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## Liquid Crystals

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# Enantiotropic nematic phases of quaternary ammonium halide salts based on trioctadecylamine

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The neat phases of a series of quaternary ammonium halides based on trioctadecylamine have been investigated by optical microscopy, differential scanning calorimetry, and <sup>2</sup>H NMR spectroscopy. Phase behaviour depends primarily on the structure of the fourth substituent on nitrogen and the thermal history of the samples. For instance, the iodide salts with methyl, ethyl, or propyl as the fourth substituent form enantiotropic *nematic* phases, while those with a proton or a longer alkyl substituent exhibit complex phase behaviour that does not include a liquid crystalline phase. Possible reasons are advanced for the unprecedented formation of nematic phases.

## 1. Introduction

When dissolved in appropriate liquids (usually water), quaternary ammonium salts are known to form many types of aggregates, including lyotropic liquid crystals, monolayers and bilayers [1, 2], branched threadlike micelles [3], and thermally reversible gels [4]. Recently thermotropic mesophase behaviour of quaternary ammonium salts [5–7] and biquaternary ammonium salts [8] with one or two long alkyl chains has been reported, and we have found that low concentrations of some quaternary ammonium salts with three or four long alkyl chains are capable of gelling a wide variety of organic liquids [9].

Unexpectedly, several of these gelators also form enantiotropic thermotropic *nematic* phases. Here, we characterize their mesophases using optical microscopy (OM), differential scanning calorimetry (DSC), and <sup>2</sup>H NMR spectroscopy.

## 2. Results

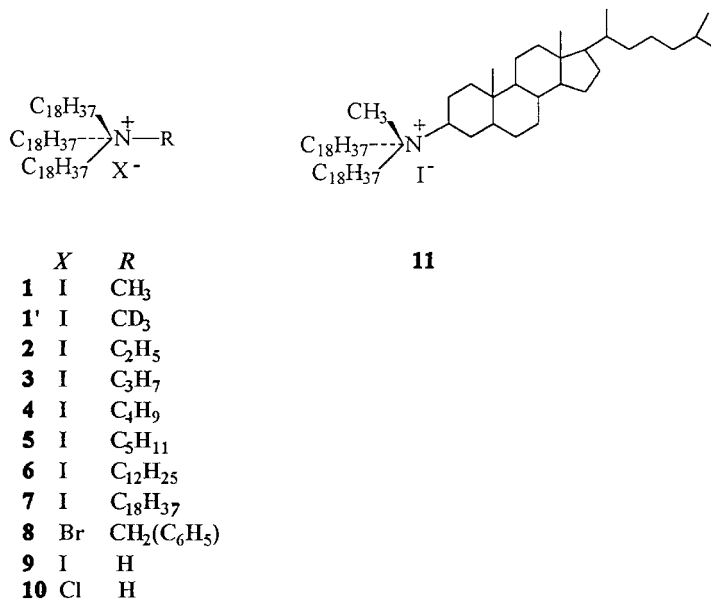
According to observations from optical microscopy, the first heating of **1** recrystallized from a solvent leads to a solid below 102°C, a deformable liquid crystal with a Schlieren texture [10] (see figure 1(a)) between 102 and 118°C, and an isotropic (non-birefringent) phase above 118°C. The liquid crystalline phases of salts **2**, **3**

and **8** have optical textures similar to that of **1** (see figure 1(b)).

