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Dicyanamide salts that adopt smectic, columnar or bicontinuous cubic liquid-crystalline mesophases

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Abstract

While dicyanamide (i.e., $[N(CN)_2]$) has been commonly used to obtain low-viscosity, halogen-free, room-temperature ionic liquids, liquid-crystalline salts containing such anions have remained virtually unexplored. Here we report a series of amphiphilic dicyanamide salts that, depending on their structures and compositions, adopt smectic, columnar or bicontinuous cubic thermotropic liquid-crystalline mesophases, even at room temperature in some cases. Thermal properties were explored using polarized light optical microscopy, differential scanning calorimetry, thermogravimetric analysis (including evolved gas analysis), and variable-temperature synchrotron X-ray diffraction. A comparison of the thermal phase characteristics of the new liquid-crystalline salts featuring "V-shaped" $[N(CN)_2]$ anions with those of structural analogues containing $[SCN]^-$, $[BF_4]^-$, $[PF_6]^-$ or $[CF_3SO_3]^-$ anions indicated that not only the size of the counterion but also its shape should be considered in the development of mesomorphic salts. Collectively, these discoveries should facilitate the design of thermotropic ionic liquid crystals that form inverted-type bicontinuous cubic and other sophisticated liquid-crystalline phases.

Keywords: liquid crystals, ionic liquids, self-assembly, mesophases, dicyanamide

Introduction

Liquid-crystalline salts or "ionic liquid crystals" (ILCs) have become the subject of intensive research, partially due to the widespread interest in ionic liquids (ILs).^[1-4] The versatility of these materials lies in the fact that they effectively combine the characteristics of liquid crystals (LCs) (e.g., anisotropic physical properties, dynamic molecular order, etc.) with those of ionic liquids (e.g., ionic conductivity, tunable physical properties, negligible vapor pressures under normal conditions, and so forth).^[1] Anion exchange is a relatively straightforward way to influence the viscosities, phase transition temperatures, and other physical properties displayed by ILs and ILCs. As such, a multitude of anions have been employed, including [BF4]⁻, [PF6]⁻, [OTf]⁻ (Tf = CF₃SO₂) and [NTf₂]⁻. While low-viscosity, molten organic salts containing dicyanamide (i.e., [N(CN)₂]⁻) anions were reported about 15 years ago by MacFarlane and co-workers,^[5, 6] only one liquid-crystalline (LC) derivative, 1,3-bis(*n*-dodecyl)-1,2,3-triazolium dicyanamide, has been disclosed thus far to the best of our

knowledge.^[7] The LC salt was reported to exhibit a smectic phase between 82 °C and 102 °C. Unlike commonly used (pseudo)spherical anions, such as Cl⁻, Br⁻, I⁻, [BF₄]⁻, [PF₆]⁻ and [ClO₄]⁻, or linear species, such as [SCN]⁻, the dicyanamide anion is shaped like the letter "V".^[8] Although the mesomeric forms of $[N(CN)_2]^-$ indicate that the negative charge is delocalized over the nitrogen atoms (Figure 1),^[9] the anion retains some Lewis basicity, in contrast to [BF₄]⁻, [PF₆]⁻, [OTf]⁻ and $[NTf_2]^{-}$.^[6, 10, 11] To better understand how the thermal properties displayed by amphiphilic salts are influenced by the $[N(CN)_2]^-$ anion, we describe the synthesis and study of a series of halogen-free dicyanamide salts that were found to adopt smectic, columnar or bicontinuous cubic thermotropic liquid-crystalline mesophases, depending on their structures and compositions. We also compare the thermal phase characteristics of the liquid-crystalline [N(CN)₂]⁻ salts to an analogue outfitted with a linear [SCN]⁻ anion and to structurally related ILCs with [BF₄]⁻, [PF₆]⁻ or [OTf]⁻ anions that have been previously reported.



Figure 1. The two mesomeric forms of the dicyanamide anion.

Results and Discussion

Molecular Design and Synthesis

To access a variety of different types of mesophases, we prepared six different $[N(CN)_2]^-$ salts (1–6) based on a *N,N,N*-trialkyl-*N*-benzylammonium motif (Scheme 1). Three parameters were varied: (i) the number of *n*-alkyloxy chains attached to the benzyl group; (ii) the length of the *n*-alkyloxy chains; and (iii) the size of the alkyl groups in the ammonium headgroup. Analogous liquid-crystalline ammonium salts were previously reported by Kato and co-workers.^[12-16] As part of a series of controls, we also investigated the thermal phase behavior of alkyl-substituted ammonium and imidazolium $[N(CN)_2]^-$ analogues (**7** and **8**, respectively)^[17] and a related $[SCN]^-$ salt (**9**) (Scheme 2).

