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Amphotropic Ionic Liquid Crystals with Low Order Parameters[†]

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Methyl-tri-*n*-decylphosphonium salts (**1P10A**, where the counterion **A** is NO_3^- or the hydrate of bromide, $Br^-\cdot H_2O$) have been shown to exhibit unique liquid-crystalline properties as neat compounds and with high concentrations (up to 20 wt %) of a small organic molecule, acetonitrile. These results indicate dual thermotropic−lyotropic (i.e., amphotropic) behavior. Optical micrographs of salts with even small amounts of acetonitrile are oily streak patterns. The low-angle peaks in X-ray diffractograms characteristic of the lamellar spacings in the smectic A phases of the neat salts are broadened but do not change their positions appreciably as the concentration of added acetonitrile is increased. The liquid-crystalline phases of both salts become oriented in strong magnetic fields. As a result, NMR experiments with the nitrate salt exhibited only one type of orientation for acetonitrile at concentrations up to ca. 10 wt %. However, two types of orientations with opposite signs of the order parameter were detected in the $Br^-\cdot H_2O$ salt at <1 wt % acetonitrile. The acetonitrile proton line width decreases by a factor of 2 between 0.7 and 13 wt % in the nitrate salt. The dual thermotropic−lyotropic behavior and relatively low order parameter of the solute suggest that these amphiphilic salts might be useful for structural studies using NMR spectroscopy.

Introduction

NMR spectra of molecules oriented in thermotropic nematic liquid crystals provide detailed information about the molecular geometry and orientation of the solute molecules.[1] However, as a result of the usually large order parameters of normal "rodlike" thermotropic liquid crystals, the spectra of molecules dissolved therein become exceedingly complicated as the number of interacting nuclei increases as a result of "strong coupling". Considerable efforts have been made to discover media with relatively low order parameters so that the dissolved molecules are "weakly coupled" and their spectra remain rather simple even when the number of interacting nuclei is large.

Order parameters of aqueous-based lyotropic liquid crystals are about an order of magnitude lower than those of normal rodlike thermotropic liquid crystals. As a result, lyotropic liquid crystals have historically been the media of choice for NMR spectroscopy of oriented molecules to obtain "first-order" spectra. However, the spectra of relatively large biomolecules dissolved even in aqueous-based lyotropic liquid crystals were not amenable to routine structural studies until the discovery of low-ordered lyotropic bicellar solutions and compressed hydrogels.[2,3] The development of techniques associated with these new media[4] and the development of nonaqueous lyotropic liquid crystals based on poly-γ-benzyl-L-glutamate[5] for dipolar structural studies of enantio- and diastereo-contents of water-insoluble molecules[6−9] have led to a renaissance and a myriad of additional possibilities.

Encouraged by these accomplishments, we have initiated efforts to discover *nonaqueous, nonpolymeric* media with low order parameters.[10,11] Such materials would facilitate the possibility of elucidating structures of large *organic* molecules not soluble in bicellar media or where chiral polymeric matrixes are undesirable. Here, we report several aspects of the *amphotropic*[12] behavior of

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[†] With awe, respect, and admiration, R.G.W. dedicates this article to Professor Ray Crist of Messiah College on the occasion of his retirement at the age of 104.

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Chart 1. Structures of 1P10A Salts

A = NO_3 **1P10NO₃**
A = Br (+H_2O) **1P10Br·H₂O**

our previously characterized methyl-tri-*n*-decylphosphonium salts (**1P10A**)[13] in which the counterion **A** is NO_3^- or Br^- (as well as one molecule of water per molecule of salt)[14] with acetonitrile as the solute, including dipolar NMR spectroscopy, optical microscopy, and X-ray diffraction studies: these salts are low-ordered *smectic* liquid crystals within a certain temperature range, and unlike normal thermotropic liquid crystals, they retain their liquid-crystalline behavior even at high solute concentrations; they exhibit dual thermotropic−lyotropic liquid-crystalline properties. (See Chart 1.)

Experimental Section

Solutions of methyl-tri-*n*-decyl phosphonium salts with NO_3 and $Br{\cdot}H_2O$ counterions[13] and varying concentrations of CH_3CN and CD_3CN (up to ca. 20 wt %) for NMR studies were prepared in 5-mm NMR tubes under a nitrogen atmosphere, and the tubes were flame-sealed immediately. Samples for optical microscopic investigations were placed in flattened Pyrex capillaries that were sealed. The capillaries were placed on a Leitz 350 heating stage and examined through crossed polars on a Leitz 585 SM-LUX-POL microscope. Temperatures were calibrated with samples of known transition/melting temperatures placed in the same capillaries.