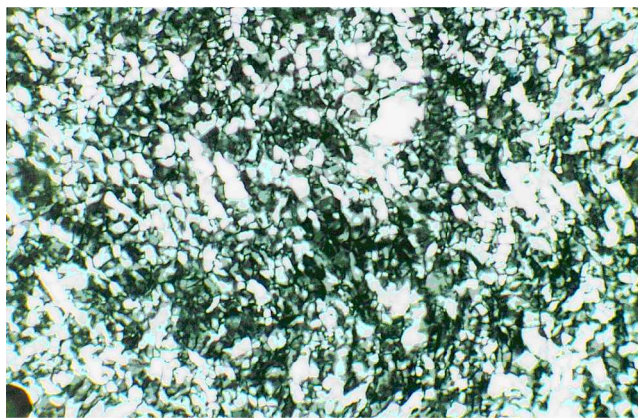
<sup>2</sup>H NMR spectra of neat *N*-trideuteriomethyl-*N,N,N*-trioctadecylammonium iodide (**1'**) were recorded on static samples using a one-pulse sequence in the isotropic and liquid crystalline phases and a quad-echo sequence in the solid phase. Above the clearing temperature, the spectra consisted of a single line, as expected, of molecules in which the quadrupolar interactions are motionally averaged. Upon cooling the sample, the singlet separated into two relatively sharp quadrupole-split lines (separation = 8400 Hz at 114°C), indicating that the molecules are aligned with respect to the external magnetic field (see figure 2(a)). An order parameter of 0.03 is calculated along the C–D bond axis assuming a zero asymmetry parameter and 180 KHz as the deuteron quadrupole coupling constant [11]. Upon further cooling the sample, the doublet transformed into a Pake-like pattern (see figure 2(b)) below the liquid crystal–solid phase transition temperature. The total spectral width is *c.* 80 KHz and the  $\delta\nu_{90}$  is *c.* 32 KHz. Consistent with the OM results, the spectral changes were completely reversible; they could be observed upon cooling or heating.

<sup>2</sup>H NMR spectra were also recorded at different temperatures while the neat **1'** sample was spun at 1 KHz about an axis making the magic angle with the magnetic field direction. In the isotropic phase (see figure 3(a)), only a single line at the chemical shift of the deuterons

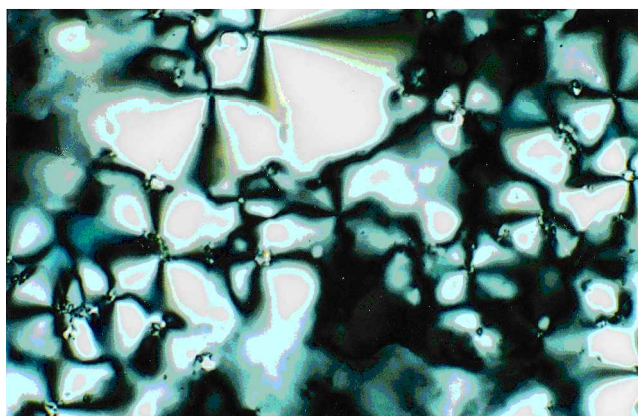
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Scheme 1.



(a)



(b)

Figure 1. (a) Optical micrograph of nematic **1** at 102°C ( $\times 420$ ); (b) optical micrograph of nematic **8** at 67°C ( $\times 420$ ).

was observed. However, due to temperature inhomogeneities, weak side bands indicative of residual nematic ordering are apparent. At *c.* 111°C in the liquid crystal phase, the spectrum consisted of an 'isotropic' singlet (centre band) flanked symmetrically by strong side bands from a quadrupolar interaction of the CD<sub>3</sub> deuterons in the oriented samples [12–15] (see figure 3(b)). The intensity of the centre band decreased while that of the side bands increased as the temperature was lowered within the liquid crystalline phase. However, it increased and that of the side bands decreased at one temperature as the sample spinning rate was increased. The behaviour can be interpreted from results on other nematics reported in the literature [12–15].

The NMR and OM data support the nematic and enantiotropic assignments of the liquid crystalline phase of **1**. By analogy, the liquid crystalline phases of **2**, **3** and **8** are nematic, also.

Some long-chain primary ammonium halides are known to form smectic phases [16, 17]. However, many simple quaternary ammonium salts with one long alkyl chain only undergo solid–solid phase transitions below their clearing temperatures [18], and the ammonium cations and halide anions in the crystals are extended bidimensionally to form an ionic layer which is sandwiched between the hydrocarbon chains [16]. Smectic-like liquid crystalline phases have also been observed for some salts with two long alkyl chains and two short alkyl groups [6, 7]. The spatial distributions of the cationic nitrogen and halide anions in the solid and smectic phases are very similar.

