. This sequence is somewhat modified from the one reported in the first investigation¹ of TxHA17, which appeared as a preliminary communication. The transitions were observed using polarizing microscopy and DSC measurements. However, the two methods were not entirely consistent; some transitions visible in the microscope were absent in the DSC thermograms and *vice versa*. The phase diagram was also very dependent on the thermal history of the sample. When TxHA17 was annealed at 77 °C overnight, only one transition at 89 °C could be detected by DSC upon heating from room temperature. Furthermore, the DSC curves depended strongly on the heating rate. Some peaks appeared while other disappeared when the rate was increased from 1 to 10 K/min. Moreover, transition processes in the region 60–75 °C changed from exothermic to endothermic when the heating rate was increased. Polarizing microscopy sometimes revealed a slow crystallization of the nematic phase which resulted in a more stable phase K'. These observations taken together indicate that the reported phase sequence does not correspond to a true thermodynamic equilibrium situation. This conclusion is further supported by adiabatic calorimetry measurements,² which are performed under thermodynamic equilibrium conditions. There, only one phase transition at 89 °C occurred upon heating.

Below, we describe our experimental findings concerning phase transitions in TxHA17. First of all, we could not observe any indications of nematic or re-entrant isotropic phases. The 2H NMR results presented in sections A–C all point in the same direction; a transition from a crystalline phase to a columnar mesophase occurs at ~ 90 °C when the sample is heated. The reverse transition (mesophase to solid phase) upon cooling takes place at ~ 60 °C due to supercooling, but no new phases could be observed. Of course, the 2H NMR experiments on a α -labeled compound alone cannot tell whether one or several crystalline phases exist below the melting temperature. In order to study such presumptive solid-state polymorphism using 2H

NMR spectroscopy, one typically needs a set of molecules deuterated at different sites along the chains.^{19,21} We have also examined TxHA17- α - d_2 contained between two glass slides with a polarizing microscope. A typical texture of a crystalline phase was observed at room temperature. On heating the sample a columnar phase grew in at ~ 90 °C. The optical texture of this liquid crystalline phase did not change until the isotropic liquid phase was reached at ~ 190 °C. The transition temperature of the mesophase/solid phase was shifted to ~ 60 °C upon cooling. No indications of nematic or reentrant isotropic liquid phases could be detected. These experiments were repeated a number of times with reproducible results. The simplest explanation to the DSC heating curve in Figure 2a, consistent with NMR and microscopy data, would be that the complex behavior below 85 °C is due to transitions between different crystalline phases. At 89 °C, a transition to a mesophase begins which apparently proceeds in two steps. Upon cooling, we did not observe any changes in enthalpy except one exothermic crystallization effect at 60 °C (see Figure 2b). This agrees well with results from the 2H NMR and polarizing microscopy measurements. The cooling behavior is in accordance with previously reported² calorimetric studies of TxHA17. The DSC thermograms observed when the virgin sample was heated differed dramatically from subsequent ones. Only two endothermic transitions in the region 78–88 °C were detected. This is also in agreement with previous results.² Finally, we increased the DSC heating rate from 1 to 10 K/min but could not find any evidence of the rate dependence discussed in ref 2.

Summary and Conclusions

Motivated by the unusual, previously reported,^{1,2} phase diagram of 2,3,7,8,12,13-hexakis(octadecanoyloxy)truxene (TxHA17), we have performed a 2H NMR investigation of this discotic mesogen. In order to do so, a molecule specifically deuterium labeled at the α -position was synthesized. The very complex phase sequence was earlier claimed^{1,2} to exhibit an inverted (nematic-columnar) sequence and a re-entrant isotropic liquid phase between 82 and 89 °C.

In our 2H NMR studies, we could not find any indications of nematic or re-entrant isotropic phases. On the contrary, the 2H NMR line shapes changed in a continuous fashion in the region –100 to 90 °C. The reduction in line width was also small in this temperature interval. A drastic motional narrowing occurred at 90 °C, which resulted in a 14 kHz wide uniaxial 2H NMR spectrum (cf. Figure 4). The spectral narrowing was interpreted as an onset of fast core rotation, which indicates a phase transition from a crystalline phase to a uniaxial discotic mesophase. The observed uniaxiality is consistent with a preliminary X-ray study² where the mesophase was reported to be of hexagonal (D_{hd}) symmetry. Deuterium NMR line shape simulations were performed in the range –100 to 90 °C, which corresponds to one or several solid phases. At low temperatures the motions of the labeled methylene sites are highly restricted whereas at elevated temperatures these sites undergo large angle librations. Moreover, the motions could not be modeled using a single, well-defined dynamic process. By employing a Gaussian libration model, the α -site fluctuations and the extent of spatial inhomogeneity could be quantified.

Nuclear spin relaxation time (T_1 and T_2) measurements confirmed the phase sequence indicated by the 2H NMR spectra. Below 90 °C the T_1 and T_2 relaxation times follow continuous curves. A discontinuous change in these parameters occurs at 90 °C due to fast molecular reorientation. By combining spin-lattice relaxation time measurements with the results of the line shape analysis, we extracted mean correlation times τ for the

local libration process. The τ values were found to be approximately 700 ps at -100°C and decreased to 100 ps at 85°C .

We have also recorded ^2H NMR spectra of benzene- d_6 dissolved in TxHA17. Below 80°C the line shapes consist of two subspectra which we associate with benzene molecules intercalated within the columns of TxHA17 and with molecules dissolved in the side chains. The exchange between these sites was found to be slow on the NMR time scale. The relative populations of the two sites are temperature dependent, and the amount of C_6D_6 in the aliphatic region increased upon heating. This behavior can be explained using entropy arguments. Above 80°C the ^2H NMR spectrum undergoes a dramatic change due to a phase transition, and a partially averaged uniaxial powder spectrum is observed. The solute molecules occupy different solvation sites also in this phase. Here, however, the exchange is fast on the NMR time scale.

Summarizing, the ^2H NMR investigations have not shown any mesophases below 90°C . At 90°C a transition takes place which results in a uniaxial discotic liquid crystalline phase (this transition is shifted to 80°C in the $\text{C}_6\text{D}_6/\text{TxHA17}$ solution). This is the only clear phase transition we monitored between -100 and 140°C employing ^2H NMR. However, indications of a solid–solid transition at $\sim 40^\circ\text{C}$ were observed in the T_2 curve (see Figure 8) and in the C_6D_6 line shapes.

The TxHA17 molecule was also studied by polarizing microscopy and DSC measurements. The microscopy observations revealed only one change in optical texture (at 90°C), which is in agreement with the NMR results. The DSC heating thermogram is on the other hand very complex. In addition to the transition at 89°C , also observed in the NMR spectra and in the polarizing microscope, the DSC heating curve (see Figure 2a) exhibits a number of peaks at lower temperatures. One of them occurs at $\sim 40^\circ\text{C}$ and probably corresponds to the solid–solid transition discussed previously. The other peaks may be explained by a complex network of transitions between different crystalline phases.

All our experiments are consistent upon cooling; the ^2H NMR line shapes of TxHA17- α - d_2 , the polarizing microscopy measurements, and the DSC cooling curve all show one transition at $\sim 60^\circ\text{C}$.

Finally, we note that a possible explanation for the discrepancy between our results and previously published data^{1,2} concerning the phase sequence could be that a small amount of impurities is left from the synthesis. The difference in clearing points (183 and 191°C , respectively) further indicates that this is indeed the case.

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