To synthesize compounds 1-6, either ethyl 3,4-dihydroxybenzoate or ethyl 3,4,5trihydroxybenzoate was first alkylated with 1-bromododecane or 1-bromooctadecane, and then converted into the corresponding benzyl alcohol using LiAlH₄. The latter was treated

with PBr₃ to prepare the corresponding benzyl bromide, which was then used to quaternize either trimethylamine or triethylamine under Menschutkin-type^[18] conditions. The resulting quaternary ammonium bromide salts were subjected to an anion exchange with either (i) $Ag[N(CN)_2]$ (which was prepared from $AgNO_3$ and $Na[N(CN)_2]$) or (ii) $Na[N(CN)_2]$ to form the corresponding dicyanamide salts. Sodium dicyanamide was used instead of silver dicyanamide to prepare 5 and 6 because the respective bromide salt precursors, 5-Br and 6-Br, required elevated temperatures to be dissolved. Subsequent combustion elemental analysis suggested to us that the bromide anions were successfully exchanged for $[N(CN)_2]^{-1}$. Quantitative ¹³C{¹H} NMR analyses, conducted under appropriate measurement conditions and in the presence of a paramagnetic relaxation agent (see the Supporting Information), supported the composition assignments. Likewise, signals were not detected in the Na1s or Br3d electron binding energy regions of the X-ray photoelectron survey spectra (XPS) that were recorded for 5 and 6 (see the Supporting Information). Dicyanamide salt 7 was prepared from the corresponding bromide salt using a slight excess of Ag[N(CN)₂], whereas compound 8 was obtained from Ionic Liquids Technologies (IoLiTec GmbH). Thiocyanate salt 9 was synthesized by reacting bromide salt 4-Br with KSCN in acetone. Additional experimental details and analytical data can be found in the Supporting Information.



Scheme 1. Synthesis of dicyanamide salts 1–6. (i) LiAlH₄, dry THF, r.t., N₂; (ii) PBr₃ (1 M in CH₂Cl₂), dry CH₂Cl₂, 0–5 °C \rightarrow r.t., N₂; (iii) N(CH₃)₃ (2 M in THF) or N(C₂H₅)₃, dry toluene, 90 °C, N₂; (iv) Ag[N(CN)₂] (1.1 eq.), EtOH/CH₃CN (1:1), r.t. \rightarrow 40 °C (for 1–4), or Na[N(CN)₂] (40 eq.), EtOH, 75 °C (for 5–6) (1: 96%, 2: 99%, 3: 99%, 4: 92%, 5: 73%, 6: 64%).



Scheme 2. Dicyanamide salts 7 and 8, and thiocyanate salt 9.

Thermal and Synchrotron X-ray Diffraction Data

The thermal properties of the bromide, dicyanamide and thiocyanate salts were examined by thermogravimetric analysis (TGA), polarized light optical microscopy (POM), and differential scanning calorimetry (DSC). The liquid-crystalline mesophases adopted by dicyanamide salts **1–8** and thiocyanate salt **9** were further investigated by synchrotron X-ray diffraction (XRD) at various temperatures to facilitate full phase identification and determination of the underlying lattice parameters, and to obtain more information about the molecular packing in the respective phases. The synchrotron measurements were performed at the PLS-II 6D UNIST-PAL Beamline of the Pohang Accelerator Laboratory (Pohang, Republic of Korea).

Thermal stability. The TGA measurements revealed that dicyanamide salts **1–6** exhibited higher thermal stabilities under an atmosphere of nitrogen when compared to their bromide salt precursors **1-Br–6-Br** (Figure 2), in accordance with previous results reported for ionic liquids.^[19, 20] Likewise, the *N*-benzyl-*N*,*N*,*N*-trimethylammonium salts were found to be more stable than their *N*-benzyl-*N*,*N*,*N*-triethylammonium analogues. The residual weight percentages recorded at 600 °C were measured to be similar across the series **1–6** as well as **1-Br–6-Br**.



Figure 2. TGA data recorded for (a) bromide salts **1-Br–6-Br** and (b) dicyanamide salts **1–6**, **7**, **8** and **10**^[21] (heating rate of 5 °C min⁻¹; N₂ atmosphere). $T_{1\%}$ represents the temperature at which 1% weight loss was measured (neglecting the initial small weight loss due to the release of H₂O (< 1% for the [N(CN)₂]⁻ salts)).

Evolved gas analysis using a TGA instrument coupled to a mass spectrometer (TGA-MS) showed that the thermal decomposition of the bromide salts at temperatures below 270 °C was accompanied by the evolution of CH₃Br and N(CH₃)₃ or C₂H₅Br and N(C₂H₅)₃ for the benzyltrimethylammonium and benzyltriethylammonium salts, respectively (Figures S14–S15). As such, we concluded that decomposition occurred through a reverse Menschutkin-type reaction where nucleophilic attack of the bromide anions on the benzyltrialkylammonium cations resulted in formation of the corresponding alkyl and benzyl bromide species.^[22] Hofmann elimination products (i.e., ethene and HBr) were not detected during the analysis of the benzyltriethylammonium salts.

The benzylammonium dicyanamide salts exhibited a different decomposition pattern. The TGA-MS data indicated that weight losses observed below 300 °C originated mainly from the expulsion of N(CH₃)₃ (in case of **1**, **3**, and **5**) or N(C₂H₅)₃ (in case of **2**, **4**, and **6**) (Figures 3 and S16). Although Kroon et al. predicted that CH₃-N(CN)₂ formed during the thermal decomposition of $[C_4mim][N(CN)_2]$ ($[C_nmim]^+ = 1$ -alkyl-3-methylimidazolium)^[23] and we

estimated the boiling points of CH_3 -N(CN)₂ and C_2H_5 -N(CN)₂ to be approximately 210 °C at atmospheric pressure from data reported by Benders and Hackmann,^[24] signals attributed to the formation of alkylated dicyanamides were not observed.^[21] Likewise, signals consistent with the formation of ethene or H-N(CN)₂ were not observed during TGA-MS analysis of the benzyltriethylammonium salts, which effectively excluded decomposition *via* Hofmann elimination, Sommelet-Hauser rearrangement or Stevens rearrangement.