X-ray diffractograms of samples flame-sealed in 0.5-mm capillaries were collected at room temperature on a Rigaku RAPID/XRD image plate system using Cu Kα radiation (λ = 1.540 56 Å). Diffractions in degrees (2θ) were converted to distances (in Å) using the Bragg relationship.

One-dimensional ^{1}H and ^{2}H NMR experiments were performed on a Bruker AVANCE 400 Spectrometer at different temperatures. A spectral width of 10 kHz and a relaxation delay of 1 s were used for the ^{1}H and ^{2}H one-dimensional experiments. Each data set was collected with 32K data points. ^{1}H data were processed with a trapezoidal window function to suppress the broad signals arising from the liquid crystals. For the samples with CH_3CN as the solute, two-dimensional ^{1}H−^{1}H COSY[15,16] and gradient-enhanced ^{1}H−^{3}C HMBC[17,18] experiments were also performed to identify the solute signals and to measure heteronuclear dipolar couplings. Spectral widths of 10 kHz were used in both dimensions for ^{1}H−^{1}H COSY experiments. One thousand twenty-four data points were collected in the t_2 dimension and 400−512 points in the t_1 domain, depending on the sample. The data were processed in both dimensions after they had been multiplied by a squared sine bell window function shifted by 90° and the data in the t_1 domain had been zero-filled to 1024 points. For ^{1}H−^{13}C HMBC experiments, spectral widths of 5 and 18 kHz were used in the ^{1}H and ^{13}C dimensions, respectively. Five hundred twelve FIDs were collected, each with 2048 data points. The delay for the evolution of the couplings was adjusted to an average $J_{CH} + 2D_{CH}$ of one- and two-bond ^{1}H−^{13}C couplings so as to optimize the sensitivity of the experiment. The data were Fourier transformed in both dimensions after being multiplied by a squared sine bell window function and zero-filled in the t_1 domain to 1024 data points. Values of the various derived dipolar couplings are included in Table 1.

Table 1[a]

	1P10NO₃		**1P10Br·H₂O**			
			0.7% CH_3CN			
parameter	1% CH_3CN	3% CH_3CN	I orientation	II orientation	1% CH_3CN	3% CH_3CN
D_{HH} (Hz)	258.7	227	202.8	−1487	210	185
$^1D_{CH}$ (Hz)	197.3	179.8	154.0	−998.2	166.3	144.3
$^2D_{CH}$ (Hz)	−52.7	−45.7	−38.3	273.8	−40.7	−36.7
angle HCH	110.7°	110.1°	110.1°	108.3°	110.7°	110.5°

[a] $^1J_{CH}$ = 136.3 Hz, $^2J_{CH}$ = −10.6 Hz.

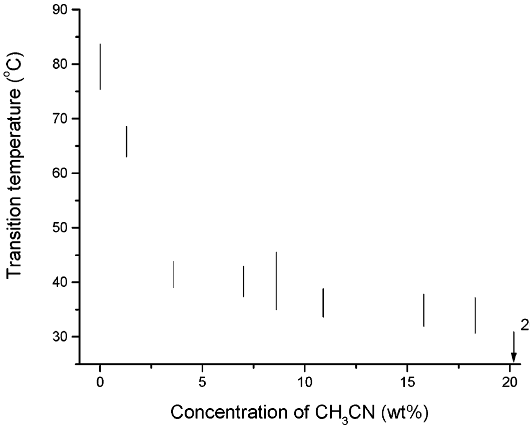

Figure 1. Transition temperature ranges (vertical lines) for CH_3CN in **1P10Br·H₂O**. The arrow indicates the lowest concentration at which the solution was observed to be no longer liquid-crystalline at room temperature.

