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Solute induced liquid crystalline behaviour of a quaternary ammonium salt and its application to structure determination

by LIANGDE LU, G. A. NAGANA GOWDA†, N. SURYAPRAKASH†,
C. L. KHETRAPAL†‡* and RICHARD G. WEISS*

Department of Chemistry, Georgetown University, Washington, DC
20057-1227, U.S.A.

†Sophisticated Instruments Facility, Indian Institute of Science,
Bangalore 560 012, India

‡National Institutes of Health, Bethesda, MD 20892, U.S.A.

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A new liquid crystalline phase, induced by the addition of small amounts of a non-mesogenic solute (such as dimethyl sulphoxide or methyl iodide) to a quaternary ammonium salt, *N*-methyl-*N,N,N*-trioctadecylammonium iodide (MTAI), has been detected by NMR and optical microscopic studies. In some cases, there is a coexistence of nematic and smectic phases. Information on the ordering of the phases in the magnetic field of the spectrometer has been derived from NMR spectra of a dissolved molecule, ¹³C-enriched methyl iodide. The low order parameter of the pure thermotropic nematic phase of the salt provides first-order spectra of the dissolved oriented molecules. Analyses of spectra of *cis,cis*-mucononitrile exemplifies the utility of the MTAI nematic phase in the determination of structural parameters of the solute.

1. Introduction

We recently reported that several simple quaternary ammonium salts with one short and three long chains form enantiotropic thermotropic nematic phases [1]. In order to explore further their properties and potential applications, one of the salts, *N*-methyl-*N,N,N*-trioctadecylammonium iodide (MTAI), was doped with small amounts of non-mesogenic solutes, such as dimethyl sulphoxide (DMSO-*d*₆), methyl iodide (¹³C-enriched) or *cis,cis*-mucononitrile. Their influence on its liquid crystalline behaviour has been investigated by ¹H, ²H, and ¹³C NMR spectroscopy, optical microscopy (OM), and differential scanning calorimetry (DSC). The results indicate that nematic phases of MTAI and related salts may provide an important tool in the determination of structural parameters of relatively complex solute molecules.

2. Experimental

MTAI, synthesized by a procedure described earlier [1], was recrystallized twice by adding acetone dropwise to a hot hexane solution; its transition temperatures were as reported [1]. The solutes DMSO-*d*₆ (MSD-isotopes 99.9 atom % D), ¹³CH₃I (ICN-biomedicals Inc., 99% ¹³C-enriched), and *cis,cis*-mucononitrile (Aldrich,

98%), were used without further purification. ²H NMR spectra of 5.8 (sample A) and 17 (sample B) wt % dimethyl sulphoxide-*d*₆, ¹³C and ¹H spectra of about 7 wt % ¹³CH₃I, and ¹H NMR spectra of 5.4 wt % *cis,cis*-mucononitrile in MTAI were recorded on a Bruker AMX-400 FT-NMR spectrometer operating at the ¹H, ²H and ¹³C frequencies of 400, 61.4 and 100 MHz, respectively, using a one-pulse sequence. The pulse-width, relaxation delay, and number of data points were 10 μs, 1 s and 32 K, respectively. Thirty-two free induction decays (FIDs) were accumulated for the ²H spectra, and 4 FIDs were averaged for ¹³C and ¹H spectra.

Heat flow and transition temperature measurements (taken as the points of maximum heat flow) were determined with a TA 2910 DSC cell base interfaced to a TA Thermal Analyst 3100 controller. Samples were heated or cooled at 2°C min⁻¹. Transition temperatures (±0.5°C, corrected) and optical textures were observed on a Leitz 585 SM-LUX-POL optical microscope equipped with crossed polarizers, a Leitz 350 heating stage, and a K-1000 Pentax 35 mm camera.

3. Results

3.1. NMR studies

3.1.1. ²H NMR studies of DMSO-*d*₆ dissolved in MTAI
²H NMR spectra of sample A, corresponding to *c.* 0.7 solute molecule per molecule of MTAI, showed a single

* Authors for correspondence.

sharp line (due to the isotropic phase) at 373 K and a quadrupolar doublet (due to aligned molecules) between 345 and 360 K. The doublet separation increased from about 1460 Hz at 360 K to about 1880 Hz at 345 K. Within 340–330 K, two quadrupolar doublets (due to two types of alignment of the solute molecules) were observed. The splittings of both doublets decreased when temperature was lowered: 1850 and 1070 Hz at 340 K; 1770 and 1000 Hz at 330 K.