Figure 3. TGA-MS data recorded for the dicyanamide salt **4** (heating rate of 5 °C min⁻¹; Ar atmosphere; 'fr.' = fragment, 'alkyl' refers to alkyl fragmentation).

Alkali metal salts containing the $[N(CN)_2]^-$ anion (e.g., $M[N(CN)_2]$; $M^+ = Na^+$, K^+ , Rb^+) have been reported to be stable to temperatures exceeding 300 °C.^[25-27] At higher temperatures, the dicyanamide undergoes trimerization and forms cyclic tricyanomelaminate ions ($[C_6N_9]^{3-}$) that contain the *s*-triazine ring system.^[26-30] FT-IR measurements showed that independently heating salts 4 or $10^{[21]}$ to 225–260 °C (i.e., temperatures that corresponded to the plateau regions in the respective TGA thermograms after the first weight loss event, Figure 2(b); see also Table S2) resulted in the attenuation of the signals recorded between 2300 and 2000 cm⁻¹, which are characteristic of the dicyanamide anion (i.e., v_s (C=N), v_{as} (C-N), $v_s(C-N)$ and $v_{as}(C=N)$) (Figures S21 and S22). This result suggested to us that the dicyanamide-containing species may undergo cyclotrimerization after the expulsion of $N(C_2H_5)_3$. Our conclusion was supported in part by the observation of a weak but clearly discernible exothermic signal in the DSC data obtained from simultaneous TGA-DSC measurements (Figures S18–S20). Moreover, the ¹H and ¹³C NMR spectra recorded for the heat-treated products featured broader peaks as compared to the starting materials (Figures S23–S26). The heat treatment apparently caused the ¹³C NMR signal from the $[N(CN)_2]^{-1}$ anions (centered at ~120 ppm in the starting materials) to disappear. Combustion elemental analyses yielded nitrogen contents that were largely consistent with the retention of the Accepted Manuscrii

dicyanamide-containing species and/or their cyclotrimerization products in the heat-treated materials (Table S3).

The benzyl group should play an important role in the thermal decomposition process of dicyanamide salts **1–6** as $[N(C_{16}H_{33})_2(CH_3)_2][N(CN)_2]$ (**7**) was found to display a significantly higher thermal stability, with the main weight loss occurring between 230 and 320 °C (Figure 2(b)). Similar decomposition temperatures were reported for $[N(CH_3)_4][N(CN)_2]$.^[31] The thermal stability and weight loss evolution of imidazolium salt $[C_{16}mim][N(CN)_2]$ (**8**) resembled that of compound **7** (Figure 2(b)). Finally, TGA analysis revealed that the thiocyanate salt **9** exhibited a significantly lower thermal stability than the analogous dicyanamide salt (i.e., **4**) (Figure S22).

Liquid-crystalline properties. POM and DSC experiments showed that all of the dicyanamide salts described above, except for compound $10^{[21]}$, are thermotropic liquid crystals, and that clearing to their isotropic liquid state occurs below the onset of their thermal decomposition. Thiocyanate salt 9 was also found to be mesomorphic. The different mesophases that were observed will be discussed in more detail below in concert with the results that were obtained from synchrotron XRD measurements. Table 1 summarizes the recorded phase transition temperatures and thermal data. Key XRD data are described in Table 2.

Smectic phases. The XRD patterns of the LC mesophases adopted by compounds 1 and 2 are characterized by three to four sharp reflections in the small-angle region, in addition to a diffuse wide-angle scattering signal centered at 4.5–4.6 Å (= h_1) (Figure 5(a)). The latter corresponds to the lateral short-range order of the molecules and is indicative of their liquidcrystalline nature. The signal could be fitted with a single Lorentzian function; shoulders or additional peaks that would distinguish different distances between the distinct molecular segments were not observed. The reciprocal *d*-spacings of the sharp small-angle reflections relate to each other as 1:2:3(:4) and originate from a layer-like ordering of the molecules (first- and higher-order reflections). This smectic phase type assignment is consistent with the focal conic texture that was observed by POM (Figure 4(a)). For both 1 and 2, good homeotropic alignment was achieved by cooling samples sandwiched between two untreated glass slides from their isotropic liquid states. These observations, in combination with the absence of any sharp XRD signals in the medium- to wide-angle region, are indicative of a smectic A phase (SmA).^[32] There is no in-plane order in a SmA phase, but the relatively intense (002) reflections that were observed for the SmA phases of 1 and 2 suggested to us that adjacent smectic layers in those phases feature well-defined interfaces.^[33] These observations are in agreement with other smectic ILCs that display high translational order but low orientational order.^[1, 34] Dicyanamide salts **7** and **8** also form SmA phases and produce "oily streaks" when viewed by POM (Figures S4 and S5), but with a lower clearing point as compared to **1** and **2** (Table 1). The differences were attributed to a beneficial effect of the benzylammonium architecture on the mesophase stability.