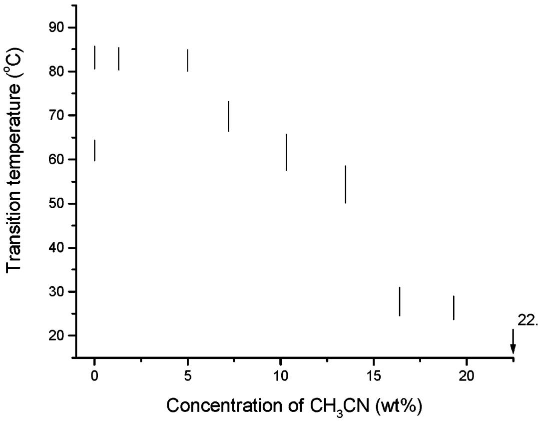

Figure 2. Transition temperature ranges (vertical lines) for CH_3CN in **1P10NO₃**. The arrow indicates the lowest concentration at which the solution was observed to be no longer liquid-crystalline at room temperature. The solid−smectic transition at 0 wt % is designated by the lower-temperature line segment.

Results and Discussion

Previously, we reported that several **1P10A** salts exhibit liquid-crystalline phases whose temperature

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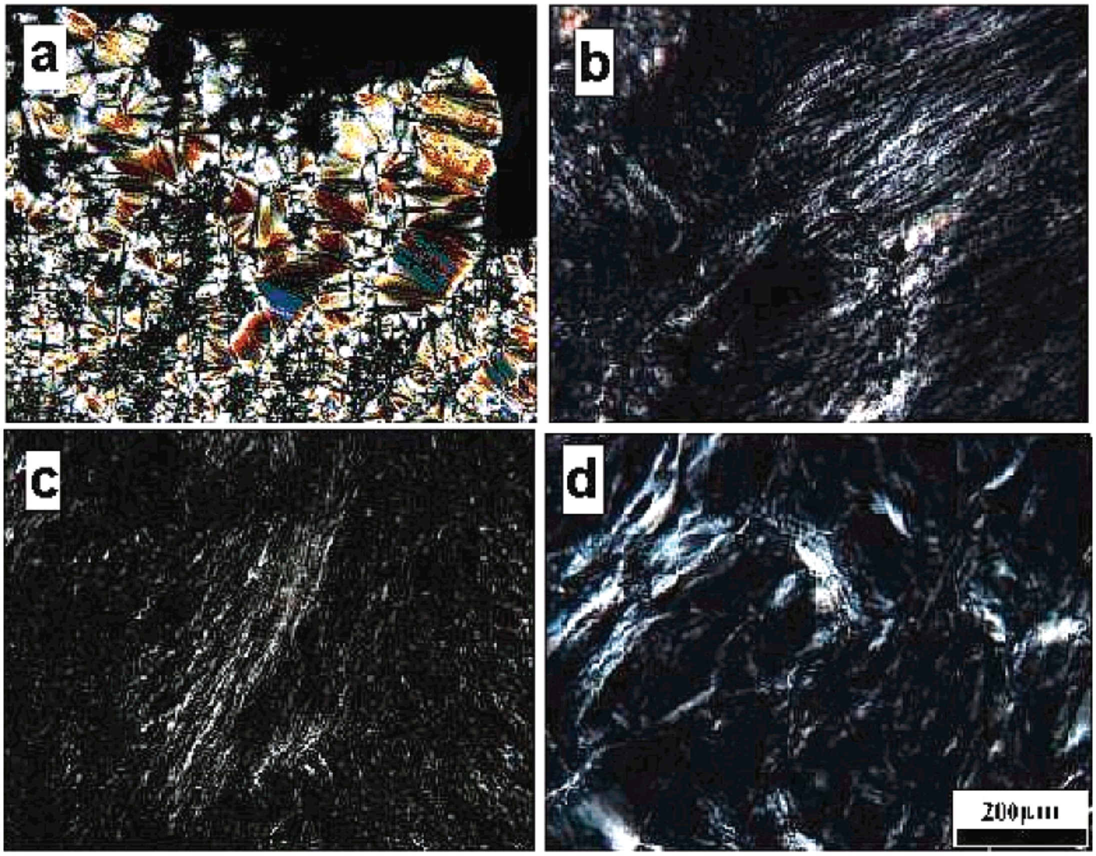

Figure 3. Room-temperature polarizing optical micrographs of (a) **1P10Br·H$_2$O** in a cell (see text for details), (b) **1P10Br·H$_2$O** between cover slips, (c) 1.3 wt % CH_3CN in **1P10Br·H$_2$O** between cover slips, (d) 10.9 wt % CH_3CN in **1P10Br·H$_2$O** between cover slips. The distance bar applies to all of the micrographs.

ranges depend on the nature of the anion **A**.[13] In all cases, the mesophase could be identified as smectic A_2 on the basis of a combination of data from X-ray diffraction and optical microscopy. A key aspect of the packing within the mesophases is the aggregation of cationic headgroups and anionic counterions in planes that are separated by the lipophilic alkyl chains.