For sample B, containing slightly more than 2 molecules of DMSO- d_6 per molecule of MTAI, an isotropic singlet and only one quadrupolar doublet (due to aligned molecules), with a constant separation of about 1500 Hz, were observed within the liquid crystalline range of temperatures. The isotropic phase appeared at 340 K and the liquid crystalline phase was evident between 327 and 339 K. The solid phase (as evidenced by the disappearance of the doublets) was below 328 and 326 K in samples A and B, respectively. However, since sharp singlets were still present at these temperatures, we conclude that at least some solute

molecules were phase-separated and remained in their liquid state. Typical spectra are shown in figures 1 and 2.

3.1.2. ^{13}C and ^1H NMR studies of $^{13}\text{CH}_3\text{I}$ in MTAI

At 347 K, the ^{13}C NMR spectrum of $^{13}\text{CH}_3\text{I}$ consisted of a quartet from molecules in the isotropic phase ($J_{\text{CH}} = 151.7\text{ Hz}$). On cooling to *c.* 343 K, another quartet from methyl iodide in a nematic environment was evident. At 332 K, a third quartet with much larger splitting appeared, corresponding to methyl iodide molecules dissolved in another phase. Finally, the quartets with the largest splitting and from the isotropic phase appeared near 318 K. Typical spectra at the four temperatures are shown in figure 3. The proton NMR spectra show analogous changes.

3.1.3. ^1H NMR studies of *cis,cis*-mucononitrile in MTAI

Proton NMR spectra of *cis,cis*-mucononitrile dissolved in the isotropic and liquid crystalline phases of MTAI are shown in figure 4. A spectrum of the same solute in

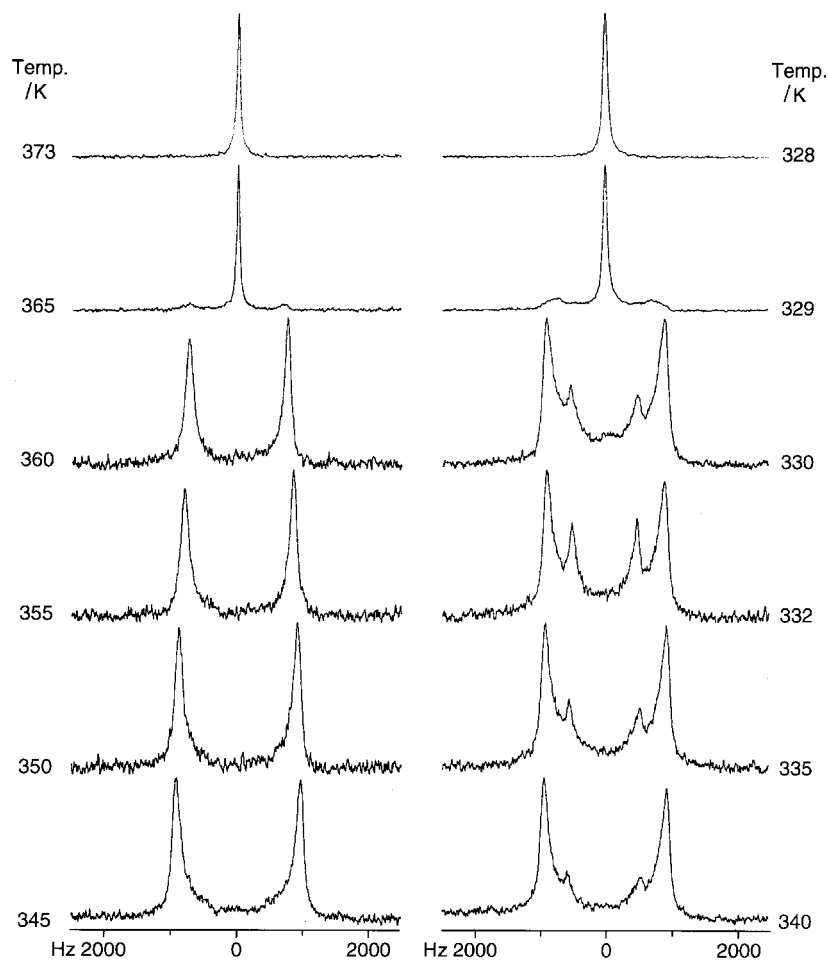


Figure 1. Deuterium NMR spectra of MTAI containing 5.8 wt % of dimethyl sulphoxide- d_6 as a function of temperature.