For amphiphilic molecules of this kind, it can be assumed that, due to nanosegregation^{[35,} ^{36]} and strong electrostatic interactions,^[37] the cationic moieties and the $[N(CN)_2]^-$ anions segregate into ionic sublayers with a head-to-head arrangement of the ionic headgroups (Figure 7(a)).^[1, 38] The alkyl chains are homogeneously distributed on either side of the ionrich layers, resulting in an alternation of ionic and aliphatic sublayers. Indeed, when calculating the cross-sectional area (or projection area) $A_{\rm M}(T)$ that is occupied by an elemental molecular assembly within the smectic layers via the relation $N \cdot [V_{mol}(T)/d(T)]$ (with V_{mol} being the molecular volume, d being the layer periodicity measured by XRD, and N being the number of molecules), the values were found to be in agreement with a bilayer structure; for N = 2, at 92 °C: $A_{\rm M} \approx 55.6$ Å² for **1** and $A_{\rm M} \approx 59.8$ Å² for **2**. At this temperature, the crosssectional area of one fully stretched aliphatic chain, σ_{ch} , equals about 22.4 Å²,^[39] indicating that the two molten alkyl chains that are connected to each cation are folded (and possibly partially interdigitated) in the aliphatic sublayers.^[40-43] The slightly larger $A_{\rm M}$ value that was calculated for 2 is consistent with its more voluminous cationic headgroup as compared to 1 (i.e., $-N^{+}(C_{2}H_{5})_{3}$ versus $-N^{+}(CH_{3})_{3}$). Larger ionic headgroups typically result in smaller smectic layer spacings due to increased chain folding and interdigitation in order to achieve a balance between the area of the cationic headgroup/anion assembly that is projected onto the smectic layer planes and the cross-sectional area(s) of the respective alkyl chain(s) attached to the cation.^[42, 44-48] In this case, however, d was found to be similar for the SmA phases adopted by 1 and 2, respectively (Table 2 and Figure 6(a)). The result suggested to us that the bulkier $-N^+(C_2H_5)_3$ headgroups may cause the ionic sublayers to expand in lateral as well as longitudinal directions due to "rippling" or "undulation" (Figure 7(a)). Such an arrangement also explains the less than expected difference in $A_{\rm M}$ between 1 and 2 when considering the estimated projection areas of the $[N(CH_3)_4]^+$ and $[N(C_2H_5)_4]^+$ cations (Table 3). Moreover, the difference in thickness of the ionic sublayers in the SmA phases of 1 and 2, respectively, was estimated to be about 1.8 Å (Figure S16), which is more than would be expected based on the relative sizes of the $-N^+(CH_3)_3$ and $-N^+(C_2H_5)_3$ headgroups (Table 3). The increase of A_M as a function of temperature (Figure 6(a)) was attributed to the known^[49] 'spreading' of the ionic sublayers with increasing temperature, a process that is accompanied by an increased folding of the alkyl chains as reflected in the temperature evolutions of the aliphatic and ionic sublayer thicknesses (Figure S16). The A_M values that were determined for **1** and **2** at temperatures close to their respective isotropization temperatures (based on linear fits of their respective $A_M(T)$ experimental data) are similar: $A_{M,limit}$ is about 63.6–64.0 Å² at 157 °C and 126 °C, respectively (Figure 6(a)). Thus, the breakdown of the ionic sublayers in the SmA phases of **1** and **2** (which feature the same alkyl chain volume per molecule) results in clearing to the isotropic liquid state and is governed by the temperature-dependent, molecular cross-sectional area.^[1, 42, 48, 50] The calculated $A_{M,limit}$ values are larger than those reported for 1-[3,4-bis(hexyloxy)benzyl]-3-methylimidazolium halides (~52.5 Å²)^[48] and for 1-(4-dodecyloxybenzyl)-3-methylimidazolium salts (~42.9–44.1 Å²),^[42] presumably because **1** and **2** each contain two long *n*-dodecyl chains per molecule. It proved challenging to obtain a more detailed structure of the ionic sublayers as the projection area of a *N*-benzyl-*N*,*N*,*N*-tri(m)ethylammonium dicyanamide headgroup is presently not known and, particularly due to the non-spherical shape of the [N(CN)₂]⁻ anion, may depend on its orientation.^[51]

Similar conclusions were obtained by gleaning the XRD data recorded for the SmA phases of compounds **7** and **8** (Table 2, Figures S8 and S9). The significantly different A_M values originate from the different molecular structures (c.f., two alkyl chains connected to the cationic headgroups *versus* one). Higher-order reflections were not observed for these salts in the small-angle region.

Columnar phases. In the small-angle region, the XRD patterns that were recorded for compounds **3**, **4** (at 56 °C), **5** and **6** are characterized by four or five sharp reflections with reciprocal *d*-spacing ratios of $1:\sqrt{3}:2:\sqrt{7}(:3)$ (Figures 5(b)–(c)), which are indicative of a columnar phase with a 2D hexagonal lattice (Col_{hex}). Fan-like textures were seen *via* POM for these Col_{hex} phases (Figures 4(b)–(d)) and, in some cases, large homeotropic areas spontaneously formed upon cooling from the isotropic liquid phase. The diffuse wide-angle X-ray scattering signal centered at 4.5–4.6 Å (= h_1) was fitted with a single Lorentzian function in each case, and sharp wide-angle signals that would indicate a regular stacking of molecules within the columns were not observed. These Col_{hex} phases can therefore be viewed as 'disordered' columnar phases (Col_{hex,d}) in which the columns are formed through nanosegregation and self-assembly of the amphiphilic molecules, with the column centers being composed of the ionic moieties and the periphery of each column being composed of the molten aliphatic chains (Figure 7(b)).