Optical micrographs of **1P10Br·H$_2$O** and **1P10NO$_3$** with various amounts of acetonitrile are birefringent as well, and the temperatures of the solid−mesophase transitions are lowered significantly and are subambient. This observation is most striking for **1P10NO$_3$**. It is liquid-crystalline at room temperature in the presence of even 1.3 wt % acetonitrile, although the onset temperature of the solid−mesophase transition of the neat salt is 59.7 °C.[19] The optically determined clearing temperatures (Figures 1 and 2) demonstrate that the amphotropic mesophases[12] persist at room temperature to nearly 20 wt % of added acetonitrile. Although the clearing temperatures decrease with increasing concentration of acetonitrile, the optical micrographs give no evidence for phase separation. Typical optical micrographs of the oily streak patterns of the salts with acetonitrile at room temperature and their patterns without solute in their mesophases are shown in Figures 3 and 4. Fanlike textures typical of smectic A_2 phases were observed for the samples loaded into heated 25-μm-thick cells by capillary action.

The X-ray diffraction patterns of **1P10Br·H$_2$O** and **1P10NO$_3$** without and with low and high concentrations of CH_3CN (Figures 5 and 6) confirm that the low-angle peaks of the smectic A_2 phases of the salts are retained throughout the range of added CH_3CN concentrations where the NMR experiments were conducted. Although the positions of the low-angle peaks do not change appreciably, the peaks do broaden, indicating less well defined lamellae, as the solute concentration is increased. At the same time, the broad high-angle peaks near 20° in 2θ (from somewhat correlated spacings between alkyl chains of the salts as well as between solute molecules) broaden at low concentrations of acetonitrile and then narrow somewhat, becoming very similar in appearance to this diffraction feature in the absence of acetonitrile. This behavior might indicate that acetonitrile is present as a part of clathrates,[20,21] especially at the 10 wt % concentration that is near a 1:1 salt/acetonitrile molecular ratio. The change in the shape and breadth of the high-angle peaks between 0

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(19) From DSC measurements. The soft crystal−mesophase transition could not be discerned by optical microscopy.

(20) Strictly speaking, clathrates refer to crystalline inclusion compounds in which one kind of molecule is surrounded by a lattice-like arrangement of another. Here, we conjecture that acetonitrile might occupy sites, partially of its own creation, within the liquid-crystalline phases, so that they are liquid-crystalline clathrates, extensions of Atwood's "liquid clathrates".[21]

