Piperidinium, Piperazinium and Morpholinium Ionic Liquid Crystals

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Piperidinium, piperazinium and morpholinum cations have been used for the design of ionic liquid crystals. These cations were combined with several types of anions, namely bromide, tetrafluoroborate, hexafluorophosphate, dodecylsulfate, bis(trifluoromethylsulfonyl)imide, diocysulfosuccinate, dicyclohexylsulfosuccinate, and dihexylsulfosuccinate. For the bromide salts of piperidinium containing one alkyl chain, the chain length was varied, ranging from 8 to 18 carbon atoms \((n = 8, 10, 12, 14, 16, 18)\). The compounds show a rich mesomorphic behavior. High-ordered smectic phases (crystal smectic E and T phases), smectic A phases, and hexagonal columnar phases were observed, depending on the type of cation and anion. The morpholinium compounds with sulfosuccinate anions showed hexagonal columnar phases at room temperature and a structural model for the self-assembly of these morpholinium compounds into hexagonal columnar phases is proposed.

Introduction

Ionic liquid crystals are a fascinating class of materials that combine the properties of both ionic liquids and liquid crystals.\(^1\)–\(^3\) It has been known for a long time that cationic surfactants with long alkyl chains not only exhibit lyotropic mesophases upon addition of a solvent, but that they can also form thermotropic mesophases upon heating.\(^4\)–\(^12\) These quaternary ammonium or phosphonium compounds form typically smectic phases, reflecting their layerlike structure with microphase segregation between the polar parts of the molecules (with the counterions in their vicinity) and the nonpolar parts formed by the molten alkyl chains.\(^13\) Although most of these smectic phases have been identified as smectic A phases, highly ordered smectic phases and crystal smectic phases have been identified as well. Later on, research on ionic liquids has revealed that mesophases are observed for these organic salts if they bear an alkyl chain of a suitable length, typically a dodecyl chain or a longer chain.\(^14\)–\(^19\)

The work on liquid-crystalline ionic liquids has shown that also the choice of the anion has a major influence on the mesophase behavior.\(^1\) Indeed, cationic surfactants contain in general chloride or bromide anions to make them water soluble, whereas for ionic liquids a much wider choice of anions is available. Many ionic liquids contain fluorinated anions like tetrafluoroborate, hexafluorophosphate, or bis(trifluoromethylsulfonyl)imide, which make these solvents hydrophobic. There are also many examples of ionic liquids with metal-containing anions. Until recently, most studies on ionic liquid crystals have been restricted to a limited number of cationic cores. Imidazolium and pyridinium salts have been by far the most popular classes of ionic liquid crystals. It has been realized that variation of the type of cationic core is a very valuable approach for tuning the mesophase behavior of these compounds. For instance, whereas most imidazolium and pyridinium salts show smectic A phases, pyrrolidinium salts show a rich mesomorphism, including highly ordered smectic phases like the crystal smectic E and T phases.\(^20\)

A major difference between the imidazolium and pyridinium salts on one hand and the pyrrolidinium salts on the other hand is that the positive charge is delocalized over the aromatic ring in imidazolium and pyridinium salts, whereas the positive charge is localized on the nitrogen atom of the five-membered heterocyclic pyrrolidinium ring.