Although no discrete columnar slices exist in the aforementioned structure, it is useful to estimate $N_{\text{hex,slice}}$, which approximates the average number of molecules that self-aggregate to

form a hypothetical slice. Values for $N_{\text{hex.slice}}$ were calculated using the relation $[h_1(T) \cdot S_{hex}(T)]/V_{mol}(T)$ (with S_{hex} being the cross-sectional area of one column, which can be estimated as $(\sqrt{3}/2)a_{\text{hex}}^2$; a_{hex} is the hexagonal lattice parameter (Table 2)). At a particular temperature, a_{hex} is consistently larger for compounds 5 and 6 when compared to 3 and 4, presumably due to the longer *n*-octadecyl chains in the former. The difference in alkyl chain volume fraction between the pairs 3:4 and 5:6 is also reflected in the different relative intensities of the small-angle XRD signals (c.f., Figures 5(b) and 5(c)). The temperature evolution of a_{hex} and $N_{\text{hex,slice}}$ is displayed in Figure 6(b). The parameters a_{hex} and S_{hex} decrease with increasing temperature as a result of increasing chain mobility and disorder, which also leads to a decrease in the value of $N_{\text{hex,slice}}$.^[52] The $a_{\text{hex}}(T)$ and $N_{\text{hex,slice}}(T)$ data that were recorded for 5 and 6 have steeper slopes than that of 3. At 120 °C, $N_{\text{hex.slice}}$ equals about four for compounds 3, 5 and 6 (Figure 6(b), Figure 7(b)). The calculated value is about 2/3 of those previously reported^[48] at the same temperature for two 1-[3,4-bis(alkyloxy)benzyl]-3methylimidazolium bromide salts ($N_{\text{hex,slice}} \sim 6$ and $N_{\text{hex,slice}} \sim 6.5$ for dodecyloxy and octadecyloxy substituents, respectively) and in agreement with the larger number of alkyl chains per molecule in the dicyanamide salts (i.e., three instead of two).

We also found a relationship between $N_{\text{hex,slice}}(T)$ and the clearing points, similar to that described above for the $A_{\text{M,limit}}$ values calculated for the SmA phases. The $N_{\text{hex,slice}}$ values determined for **3**, **5** and **6** are similar at temperatures close to their respective isotropization temperatures. The data suggested to us that at least 3.6–3.7 molecules need to aggregate to form the supramolecular columns in the Col_{hex} phase (Figure 6(b)).

Based on its XRD pattern, the liquid-crystalline phase adopted by thiocyanate salt **9** was also identified as a Col_{hex} phase (POM images can be found in Figure S6). The (21) and (30) reflections or the h_2 scattering signal mentioned above were not observed (Table 2). The $N_{\text{hex,slice}}$ value showed a similar temperature evolution as the dicyanamide salts discussed above (Figure S19).

Bicontinuous cubic phases. In addition to its Col_{hex} phase, another LC mesophase was detected for salt 4. When a pristine POM sample of 4 was heated and annealed, it lost all birefringence (Figure S2) but remained viscous. Further heating caused transition to a higher-temperature Col_{hex} phase and the appearance of a texture (Figures 4(e)–(f) and S3). These observations suggested to us that a cubic, optically isotropic LC mesophase had formed. Judging from the position of the cubic phase in the phase sequence $Cub \rightarrow Col_{hex}$ and from the disappearance of the cubic phase for longer chain lengths (no cubic phase was observed for 6), the possibility of a micellar cubic phase can be excluded and an "inverted-type",

multicontinuous structure can be assumed.^[53-55] The XRD pattern of the cubic phase is displayed in Figures 5(d) and S11. Up to 11 small-angle reflections were observed, with reciprocal *d*-spacing ratios of $\sqrt{6}:\sqrt{8}:\sqrt{14}:\sqrt{16}:\sqrt{20}:\sqrt{22}:\sqrt{24}:\sqrt{26}:\sqrt{38}:\sqrt{48}:\sqrt{50}$. These signals could be indexed as reflections (211), (220), (321), (400), (420), (332), (422), (431), (532) / (611), (444), and (543) from a body-centered cubic lattice with *Ia* $\overline{3}d$ symmetry ('double gyroid phase').^[56] The peak intensity distribution of the XRD pattern, which included an intense reflection at small angles (i.e., (211)) and a progressively decreasing intensity with increasing diffraction angle (up to reflection (400)), matches that of previously reported thermotropic Cub_v(*Ia* $\overline{3}d$) phases adopted by polyphilic LCs.^[57, 58]