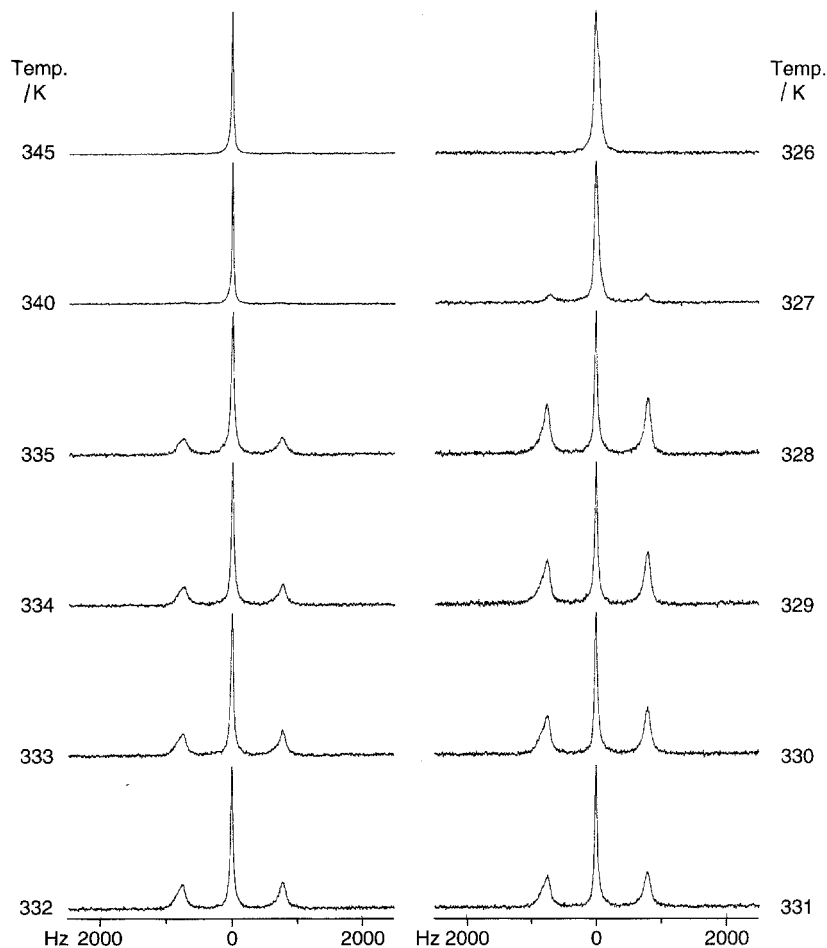


Figure 2. Deuterium NMR spectra of MTAI containing 17 wt % of dimethyl sulphoxide- d_6 as a function of temperature.

a 'normal' thermotropic nematic phase (from Merck ZLI-1167) [2] is also shown for comparison.

3.2. Optical microscopy results

A sample of 20 wt % DMSO in MTAI, sandwiched between pyrex discs, showed a solid phase with a few isotropic droplets at the glass surfaces below 330 K, and an isotropic phase when heated above 344 K. Upon cooling, a smectic-like texture [2] appeared below 330 K (figure 5), transformed into another texture near 325 K (figure 6), and finally crystallized at *c.* 322 K. Similar behaviour was found for a 14 wt % sample. At 4.7 wt % DMSO in MTAI, the solid phase below 332 K appeared similar to that of the higher dopant samples, but its texture above 344 K was like that of the nematic phase of pure MTAI, and remained so to its clearing transition at 393–394 K. The cooled isotropic phase behaved very similarly to pure MTAI.

When lateral pressure was applied to one of the disks at a temperature where both birefringent phases coexisted, they did not mix or coalesce into one pattern. Attempts to record optical patterns of samples of

methyl iodide in MTAI at elevated temperatures were unsuccessful since the solute evaporated rapidly.

3.3. DSC results

Thermograms of MTAI samples containing 4.7, 9.3, 14 and 20 wt % DMSO were recorded. Each contained at least one more transition than the three thermograms of pure MTAI [1] when heated between 300 and 405 K. The new transitions included a solid–solid *exotherm* near 328–331 K. In all cases, the solid–mesophase transition was highest in enthalpy change. Since some of the DMSO was always in an isotropic phase (while presumably saturated with MTAI), it is not possible to calculate precisely the heats of transition from the MTAI-rich anisotropic components. However, as expected, the sums of the heats of transition were always significantly lower than those from pure MTAI even when it was assumed that only the mass fraction of MTAI contributes to the transitions.