By contrast, **1–3** and **8**, ammonium salts with *three* long chains and a short one (designated the 'fourth'

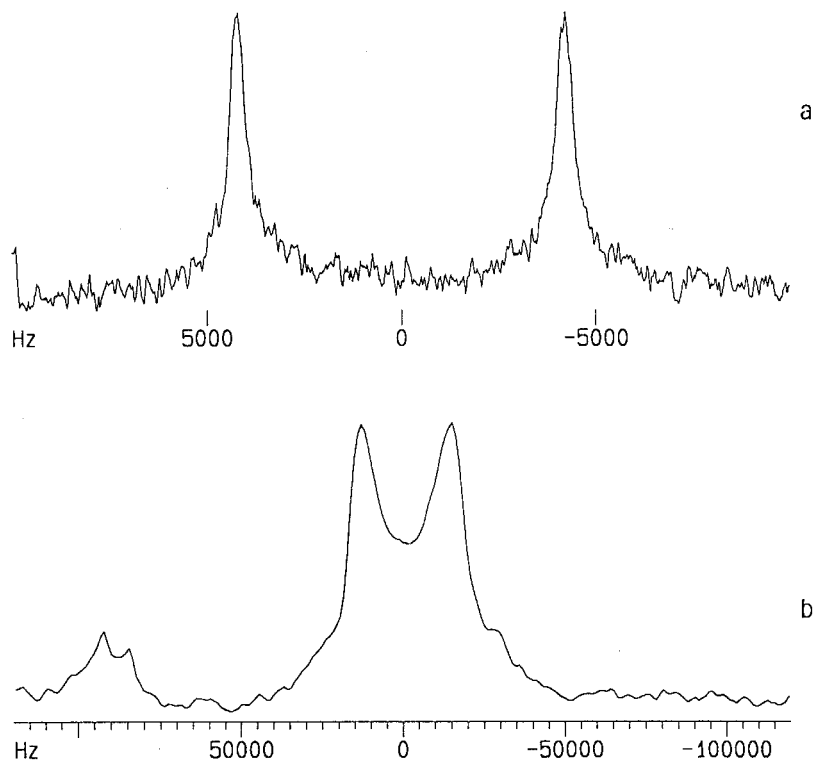


Figure 2.  $^2\text{H}$  NMR spectra at 46 MHz of neat **1'** in different phases. (a) Nematic phase at  $114^\circ\text{C}$ ; (b) solid phase at  $25^\circ\text{C}$ .

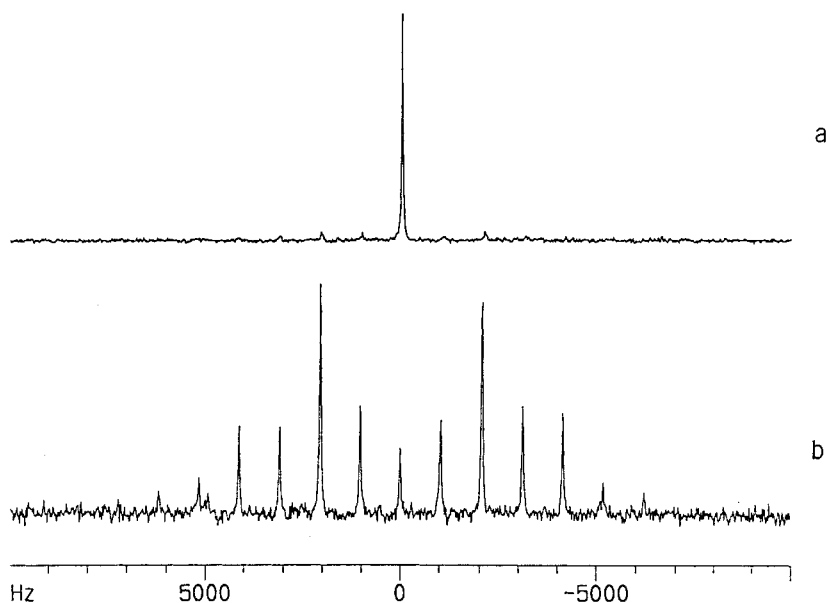


Figure 3.  $^2\text{H}$  NMR spectra of neat **1'** with 1 KHz spinning rates at the magic angle. (a)  $T \approx 120^\circ\text{C}$ ; (b)  $T \approx 111^\circ\text{C}$ .

group), form enantiotropic and thermotropic nematic phases. Several of the other molecules in the scheme are polymorphous between room temperature and their clearing temperatures.