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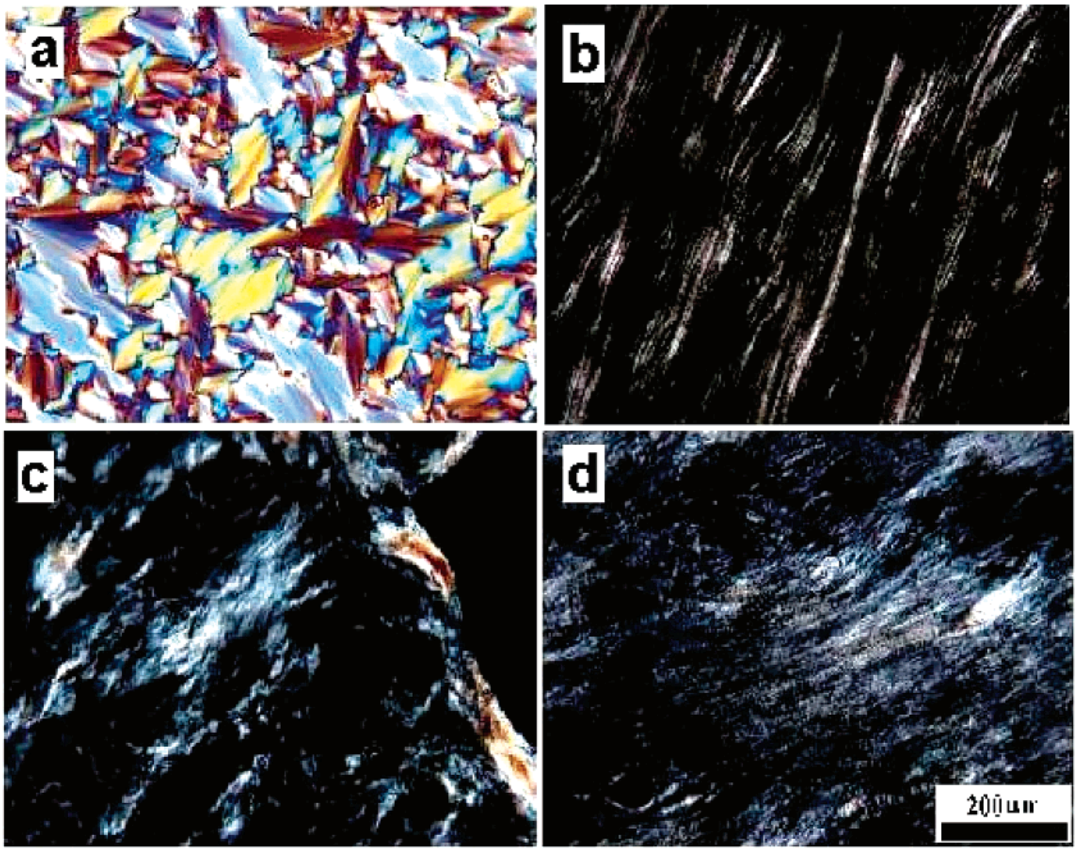

Figure 4. Polarizing optical micrographs of (a) **1P10NO$_3$** in a cell at 60 °C (in its liquid-crystalline phase) upon cooling from the isotropic phase (see text for details), (b) **1P10NO$_3$** between cover slips upon application of lateral force at 61 °C (in its liquid-crystalline phase) upon cooling from the isotropic phase, (c) 1.3 wt % CH$_3$CN in **1P10NO$_3$** between cover slips at room temperature, (d) 10.3 wt % CH$_3$CN in **1P10NO$_3$** between cover slips at room temperature. The distance bar applies to all of the micrograghs.

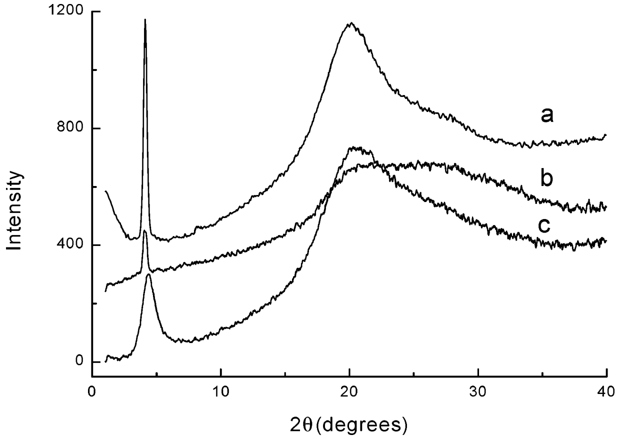

Figure 5. X-ray diffraction patterns and *d* values of the low-angle peaks in parentheses for **1P10Br·H$_2$O** with (a) 0 wt % (21.4 ± 0.2 Å), (b) 1.5 wt % (21.8 ± 0.1 Å), and (c) 10.0 wt % (20.1 ± 0.1Å) CD$_3$CN. The curves have been offset along the *Y* axis for clarity.

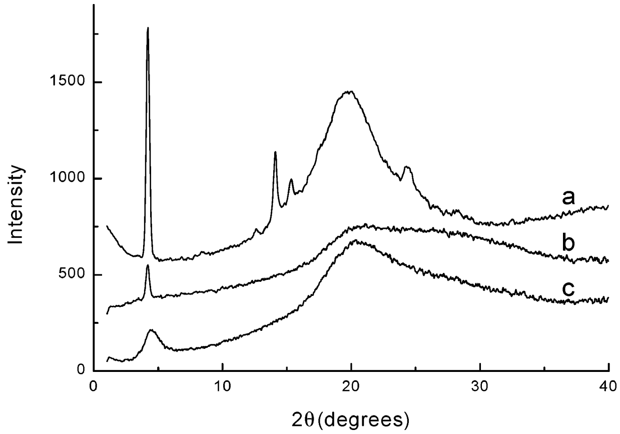

Figure 6. X-ray diffraction patterns and *d* values of the low-angle peaks in parentheses for **1P10NO$_3$** with (a) 0 wt % (20.9 ± 0.2 Å), (b) 1.5 wt % (21.0 ± 0.1 Å), and (c) 10.0 wt % (20.1 ± 0.1Å) CD$_3$CN. The curves have been offset along the *Y* axis for clarity. Note that the sample in a is crystalline.