Although more transitions were in evidence by DSC than by optical microscopy, there was good agreement

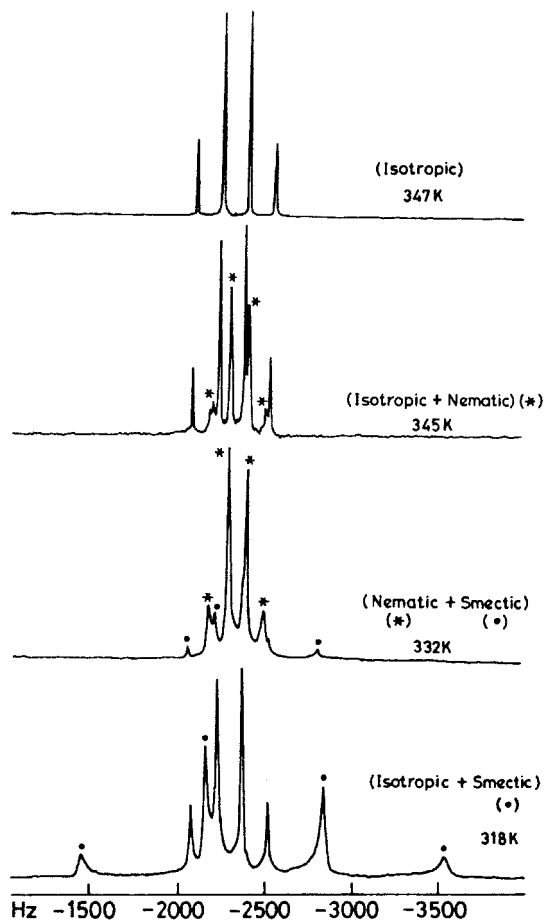


Figure 3. ^{13}C NMR spectra of 7 wt % of $^{13}\text{CH}_3\text{I}$ in MTAI as a function of temperature.

between the temperatures of the two methods where comparisons were possible.

4. Discussion

The experimental results indicate the coexistence of two liquid crystalline phases within certain temperature and solute concentration limits. In hypothesis, the two doublets in the NMR spectra could be from solute molecules in two different environments within one phase, or from two different phases. The optical microscopy observations confirm the latter situation. By comparison, pure MTAI forms only one liquid crystalline phase that is nematic [1]. On this basis, it is concluded that at least one of the liquid crystalline phases is induced by addition of a non-mesogenic solute to MTAI at a particular temperature and concentration. When the solute concentration exceeds an upper limit, the induced phase is formed†.

†Phase induction has been effected by addition of benzene to MTAI, also, but the results have not been quantified.

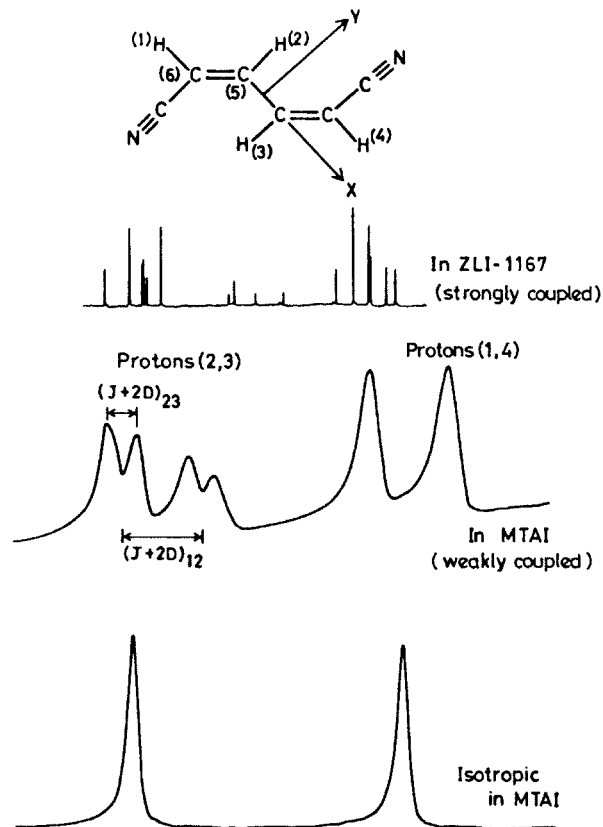


Figure 4. Proton NMR spectra of *cis,cis*-mucononitrile: (top trace) in ZLI-1167, (central trace) 5.4 s % in MTAI and (bottom trace) isotropic phase in MTAI.

The solute-induced liquid crystalline phase is smectic; it is immiscible with the other liquid crystalline phase whose spontaneous alignment in the magnetic field of the NMR spectrometer and mosaic optical pattern are compatible with its being nematic. If both phases were nematic, they should have been miscible and the optical pattern of the second phase would have been different.

In thermotropic nematic liquid crystals, the magnitude of order parameters normally increases as the temperature is lowered. In the present case, when two quadrupole split doublets are observed in the ^2H NMR spectra of DMSO-d_6 oriented in the liquid crystalline phases of MTAI, the decrease of both doublet separations with decreasing temperature indicates solvent-solute interactions in the system.