Heating and cooling thermograms of **1** are shown in figure 4. During the first heating and cooling run, solid–solid, solid–liquid crystalline and liquid crystalline–

isotropic phase transitions can be identified (see the table). The greater complexity in subsequent thermograms appears to be associated with some thermal decomposition, especially of salts with a shorter alkyl group; thermograms of salts with a longer alkyl group were simpler in subsequent cycles. To determine whether adventitious water plays a role in the phase behaviour

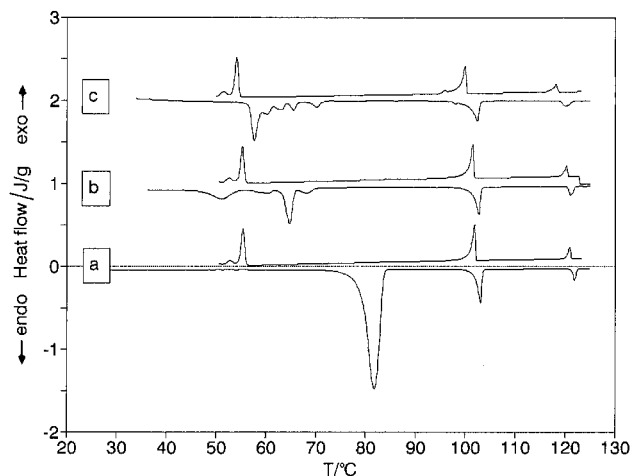


Figure 4. Thermograms of **1**: (a) first heat/cool cycle (solvent precipitated material); (b) second cycle recorded immediately after first; (c) fourth cycle recorded 4 months after second. The fifth cycle recorded immediately after the fourth is almost the same as (b), but the transitions between 100 and 125°C are broadened as in (c), indicating some decomposition.

of the salts, a thermal gravimetric analysis of **6** was performed. From 40 to 90°C, less than 0.013 per cent of sample weight was lost (i.e. an amount within experimental error of zero).

These results are a consequence of both chemical and morphological changes. For the sake of consistency, the reported DSC data are taken from first heating scans. The very small entropy changes ( $7.4\text{--}11.6\text{ J K}^{-1}\text{ mol}^{-1}$ ) during the liquid crystal to isotropic transitions of **1**, **2**, **3** and **8** are consistent with the nematic assignment. Although there is ample precedent for formation of thermotropic *smectic* phases by ammonium salts, we are unaware of any that form thermotropic *nematic* phases.

Based on X-ray data from **8**, the only molecule in the scheme from which good quality single crystals have been obtained thus far, the packing arrangement is 'zigzag' lamellae with one octadecyl chain projected (via a *gauche* kink at the C<sub>2</sub>–C<sub>3</sub> bond) almost perpendicular to other two parallel all-*trans* chains [19]. This conformation is *not* amenable to liquid crystal phase formation. If the three long chains were projected parallel after melting (resulting in a rod-shaped molecule), a *smectic* phase should be preferred [1]. Since one does not and since the heat of melting from the solid to nematic phases is exceedingly large ( $153\text{ J g}^{-1}$ ), large structural and organizational changes must be occurring. A reasonable hypothesis is that a rod-like molecular shape is achieved by projecting two octadecyl chains in one direction and the other chain and the benzyl group along a diametrically opposed direction.