and high weight percentage concentrations of acetonitrile, as well as two orientations for acetonitrile molecules in the bromide hydrate (Table 1), are consistent with a subtle change of packing at low concentrations: At the lower concentrations, some salt molecules are not in contact with acetonitrile molecules and others are; thus, a distribution of (related) packing arrangements exists within the phase.

At all concentrations examined, the ^{1}H NMR spectra of the CH$_3$CN solute in the NO$_3^-$ salt show a triplet due to H−H dipolar coupling. Our observation that the NO$_3^-$ salt exhibits a single orientation with respect to the magnetic field is further substantiated by the single quadruple−split doublet in the ^{2}H NMR spectra of solutions containing CD$_3$CN as the solute. Typical spectra of 1.5 and 10 wt % CD$_3$CN are shown in Figure 7. The spectra of the solute in the **1P10Br·H$_2$O** salt also showed a single set of signals for solute concentrations higher than about 1 wt %. However, at ≤1 wt % concentrations, the spectra contained a small additional set of signals, indicating that the **1P10Br·H$_2$O** salt exhibits two orientations. This might indicate that the

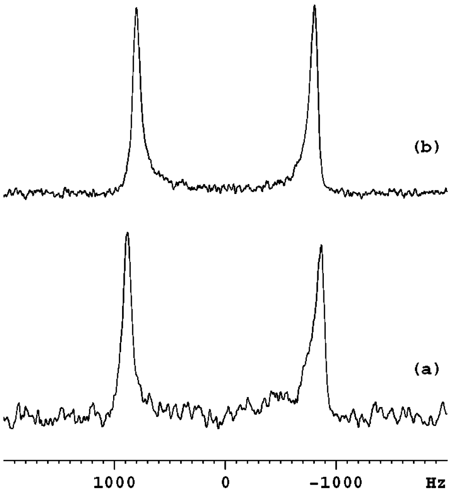

Figure 7. ^{2}H NMR spectra of (a) 1.5 and (b) 10 wt % CD_3CN in **1P10NO$_3$** showing quadrupole split doublets due to orientation.

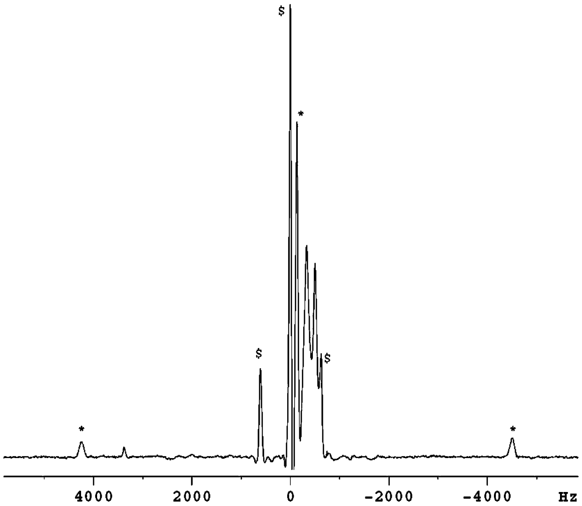

Figure 8. ^{1}H NMR spectrum of 0.7 wt % CH_3CN in **P10Br·H$_2$O** showing two types of solute orientations (lines marked with * and $).

solute molecules are sequestered in two different environments within the singly oriented salt at low solute concentrations. This possibility is supported by the fact that the central peaks in the two orientations do not overlap and are separated by 0.33 ppm. The larger population is associated with the smaller orientation parameter (Figure 8). On the basis of analogous NMR studies of DMSO containing small amounts of water and **1P10Br·H$_2$O** with added DMSO,[22] we strongly suspect that association of some of the acetonitrile molecules with water is responsible for one of the two "orientations".