In order to explore whether also ionic liquids crystals based on other aliphatic heterocycles exhibit unusual mesophases, we investigated piperidinium, piperazinium, and morpholinium salts, which are all composed of a six-membered heterocycle. To the best of our knowledge, only one study has been previously published on liquid-crystalline piperazinium salts,\(^21\) whereas no examples of liquid-crystalline piperidinium and morpholinium salts have been described in the literature yet. Ionic liquids based on piperidinium, piperazinium, and morpholinium salts have received only limited attention.\(^22\)–\(^28\) A second objective of this work was to develop strategies to lower the melting points of ionic liquid crystals to such an extent that they exhibit a mesophase at ambient temperatures. Therefore, dodecylsulfate and different dialkylsulfosuccinates like dioctylsulfosuccinate, dicyclohexylsulfosuccinate, and dihexylsulfosuccinate have been combined with the cationic cores, besides the more classical anions bromide, tetrafluoroborate, hexafluorophosphate, and bis(trifluoromethylsulfonyl)imide. It has been shown in the literature that replacement of chloride ions by dodecylsulfate anions can lead to a dramatic reduction in the transition temperatures of ionic metallomesogens.\(^29\) Bis(2-ethylhexyl)sulfosuccinate has successfully been used to transform a perylene dye into a liquid-crystalline material with a very wide mesophase range.\(^30\) Materials that show mesophase behavior at room temperature have distinct advantages compared to compounds that melt at high temperatures. These materials are accessible for study by different physical methods and there are no problems with thermal decomposition of the compounds at room temperature. Moreover, ionic liquid crystals with low melting points can find application as anisotropic ionic conductors.\(^31\) In the case of columnar phases, there will be a higher conductivity along the column axis than perpendicular to it. Room-temperature ionic liquid crystals are also being investigated as electrolytes in dye-sensitized solar cells (Grätzel cells).\(^32\)
Experimental Methods

General Information. Defect textures of the mesophases were observed with an Olympus BX60 polarizing microscope equipped with a LINKAM THMS600 hot stage and a LINKAM TMS93 programmable temperature controller. DSC traces were recorded with a Mettler-Toledo DSC822e module (heating/cooling rate of 10 °C min⁻¹; He atmosphere). Powder X-ray diffractograms were recorded on a Bruker AXS D8 Discover diffractometer mounted with a copper X-ray ceramic tube, working at 1.6 kW. The emitted Cu Kα radiation (λ = 1.5418 Å) was focused on the sample by a Göbel mirror. All the samples (without a thermal history) were prepared by spreading the powders on a thin cleaned silicon wafer. Diffractograms were recorded using the Bragg-Brentano reflection geometry (θ/2θ setup) at an angular resolution (in 2θ) of 0.03° per step. The deviation between the temperature on the surface of the sample holder and the set temperature was about 3%. The scattering signal was recorded with a one-dimensional detector (LynxEye detector). Indexation of the powder X-ray diffractograms was performed with the WinXPOW program package with the Index and Refine program using Werner’s TREOR algorithm program (allowed 2θ error in matching the experimentally observed peaks = 0.05°)  \(^{33,34}\). The synthesis of the ionic liquid crystals and their characterization are described in the Supporting Information.

Results and Discussion

An overview of all the piperidinium, piperazinium, and morpholinium compounds that were investigated is given in Scheme 1. The thermal properties of all the compounds were examined by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction on powder samples (PXRD). The transition temperatures and thermal data for all these compounds are summarized in Table 1. For the sake of brevity, dodecylsulfate, bis(trifluoromethylsulfonyl)imide (or bistriflimide), dioctylsulfosuccinate, dicyclohexylsulfosuccinate, and dihexylsulfosuccinate are abbreviated as DOS, NTf₂, DOSS, DcHSS, and DHSS, respectively.

For some compounds, two or more crystalline phases were observed. This is not unusual as crystal polymorphism and the existence of conductive plastic crystal phases (rotationally disordered phases) of pyrrolidinium-based ionic liquids have been reported by several authors in the past. \(^{35-30}\)

For the piperidinium compounds containing one alkyl chain, the bromide salts with short alkyl chains (n = 8–12; 1a–3a, respectively) were not liquid-crystalline. On heating the compounds, a plastic crystalline phase was observed, which transformed into an isotropic liquid upon further heating. The bromide salts with long alkyl chains (n = 14–18; 4a–6a, respectively) showed a crystal smectic T phase. The tetrafluoroborate (4b) and DOS (4e) salts showed a crystal smectic T phase. The hexafluorophosphate (4c) and all the sulfosuccinate (4f, 4g, and 4h) salts were not liquid-crystalline.