The structural model for such cubic phases is based on two interpenetrating, branched 3D networks of opposite chirality, separated by a type G infinite periodic minimal surface (IPMS). Both networks are comprised of short channel segments. Each cubic unit cell contains 24 of those segments, which are linked in a coplanar manner at junctions where three segments join. The differential 3D electron density map that was constructed by Kato, Ungar, Ohno and co-workers for two taper-shaped ILCs with $[BF_4]^-$ or $[PF_6]^-$ anions, respectively, elegantly showed that the anions are located primarily in the center of the channels, close to the cationic headgroups, with the channels being enclosed by the aliphatic continuum.^[14] A similar structure can be envisioned for the $\operatorname{Cub}_{V}(Ia\overline{3}d)$ phase adopted by compound 4. It should be noted that the volume of $[N(CN)_2]^{-1}$ is intermediate that of $[BF_4]^{-1}$ and $[PF_6]^{-1}$ (Table 3), yet with a different shape. Theoretically, the distance between two ternary junctions equals $(1/\sqrt{8})a_{\text{Cub}}$, with a_{Cub} being the cubic lattice parameter. The actual arrangement may be more complex because, at the junctions, the channel segments may not perfectly fuse together and are most probably separated by short gaps^[48, 59-61] which complicates an estimation of the number of molecules that are organized in a cylindrical fashion and bridge two junction points.^[62] Nevertheless, it can be assumed that the local structure of the Col_{hex} phase of **4** is retained during the Colhex-to-Cuby phase transition upon cooling. Douce et al. pointed out that such a transformation may take place through regular column undulations and interconnections, which significantly increase with decreasing temperature.^[48, 63] Similar to that observed during analyses of the columnar phases (see above), a broad scattering signal that was centered at ca. 9.5 Å (i.e., h_2 , see Figure S20) was detected apart from the wide-angle scattering signal h_1 . Finally, by comparing the volume of one cubic unit cell, V_{Cub} , and the molecular volume, $V_{\rm mol}$, we estimated the total number of molecules per cell at a given temperature as $N_{\text{Cub}} \approx V_{\text{Cub}}(T)/V_{\text{mol}}(T)$ (Table 2). As can be seen from Figure 6(c), this number decreases with increasing temperature. The calculated N_{Cub} values were found to be approximately 2/3 of those reported^[48] for 1-[3,4-bis(dodecyloxy)benzyl]-3-methylimidazolium bromide, which contains two alkyl chains per molecule.

Table 1. Phase transition temperatures and thermal data recorded for dicyanamide salts **1–8** and for thiocyanate salt **9**.

| Cpd. | Transition ^[a] | $T (^{\circ}C)^{[b]}$ | Δ <i>H</i> (kJ mol ⁻¹) ^[c] |
|------|---|-----------------------|--|
| 1 | $Cr \rightarrow SmA$ | 78 ^[d] | 30.5 |
| | $SmA \rightarrow Iso$ | 157 | 0.6 |
| 2 | $Cr \rightarrow SmA$ | 66 ^[e] | 27.9 |
| | $SmA \rightarrow Iso$ | 126 ^[f] | 1.3 |
| 3 | $Cr \rightarrow Col_{hex}$ | 22 | 38.0 |
| | $\operatorname{Col}_{\operatorname{hex}} \to \operatorname{Iso}$ | 155 ^[f] | 0.9 |
| 4 | $\operatorname{Cr} \to \operatorname{Cub}_{\operatorname{V}}(Ia\overline{3}d)$ | 24 | 36.1 |
| | $\operatorname{Cub}_{V}(Ia\overline{3}d) \rightarrow \operatorname{Col}_{\operatorname{hex}}$ | 41 | 0.9 |
| | $\operatorname{Col}_{\operatorname{hex}} \to \operatorname{Iso}$ | 84 ^[g] | 1.0 ^[g] |
| 5 | $Cr \rightarrow Col_{hex}$ | 68 | 82.8 |
| | $\operatorname{Col}_{\operatorname{hex}} \to \operatorname{Iso}$ | 145 ^[f] | 0.5 |
| 6 | $Cr \rightarrow Col_{hex}$ | 69 | 76.3 |
| | $\operatorname{Col}_{\operatorname{hex}} \to \operatorname{Iso}$ | 133 ^[f] | 0.4 |
| 7 | $Cr \rightarrow SmA$ | 47 ^[h] | 20.2 |
| | $SmA \rightarrow Iso$ | 83 | 1.5 |
| 8 | $Cr \rightarrow SmA$ | 65 | 68.7 |
| | $SmA \rightarrow Iso$ | 111 | 0.7 |
| 9 | $Cr \rightarrow Col_{hex}$ | 25 ^{[f][i]} | 33.0 |
| | $\operatorname{Col}_{\operatorname{hex}} \to \operatorname{Iso}$ | 91 ^[f] | 0.4 |

^[a] Abbreviations: Cr = crystalline phase; SmA = smectic A phase; Cub_V($Ia\bar{3}d$) = bicontinuous cubic phase (space group $Ia\overline{3}d$); Col_{hex} = hexagonal columnar phase (plane group p6mm); Iso = isotropic liquid phase. ^[b] Onset temperatures obtained by DSC during the second heating run (unless indicated otherwise) at a heating rate of 10 °C min⁻¹ and under an atmosphere of N₂. The first heating run was performed from 25 °C to 165 °C (1–6), 110 °C (7) or 130 °C (8–9); the first cooling was run to -20 °C; subsequent heating/cooling cycles were run between -20 °C and 165 °C (1–6), 110 °C (7) or 130 °C (8–9). ^[c] Enthalpy change. ^[d] During the 2nd heating run, melting was preceded by an endothermic solid-to-solid transition with a peak temperature of 48 °C ($\Delta H = 5.8$ kJ mol⁻¹) and was immediately followed by an exothermic recrystallization event with a peak temperature of 57 °C ($\Delta H = -0.6$ kJ mol⁻¹). ^[e] During the 2nd heating run, melting was preceded by an exothermic recrystallization event with a peak temperature of 34 °C (ΔH = -12.1 kJ mol⁻¹). ^[f] Peak temperature. ^[g] Value from the 1st heating run; no signal was observed during the 2nd heating run. ^[h] During the 2nd heating run, the transition to the SmA phase was preceded by a melting peak ($T_{\text{onset}} = 36 \text{ °C}, \Delta H = 33.8 \text{ kJ mol}^{-1}$) which was immediately followed by an exothermic signal that may stem from rapid recrystallization ($T_{\text{onset}} = 41$ °C, $\Delta H = -4.5 \text{ kJ mol}^{-1}$). ^[i] During the 2nd heating run, melting was preceded by an endothermic solid-to-solid transition with a peak temperature of 10 °C (ΔH = 2.5 kJ mol^{-1}).