The HCH angle derived from the H−H and C−H dipolar couplings obtained from two-dimensional HMBC experiments (Figure 9) varied between 110.1° and 110.7° (Table 1) in the liquid-crystalline phases of both **1P10A** salts. The order parameters of the symmetry axis of acetonitrile in the nitrate salt and that of the small orientation in the bromo hydrate are significantly smaller than that in a normal rodlike thermotropic liquid crystal[1,23] but larger than those in an ammonium salt reported earlier.[11] The acetonitrile proton line width decreases by a factor of 2 between 0.7 and 13 wt % in the nitrate salt but still is ca. 10 Hz.

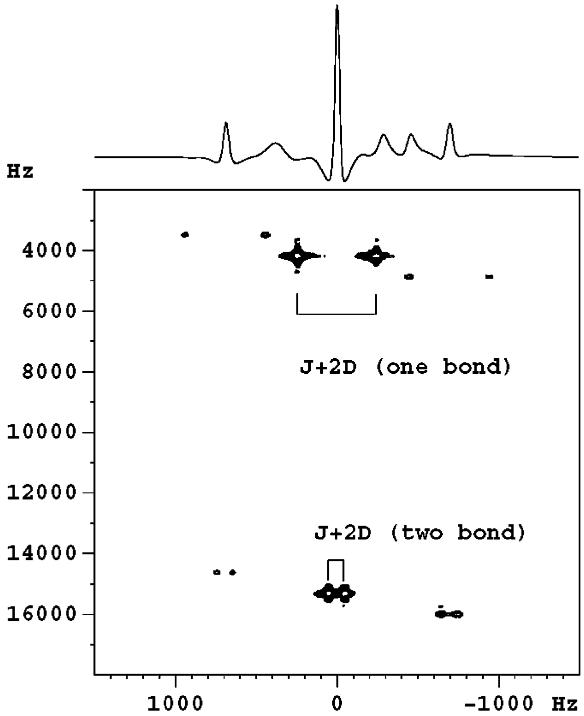

Figure 9. Typical ^{1}H−^{13}C HMBC spectrum of 3 wt % CH_3CN in **1P10NO$_3$** showing one- and two-bond ^{1}H−^{13}C dipolar splittings.

The data in Table 1 show that, when two orientations are present in the bromide hydrate salt host, the order parameters of the symmetry axis of the solute are of opposite sign. The larger orientation parameter provides a value for the HCH bond angle that is lower than that from the lower orientation parameter. The angle calculated in a normal uniaxial thermotropic liquid crystal is nearly 109°.[1] It is interesting to mention that the value of the HCH bond angle in acetonitrile determined in the thermotropic liquid crystal 1,4′(*p*-terphenyl)-bis-[2,3,4-tri(dodecyloxy)benzal]imine is also 109.8°,[24] and that determined in a lyotropic liquid crystal composed of a 25.91:6.24:67.85 (wt/wt/wt) mixture of potassium laurate, decanol, and D_2O is around 109°.[25] The variations of the HCH bond angles in different liquid crystals can be attributed to different solvent−solute interactions.

The results also indicate that the nonmesogenic solute, acetonitrile, induces liquid crystallinity, making the **1P10A** salts amphotropic.[12] Unlike in normal thermotropic liquid crystals, the liquid-crystalline behavior persists even at large concentrations of the "solute". This observation also accounts for the appearance of the mesogenic phase with opposite diamagnetic anisotropy. Thus, both **1P10A** salts form a lyotropic liquid crystal with the nonmesogenic solute acting as one of the ingredients.

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Conclusions

Optical micrographs and X-ray diffractograms of **$1P10Br\cdot H_2O$** and **$1P10NO_3$** confirm that they retain their liquid-crystalline phases, albeit at much lower temperatures, in the presence of as much as ca. 20 wt % of an added solute, acetonitrile.

The low order parameter of the acetonitrile molecules and the amphotropic behavior of the phosphonium salts suggest that these host systems might be useful for structural studies using NMR spectroscopy. In addition, the reduction in the ^1H line width observed when the acetonitrile concentration is increased in the NO_3^- salt suggests that additional “tuning” of these systems might lead to narrower lines that will be amenable to NMR analyses of structures with more complex spins systems. In that regard, we have found that several other small solute molecules, such as dimethyl sulfoxide and methanol, are also lyotropic partners with the **1P10A** salts.[22] Studies on these systems will be reported in the future.

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