As the length of the fourth group on nitrogen increases from one to three carbon atoms, the nematic temperature range decreases; liquid crystallinity is lost when the fourth group is butyl or longer *or* when it is replaced by a proton (see figure 5, and the tertiary ammonium salts, **9** and **10**). The homologues with a longer fourth chain, **4** and **5**, give evidence for a plastic phase, similar to that reported for the tetrabutylammonium halides [20, 21]: at elevated temperatures, but below their melting points, they are soft, deformable solids.

**1** and **2** have very high clearing temperatures and very high total enthalpy changes (see figure 6 which includes all transitions between room temperature and the clearing temperature for the first heating). Only solid–solid and solid–isotropic phase transitions are observed for **11**, a molecule like **1** but in which one flexible octadecyl chain is replaced by a rigid cholestanyl group. However, cholestanyl dioctadecylammonium iodide, a structural relative of the non-mesogenic **9**, forms a *smectic* phase [4]. Clearly, the interplay between structure and mesomorphism in these salts is very subtle and will require further examples before all of the underlying factors can be identified.

### 3. Conclusions

A series of quaternary ammonium halides with three long (octadecyl) chains have been shown to exhibit very complicated thermal behaviour which depends on the length and the structure of the fourth substituent on nitrogen. In particular, some of the salts with shorter fourth alkyl chains form enantiotropic, thermotropic nematic phases. Although there is precedent for *smectic* mesomorphism in related molecules, we are unaware of any other examples of nematic phase formation by simple ammonium salts; future efforts are likely to uncover more.

## 4. Experimental

### 4.1. Analysis

Heat flow, transition temperatures and weight loss measurements were determined with a TA 2910 DSC cell base and a TA 2050 TGA interfaced to a TA Thermal Analyst 3100 controller. Temperatures were calibrated with an indium standard. Samples were heated or cooled at  $2^\circ\text{C min}^{-1}$  using a steady nitrogen flow. Clearing temperatures (m.p.) and optical textures were detected on a Leitz 585 SM-LUX-POL optical microscope equipped with crossed polars, a Leitz 350 heating stage and a K-1000 Pentax 35mm camera (total magnification:  $\times 500$ ).  $^2\text{H}$  NMR spectra of trideuterio **1** (**1'**) were recorded on a Bruker DSX-300 spectrometer operating at 46 MHz. Elemental analyses were determined by Desert Analytics, Tucson, Arizona.



## 4.2. Synthesis of the ammonium salts

**Synthesis of 1.** Trioctadecylamine [7] (100 mg, 0.13 mmol) was dissolved in THF (1.5 ml), and CH<sub>3</sub>I (0.1 ml, 1.6 mmol) was added. The solution was stirred in a nitrogen atmosphere at 38–40°C for 3 h. A white solid (95 mg, 80 per cent), m.p. 118–121°C, was obtained after the solvent was evaporated under vacuum, and the residue was recrystallized in anhydrous ethanol. IR (KBr) 2917 (vs), 2859 (vs), 1473 (w)cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.52–3.38 (m, 6 H, CH<sub>2</sub>), 3.31 (s, 3 H, CH<sub>3</sub>), 1.76–0.82 (m, 105 H, heptadecyl chains). Analysis calculated for C<sub>55</sub>H<sub>114</sub>N<sup>+</sup>I<sup>-</sup>: C, 72.09; H, 12.54; N, 1.53. Found: C, 72.28; H, 12.79; N, 1.52 per cent.

The remaining quaternary ammonium halides were synthesized by modification of the above procedure.

**1'**: m.p. 119–120°C. IR (KBr) 2917 (vs), 2851 (vs), 1476 (w)cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.63–3.22 (m, 6 H, CH<sub>2</sub>), 1.76–0.82 (m, 105 H, heptadecyl chains).

**2**: m.p. 125.0–127°C. IR (KBr) 2917 (vs), 2849 (vs), 1469 (w), 1388 (w)cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS) δ 3.61–3.53 (q, 2 H, CH<sub>2</sub>, *J*=7.0 Hz), 3.34–3.27 (m, 6 H, CH<sub>2</sub>), 1.77–0.8 (m, 113 H, heptadecyl chains). Analysis calculated for C<sub>56</sub>H<sub>116</sub>N<sup>+</sup>I<sup>-</sup>: C, 72.29; H, 12.57; N, 1.51. Found: C, 72.25; H, 12.57; N, 1.50 per cent.