Table 2. Summary of synchrotron XRD data recorded for the LC mesophases adopted by dicyanamide salts **1–8** and thiocyanate salt **9**, including calculated structural parameters.

| Cpd. | Type of LC mesophase | <i>T</i> (°C) | d _{obs.} (Å) ^[a] | I ^[b] | hkl ^[c] | $d_{ m calcd.}$ $({ m \AA})^{[m a]}$ | Structural parameters of the LC mesophases ^[d] |
|------|---|-------------------|--------------------------------------|--------------------------|--------------------|---------------------------------------|---|
| 1 | SmA | 92 | 36.65 | VS (sh) | 001 | 36.66 | d = 36.66 Å |
| | | | 18.33 | S (sh) | 002 | 18.33 | $V_{ m mol} pprox 1020 \ { m \AA}^3$ |
| | | | 12.22 | M (sh) | 003 | 12.22 | $A_{\rm M} \approx 55.6 \ {\rm \AA}^2$ |
| | | | 4.5 | br | h_1 | | $\sigma_{ m ch} \approx 22.4 \ { m \AA}^2$ |
| 2 | SmA | 92 | 36.59 | VS (sh) | 001 | 36.58 | d = 36.58 Å |
| | | | 18.30 | S (sh) | 002 | 18.29 | $V_{ m mol} \approx 1093 \ { m \AA}^3$ |
| | | | 12.19 | M (sh) | 003 | 12.19 | $A_{\rm M} \approx 59.8 \ {\rm \AA}^2$ |
| | | | 9.14 | VW (sh) | 004 | 9.15 | $\sigma_{ m ch} \approx 22.4 \ { m \AA}^2$ |
| | | | 4.6 | br | h_1 | | |
| 3 | Col _{hex} | 83 | 32.92 | VS (sh) | 10 | 32.92 | $a_{\rm hex} = 38.01 \text{ Å}$ |
| | | | 18.99 | S (sh) | 11 | 19.00 | $V_{ m mol} \approx 1333 \ { m \AA}^3$ |
| | | | 16.45 | M (sh) | 20 | 16.46 | $S_{\rm hex} = 1251 \text{ Å}^2$ |
| | | | 12.43 | VW (sh) | 21 | 12.44 | $N_{\rm hex,slice} \approx 4.2$ |
| | | | 10.96 | VW (sh) | 30 | 10.97 | |
| | | | 9.1 | br | h_2 | | |
| | | | 4.5 | br | h_1 | | |
| 4 | $\operatorname{Cub}_{V}(Ia\overline{3}d)$ | 45 ^[e] | 35.14 | VS (sh) | 211 | 35.15 | $a_{\rm Cub} = 86.10 \text{ Å}$ |
| | | | 30.43 | S (sh) | 220 | 30.44 | $V_{ m mol} \approx 1367 \ { m \AA}^3$ |
| | | | 23.03 | M (sh) | 321 | 23.01 | $V_{\rm Cub} = 638267 \text{ Å}^3$ |
| | | | 21.54 | M (sh) | 400 | 21.52 | $N_{ m Cub} \approx 467$ |
| | | | 19.26 | M (sh) | 420 | 19.25 | |
| | | | 18.36 | M (sh) | 332 | 18.36 | |
| | | | 17.57 | M (sh) | 422 | 17.58 | |
| | | | 16.89 | M (sh) | 431 | 16.89 | |
| | | | 13.95 | VW (sh) | 532, 611 | 13.97 | |
| | | | 12.43 | VW (sh) | 444 | 12.43 | |
| | | | 12.17 | VW (sh) | 543 | 12.18 | |
| | | | 18 | br (ξ = | $D^{[\mathrm{g}]}$ | | |
| | | | | 10.4 nm ^[f]) | | | |
| | | | 9.5 | br | h_2 | | |
| | | | 4.5 | br | h_1 | | |
| | Col _{hex} | 56 (upon | 33.86 | VS (sh) | 10 | 33.86 | $a_{\rm hex} = 39.10 \text{ Å}$ |
| | | cooling) | 19.54 | S (sh) | 11 | 19.55 | $V_{ m mol} \approx 1388 \ { m \AA}^3$ |
| | | | 16.93 | M (sh) | 20 | 16.93 | $S_{\text{hex}} = 1324 \text{ Å}^2$ |
| | | | 12.80 | VW (sh) | 21 | 12.80 | $N_{\rm hex,slice} \approx 4.3$ |
| | | | 9.4 | br | h_2 | | |
| | | | 4.5 | br | h_1 | | |