For the piperidinium compounds containing two alkyl chains, the bromide (7a), tetrafluoroborate (7b), and hexafluorophosphate (7c) salts showed a crystal smectic E/T phase; the DOS salt (7e) showed a hexagonal columnar phase, while the NTf₂ (7d) and all the sulfosuccinate (7f, 7g, and 7h) salts were not liquid-crystalline.

For the morpholinium compounds, the bromide (8a), tetrafluoroborate (8b), and the DOS (8e) salts showed a crystal smectic E/T phase at lower temperatures and a smectic A phase at higher temperatures (the bromide salt 8a also showed a plastic crystalline phase below the crystals smectic E/T phase). The NTf₂ salt (8d) was not liquid-crystalline. The hexafluorophosphate salt (8c) showed a crystal smectic E/T phase, while all the sulfosuccinate salts (8f, 8g, and 8h) showed a hexagonal columnar phase at room temperature and melted between 120–147 °C to an isotropic liquid.

For the piperazinium compounds, the bromide (9a), tetrafluoroborate (9b), hexafluorophosphate (9c), and NTf₂ (9d) salts were not liquid-crystalline. The DOS (9e) and all the sulfos-
TABLE I: Transition Temperatures and Thermal Data for the Piperidinium, Piperazinium and Morpholinium Salts

<table>
<thead>
<tr>
<th>compd</th>
<th>cation</th>
<th>n°anion</th>
<th>transition ( T ) (°C)</th>
<th>( \Delta H ) (kJ mol(^{-1}))</th>
<th>( \Delta S ) (J K(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a piperidinium 8 Br(^-)</td>
<td>Cr ( \rightarrow ) X</td>
<td>104</td>
<td>30.5</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>2a piperidinium 10 Br(^-)</td>
<td>X ( \rightarrow ) I</td>
<td>198</td>
<td>38.2</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>3a piperidinium 12 Br(^-)</td>
<td>X ( \rightarrow ) I</td>
<td>98</td>
<td>34.5</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>4a piperidinium 14 Br(^-)</td>
<td>Cr ( \rightarrow ) T</td>
<td>88</td>
<td>61.9</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>5a piperidinium 16 Br(^-)</td>
<td>Cr ( \rightarrow ) Cr</td>
<td>76</td>
<td>11.9</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>6a piperidinium 18 Br(^-)</td>
<td>Cr ( \rightarrow ) T</td>
<td>100</td>
<td>75.4</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>4b piperidinium 14 BF(_4)(^-)</td>
<td>Cr ( \rightarrow ) Cr</td>
<td>41</td>
<td>5.4</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>4c piperidinium 14 PF(_6)(^-)</td>
<td>Cr ( \rightarrow ) Cr</td>
<td>82</td>
<td>64.7</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>4d piperidinium 14 NTf(_2)(^-)</td>
<td>Cr ( \rightarrow ) I</td>
<td>86</td>
<td>3.7</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>4e piperidinium 14 DOS</td>
<td>Cr ( \rightarrow ) Cr</td>
<td>51</td>
<td>20.6</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>4f piperidinium 14 DOSS</td>
<td>Cr ( \rightarrow ) Cr</td>
<td>41</td>
<td>6.5</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>4g piperidinium 14 DcHSS</td>
<td>Cr ( \rightarrow ) Cr</td>
<td>56</td>
<td>39.1</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>4h piperidinium 14 DHSS</td>
<td>Cr ( \rightarrow ) I</td>
<td>41</td>
<td>2.0</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>7a piperidinium 14 Br(^-)</td>
<td>Cr ( \rightarrow ) Cr</td>
<td>70</td>
<td>6.9</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>7b piperidinium 14 BF(_4)(^-)</td>
<td>SmX ( \rightarrow ) X</td>
<td>89</td>
<td>62.8</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>7c piperidinium 14 PF(_6)(^-)</td>
<td>SmX ( \rightarrow ) X</td>
<td>80</td>
<td>36.4</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>7d piperidinium 14 NTf(_2)(^-)</td>
<td>SmX ( \rightarrow ) X</td>
<td>119</td>
<td>10.2</td>
<td>16</td>
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<tr>
<td>7e piperidinium 14 DOS</td>
<td>SmX ( \rightarrow ) Cr</td>
<td>114</td>
<td>13.2</td>
<td>25</td>
<td></td>
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<tr>
<td>7f piperidinium 14 DOSS</td>
<td>SmX ( \rightarrow ) Cr</td>
<td>163</td>
<td>16.8</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>7g piperidinium 14 DcHSS</td>
<td>SmX ( \rightarrow ) Cr</td>
<td>53</td>
<td>4.1</td>
<td>11</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \) n is the number of carbon atoms in the terminal alkyl chain(s). \( ^b \) DOS, dodecylsulfate; DOSS, dodecylsulfosuccinate; DcHSS, dicyclohexylsulfosuccinate; DHSS, dihexylsulfosuccinate. \( ^c \) Abbreviations: Cr, Cr\(_1\), Cr\(_2\), Cr\(_3\) = crystalline phase, \( T = \) crystal smectic T phase; Cr\(_h\) = hexagonal columnar phase; SmX = crystal smectic E to T phase; SmA = smectic A phase; I = isotropic liquid; Dec = decomposition. \( ^d \) Onset temperatures obtained by DSC at heating/cooling rates of 10°C min\(^{-1}\) (He atmosphere). For 4c, 7c, 7f, 7h, 8d, and 8i, values were taken from the second heating run. For all other compounds, values were taken from the first heating run. During the first cooling run, 4f, 4g, 4h, 7f, 7g, 7h, 9f, 9g, and 9h were cooled to \(-20\)°C, and all other compounds were cooled to \(25\)°C. \( ^e \) Peak temperature.