**3**: m.p. 103.5–105.5°C. IR (KBr) 2917 (vs), 2849 (vs), 1463 (w), 1373 (w)cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.47–3.16 (m, 8 H, CH<sub>2</sub>), 1.93–0.76 (m, 110 H, heptadecyl chains). Analysis calculated for C<sub>57</sub>H<sub>118</sub>N<sup>+</sup>I<sup>-</sup>: C, 72.49; H, 12.59; N, 1.48. Found: C, 72.66; H, 12.69; N, 1.51 per cent.

**4**: m.p. 101.5–105.0°C. IR (KBr) 2919 (vs), 2849 (vs), 1464 (w), 1373 (w)cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.52–3.20 (m, 8 H, CH<sub>2</sub>), 1.82–0.74 (m, 113 H, heptadecyl chains). Analysis calculated for C<sub>58</sub>H<sub>120</sub>N<sup>+</sup>I<sup>-</sup>: C, 72.68; H, 12.62; N, 1.46. Found: C, 73.00; H, 12.91; N, 1.63 per cent.

**5**: m.p. 102–106°C. IR (KBr) 2917 (vs), 2849 (vs), 1472 (w)cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.53–3.11 (m, 8 H, CH<sub>2</sub>), 1.86–0.62 (m, 122 H, heptadecyl chains). Analysis calculated for C<sub>59</sub>H<sub>122</sub>N<sup>+</sup>I<sup>-</sup>: C, 72.87; H, 12.64; N, 1.44. Found: C, 72.85; H, 12.80; N, 1.47 per cent.

**6**: m.p. 100.5–102°C. IR (KBr) 2920 (vs), 2857 (vs), 1473 (w), 1381 (w)cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.65–2.99 (m, 8 H, CH<sub>2</sub>), 1.91–0.49 (m, 134 H, heptadecyl chains). Analysis calculated for C<sub>66</sub>H<sub>136</sub>N<sup>+</sup>I<sup>-</sup>: C, 74.04; H, 12.80; N, 1.31. Found: C, 74.03; H, 12.63; N, 1.33 per cent.

**7**: m.p. 113.5–114.5°C. IR (KBr) 2918 (vs), 2855 (vs), 1471 (w), 1386 (w)cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.48–3.16 (m, 8 H, CH<sub>2</sub>), 1.78–0.81 (m, 148 H, heptadecyl chains). Analysis calculated for C<sub>72</sub>H<sub>148</sub>N<sup>+</sup>I<sup>-</sup>: C, 74.88; H, 12.92; N, 1.21. Found: C, 74.61; H, 13.07; N, 1.22 per cent.

**8**: m.p. 89–89.5°C. IR (KBr) 2916 (vs), 2851 (vs), 1473 (w), 1386 (w)cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.74–7.36 (m, 4 H, aromatic H), 5.19–4.76 (s, 2 H, CH<sub>2</sub>), 3.69–3.12 (m, 6 H, CH<sub>2</sub>), 2.05–0.67 (m, 104 H, heptadecyl chains).

Analysis calculated for C<sub>61</sub>H<sub>118</sub>N<sup>+</sup>Br<sup>-</sup>: C, 77.49; H, 12.58; N, 1.48. Found: C, 77.66; H, 12.46; N, 1.56 per cent.

Syntheses of **9** and **10**. Trioctadecylamine in methylene chloride or benzene was treated with 47 per cent HI<sub>(aq)</sub> or gaseous HCl to produce **9** and **10**, respectively.

**9**: m.p. 81.5–85°C. IR (KBr) 2920 (vs), 2851 (vs), 2662 (NH<sup>+</sup>, m), 1474 (w), 1383 (w)cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.24–2.57 (m, broad, 6 H, CH<sub>2</sub>), 1.99–0.76 (m, 108 H, heptadecyl chains).