Earlier studies [3–9] on non-ionic nematic liquid crystals with strongly polar end groups, like cyano, and containing rather non-polar solutes have shown that smectic A phases can be induced even when neither component shows smectic behaviour. Additionally, there is precedence for mixtures of non-ionic, non-mesogenic molecules forming thermotropic nematic phases [10]. In hindsight, the induction of a smectic phase of MTAI is not surprising since most related ammonium salts



Figure 5. Optical micrograph ($\times 200$ total magnification) between crossed polarizer of MTAI containing 20 wt % of dimethyl sulphoxide on being cooled from the isotropic phase to 329 K.

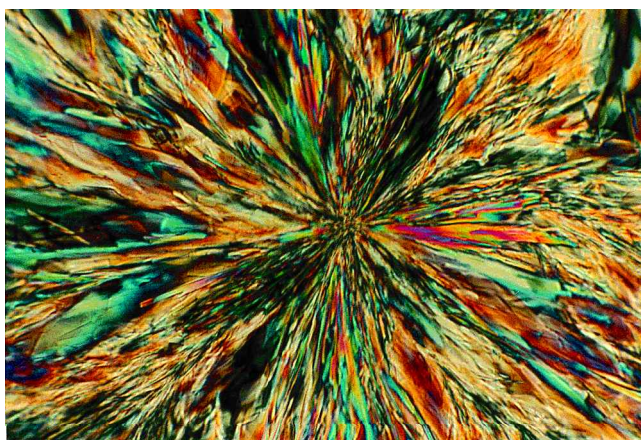


Figure 6. Optical micrograph as in figure 5, but at 322 K.

with one or two long alkyl chains prefer to form lamellar assemblies when pure or in concentrated lyotropic phases [9, 11].

From the proton and ^{13}C NMR spectra of $^{13}\text{CH}_3\text{I}$, the values of the H–H and ^{13}C –H direct dipolar and the indirect ^{13}C –H couplings were determined. The values for the nematic phase at 338 K and those for the smectic phase at 318 K are reported in the table.

The dipole couplings, D_{HH} and D_{CH} , have been used to determine the HCH bond angles and the order

Table. Values (in Hz) of the indirect ^{13}C H couplings and the direct dipolar couplings for $^{13}\text{CH}_3\text{I}$ at 338 and 318 K.

Nematic phase (338 K)			Smectic phase (318 K)		
J_{CH}	D_{CH}	D_{HH}	J_{CH}	D_{CH}	D_{HH}
150.7	–332.3	–170.6	150.7	–418.7	–541.3

parameters in both phases using expressions reported in the literature [12]. The angles, 110.2° and 110.3 , thus obtained, are smaller by about 1° than those from studies in other thermotropic liquid crystals [12, 13]. The difference in magnitudes is attributed to variations in solvent–solute interactions (as mentioned above). A dependence of HCH bond angle in methyl halides on solvent has been observed previously [13]. We note that the value of the HCH bond angle in methyl iodide, as determined above, is similar to the angle obtained for methanol, where weak molecular interactions are known [12]. The order parameters (SC_3), along the 3-fold symmetry axis, are -0.0167 (nematic) and -0.0531 (smectic). The negative sign indicates negative diamagnetic susceptibility anisotropy of the liquid crystal.

The proton spectrum of mucononitrile in ZLI-1167 (top trace, figure 4) is ‘strongly’ coupled and it is difficult to assign the line to specific protons. The spectrum in MTAI (middle trace, figure 4) in the nematic phase shows essentially two groups of lines corresponding to protons (2,3) and (1,4) as shown in the figure, centred nearly round the isotropic positions of these protons (bottom trace, figure 4). The splittings within the two groups of lines provide $(J + 2D)_{12}$ and $(J + 2D)_{23}$ to the first order, as shown in the figure; $(J + 2D)_{14}$ falls within the line width.

5. Conclusions

NMR, OM, and DSC data on MTAI containing relatively small amounts of non-mesogenic solutes indicate the induction of smectic phases. The order parameter in the nematic phase is only about 3% of that of a normal thermotropic nematic phase consisting of rod-like molecules, and is comparable to the values for lyotropic nematic phases. As a result, MTAI has potential applications for obtaining first-order proton NMR spectra of dissolved oriented molecules. The spectra are much simpler than those in ‘normal’ thermotropic solvents which are invariably ‘strongly’ coupled and, hence, difficult to analyse. A preliminary study of mucononitrile oriented in this phase demonstrates such an application. Efforts to decrease the line-widths and to analyse the spectra of more complex systems are in progress.

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