uccinate (8f, 8g, and 8h) salts showed smectic A phases and the DcHSS salt (9g) showed an additional crystal smectic E/T phase at lower temperatures.

The smectic A phases and the hexagonal columnar phases were identified on the basis of their optical defect textures, observed by POM. The smectic A phases showed oily streak or focal conic textures (Figure 1); the hexagonal columnar phases showed beautiful pseudo focal conic fan textures with nonmerging extinction crosses (Figure 1). The crystal smectic T phases were identified using POM observations combined with PXRD measurements (see below). The crystal smectic T phases showed lancet textures with large homeotropic domains (Figure 1). The high-ordered mesophases of compounds 7a, 7b, 7c, 8a, 8b, 8c, 8e, and 9g could not be unequivocally identified. The mesophases of these compounds were assigned as being crystal smectic E or T phases (no distinction could be made between the two possibilities). The reason why we assigned the phases as being crystal smectic E/T is as follows. Using POM, lancet, and/or mosaic textures with large (pseudo) homeotropic domains were observed (Figure 1). Together with the fact that these phases were highly viscous, this points at crystal smectic B, E, or T phases. Because of the appearance of large (pseudo) homeotropic domains, tilted high-ordered smectic phases (SmI, SmF, H, G, J, and K phases) could be excluded. In addition, analogous pyrrolidinium ionic liquid crystals only showed crystal smectic T or E phases.20 A hexagonal two-dimensional ordering of the ions seems to be less favorable for such compounds, while ordering of ions in a square or rectangular two-dimensional network with cations and anions at the corners and centers allows a strict alternation of positive and negative charges. Therefore, the phases are most probably crystal smectic E or T (and not hexatic, such as crystal smectic B). Unfortunately, the powder X-ray diffractograms of these compounds did not show a sufficient number of well-resolved diffraction peaks to make a clear distinction between a crystal smectic E or T phase possible (see below). It should be noted that there is only a small difference between these two high-ordered phases. In both cases, the molecules are arranged into layers. Within the layers, the ions are arranged into a rectangular lattice for the crystal smectic E phase, while for the crystal smectic T phase, the ions are arranged into a square lattice (Figure 2).