**10**: m.p. 100.0–103.5°C. IR (KBr) 2916 (vs), 2851 (vs), 2448 (NH<sup>+</sup>, m), 1471 (w), 1383 (w)cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.15–2.78 (m, broad, 6 H, CH<sub>2</sub>), 1.96–1.65 (m, broad, 6 H, CH<sub>2</sub>), 1.60–0.76 (m, 113 H, hexadecyl chains).

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## References

- [1] KUNITAKE, T., KIMIZUKA, N., HIGASHI, N., and NAKASHIMA, N., 1984, *J. Am. chem. Soc.*, **106**, 1978.
- [2] EVERAARS, M. D., MARCELIS, A. T. M., and SUDHOLTER, E. J. R., 1995, *Colloids Surfaces A: Physicochem. Eng. Aspects*, **102**, 117.
- [3] DANINO, D., TALMON, Y., LEVY, H., BEINERT, G., and ZANA, R., 1995, *Science*, **269**, 1420.
- [4] LU, L., and WEISS, R. G., 1995, *Langmuir*, **11**, 3630.
- [5] PALEOS, C. M., MARGOMENOU-LEONIDOPOULOU, G., BABILIS, D., and CHRISTIAS, C., 1987, *Mol. Cryst. liq. Cryst.*, **146**, 121.
- [6] PALEOS, C. M., ARKAS, M., SEGHRUCHNI, R., and SKOULIOS, A., 1995, *Mol. Cryst. liq. Cryst.*, **268**, 179.
- [7] ALAMI, E., LEVY, H., ZANA, R., WEBER, P., and SKOULIOS, A., 1993, *Liq. Cryst.*, **13**, 201.
- [8] FULLER, D., SHINDE, N. N., TIDDY, G. J., ATTARD, G. S., and HOWELL, O., 1996, *Langmuir*, **12**, 1117.
- [9] LU, L., and WEISS, R. G., *J. chem. Soc., chem. Commun.*, 1996, 2029.
- [10] DEMUS, D., and RICHTER, L., 1978, *Textures of Liquid Crystals* (Verlag Chemie), pp. 166–211.
- [11] KHETRAPAL, C. L., and DIEHL, P., 1969, *NMR-Basic Principles and Progress* (Springer Verlag), Vol. 1.
- [12] NAGANA GOWDA, G. A., WEISS, R. G., and KHETRAPAL, C. L., 1991, *Liq. Cryst.*, **10**, 659.
- [13] ARUN KUMAR, B. S., SURYAPRAKASH, N., RAMANATHAN, K. V., and KHETRAPAL, C. L., 1987, *Chem. Phys. Lett.*, **136**, 227.
- [14] ARUN KUMAR, B. S., RAMANATHAN, K. V., and KHETRAPAL, C. L., 1988, *Chem. Phys. Lett.*, **149**, 307.
- [15] ARUN KUMAR, B. S., RAMANATHAN, K. V., KHETRAPAL, C. L., OPELLA, S. J., and BECKER, E. D., 1990, *J. Magn. Reson.*, **86**, 516.
- [16] BUSICO, V., CORRADINI, P., and VACATELLO, M., 1982, *J. phys. Chem.*, **86**, 1033.
- [17] GAULT, J. D., GALLARDO, H. A., and MILLER, H. J., 1985, *Mol. Cryst. liq. Cryst.*, **130**, 163.
- [18] IWAMOTO, K., OHNUKI, Y., SAWADA, K., and SENO, M., 1981, *Mol. Cryst. liq. Cryst.*, **73**, 95.
- [19] BACHMAN, R., COCKER, M. T., LU, L., and WEISS, R. G., to be published.
- [20] PAJAK, Z., and SZAFRANSKA, B., 1993, *Phys. Stat. Sol. (a)*, **136**, 371.
- [21] WANG, Q., HABENSCHUSS, A., XENOPOULOS, A., and WUNDERLICH, B., 1995, *Mol. Cryst. liq. Cryst.*, **264**, 115.