All the liquid-crystalline piperidinium, morpholinium, and piperazinium compounds were studied by X-ray diffraction on powder samples for further identification of the mesophases and
to obtain more information about the molecular packing in the mesophases. Table 2 gives an overview of the Bragg reflections collected from the X-ray diffractograms of all the mesomorphic compounds.

The diffractograms of the smectic mesophases show several sharp reflections at small angles, which could be indexed as reflections of a hexagonal lattice (for a hexagonal lattice: \( d_{hkl} = a/(\sqrt{3}) \)) (see Table 2). In the wide-angle region, a diffuse signal, centered at about 4.7 Å, was observed, corresponding to the lateral short-range order of the disordered (molten) aliphatic chains. In addition, a weak signal at about 5.0 Å was observed, which was assigned to the stacking periodicity along the columnar axis, \( h \) (see Table 2).

The most interesting part of this study was the observation of room temperature hexagonal columnar phases for the morpholinium compounds with sulfosuccinate counterions. Therefore, the hexagonal columnar phases of the morpholinium compounds deserves a further discussion. Upon the basis of the parameters obtained by PXRD, a molecular model is presented in the following section. Providing the correct repeating distance along the column (\( h \)) is known, the effective number of molecules (\( Z \)) per repeat distance (or slice) can be determined by the relationship between the columnar cross-section area (\( S \)) and the molecular volume (\( V_M \)), according to \( h \cdot S = Z \cdot V_M \). \( V_M \) can be calculated as \( V_M = f(M/0.6022) \), where \( M \) is the molecular mass (g mol\(^{-1}\)) and \( f \) is a temperature correction factor (\( f = \text{the flux} \times 10^{-4}T; T \) is in °C). \( S \) can be deduced from the lattice parameter \( a \) via the relation \( S = a^2/2\sqrt{3} \). Thus, for the hexagonal columnar phases of the morpholinium sulfosuccinate salts 8f, 8g, and 8h, the equivalent of about three molecules are found in a slice that is about 5 Å thick (see Table 2). A molecular model for the hexagonal columnar phase of the morpholinium DHSS salt 8h is shown in Figure 3. By assembling three molecules, a disklike shape is obtained. These discs stack into a column, and the columns are arranged into a hexagonal lattice to form a hexagonal columnar mesophase. The dimensions of the slices are in good agreement with the molecular dimensions of morpholinium compound 8h. The diameter of a column \( 2r = a \) is 27.5 Å (see Table 2), and for the molecular model shown in Figure 3, a value of about 28 Å was
obtained. The molecular packing of the morpholinium compounds 8f and 8h in the hexagonal columnar phases is analogous.

**Conclusions**

We have synthesized the first series of thermotropic ionic liquid crystals based on the piperidinium, morpholinium, and piperazinium cores. These compounds show a rich mesomorphic behavior, including ordered smectic phases (crystal smectic T and E phases), disordered smectic A phases, and hexagonal columnar phases. It was shown for the piperidinium core that a minimum alkyl chain length of 14 carbon atoms was necessary to induce smectic phases. In general, both the cationic core and the anion type have a great influence on the mesomorphic behavior. For the piperidinium compounds, only high-ordered crystal smectic phases were observed (except for the dodecyl-
sulfate salt of the piperidinium compound with two tetradecyl chains, which showed a hexagonal columnar phase. For the piperazinium compounds, only disordered smectic A phases were observed (except for the DeHSS salt, which also showed a high-ordered crystal smectic phase below the smectic A phase). The best results were obtained for the morpholinium compounds, which all showed liquid crystal phases (except the bistriflimide salt). For the large sulfosuccinate salts of the morpholinium compounds, hexagonal columnar phases were observed at room temperature, which were stable over a wide temperature range. Via powder X-ray diffraction and consecutive molecular modeling, it was shown that via self-assembly of three molecules, a disklike shape is obtained, which is suitable for the formation of hexagonal columnar phases.

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Supporting Information Available: Synthesis and characterization of the precursors and the piperidinium, piperazinium, and morpholinium salts. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


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