| 5 | Col _{hex} | 92 | 37.74 | VS (sh) | 10 | 37.74 | $a_{\rm hex} = 43.58 \text{ Å}$ |
|---|--------------------|----|-------|---------|-------|-------|--|
| | | | 21.80 | M (sh) | 11 | 21.79 | $V_{ m mol} \approx 1782 \ { m \AA}^3$ |
| | | | 18.87 | M (sh) | 20 | 18.87 | $S_{\text{hex}} = 1645 \text{ Å}^2$ |
| | | | 14.26 | M (sh) | 21 | 14.26 | $N_{\rm hex, slice} \approx 4.2$ |
| | | | 12.58 | W (sh) | 30 | 12.58 | |
| | | | 11.1 | br | h_2 | | |
| | | | 4.6 | br | h_1 | | |
| 6 | Col _{hex} | 92 | 38.44 | VS (sh) | 10 | 38.44 | $a_{\rm hex} = 44.39 \text{ Å}$ |
| | | | 22.18 | M (sh) | 11 | 22.19 | $V_{ m mol} \approx 1855 \ { m \AA}^3$ |
| | | | 19.22 | M (sh) | 20 | 19.22 | $S_{\text{hex}} = 1706 \text{ Å}^2$ |
| | | | 14.53 | M (sh) | 21 | 14.53 | $N_{\rm hex,slice} \approx 4.2$ |
| | | | 12.81 | W (sh) | 30 | 12.81 | |
| | | | 11.1 | br | h_2 | | |
| | | | 4.6 | br | h_1 | | |
| 7 | SmA | 80 | 29.34 | VS (sh) | 001 | 29.34 | <i>d</i> = 29.34 Å |
| | | | 4.5 | br | h_1 | | $V_{ m mol} \approx 970 \ { m \AA}^3$ |
| | | | | | | | $A_{\rm M} \approx 66.1 \ {\rm \AA}^2$ |
| | | | | | | | $\sigma_{ m ch} \approx 22.2 \ { m \AA}^2$ |
| 8 | SmA | 80 | 34.14 | VS (sh) | 001 | 34.14 | <i>d</i> = 34.14 Å |
| | | | 4.5 | br | h_1 | | $V_{\rm mol} \approx 646 \text{ Å}^3$ |
| | | | | | 1 | | $A_{\rm M} \approx 37.8 \text{ Å}^2$ |
| | | | | | | | $\sigma_{\rm ch} \approx 22.2 \ {\rm \AA}^2$ |
| 9 | Colhar | 60 | 33.45 | VS (sh) | 10 | 33.45 | $a_{\rm hor} = 38.63 \text{ Å}$ |
| - | nex | 20 | 19.28 | S(sh) | 11 | 19.31 | $V_{\rm mol} \approx 1369 \text{ Å}^3$ |
| | | | 16.71 | M (sh) | 20 | 16.73 | $S_{\text{hex}} = 1292 \text{ Å}^2$ |
| | | | 4.5 | br | h_1 | | $N_{\rm hexslice} \approx 4.2$ |
| | | | | | - | | non,since |

^[a] The $d_{obs.}$ and $d_{calcd.}$ values refer to the measured and calculated diffraction spacings, respectively. For the SmA phases: $d_{\text{calcd.}} = \langle d_{001} \rangle = [\Sigma_l d_{00l} l] / N_{00l}$, in which N_{00l} = the number of (00*l*) reflections. For the Col_{hex} phases: $d_{hk,\text{calcd.}} = [(\sqrt{3}/2)a_{\text{hex}}]/(h^2 + k^2 + hk)^{V_2}$, in which the hexagonal lattice parameter a_{hex} was calculated from the peak position of the most intense reflection at the smallest Bragg angle (i.e., (10)). For the Cub_V phase: $d_{hkl,\text{calcd.}} = d_{hkl,\text{calcd.}} = d_{hkl,\text{calcd.}}$ position of the most interse reflection at the smallest Bragg angle (i.e., (10)). For the Cuby phase, $a_{hkl,calcd.} = a_{Cub}/(h^2 + k^2 + l^2)^{\frac{1}{2}}$, in which the cubic lattice parameter a_{Cub} was calculated from the peak positions of all observed reflections. ^[b] I is the intensity of each reflection: VS, very strong; S, strong; M, medium; W, weak; VW, very weak; sh, sharp reflection; br, broad reflection. ^[c] hkl are the Miller indices of the reflections. h_1 indicates the center position of the diffuse wide-angle signal. h_2 : see text. D: see text. ^[d] V_{mol} is the molecular volume. Due to the lack of dilatometry data, $V_{mol}(T)$ was estimated as (M/0.6022)f, in which M is the molecular mass (in g mol⁻¹) and f is a temperature-correcting factor ($f = 0.9813 + 7.474 \times 10^{-4}T$ with T in °C) (see Section 4.1 in the Supporting Information). $A_{\rm M}$ is the cross-sectional molecular area as calculated from $A_{\rm M}(T)$ = $2V_{\rm mol}(T)/d(T)$ (see text). $\sigma_{\rm ch}$ is the cross-sectional area of one fully stretched aliphatic chain.^[39] $a_{\rm hex}$ is the hexagonal lattice parameter. S_{hex} is the 2D hexagonal lattice area, i.e. the cross-sectional area of one column in the Col_{hex} phase (= $(\sqrt{3}/2)a_{hex}(T)^2$). $N_{hex,slice}$ is the number of molecules within one hypothetical slice of a column in the Col_{hex} phase, with an assumed height h_1 , and was estimated as $[h_1(T) \cdot S_{hex}(T)]/V_{mol}(T)$ (see text). a_{Cub} is the cubic lattice parameter. V_{Cub} is the volume of the cubic cell (= $a_{\text{Cub}}(T)^3$). N_{Cub} is the number of molecules within the cubic cell and was estimated as $V_{\text{Cub}}(T)/V_{\text{mol}}(T)$. For comparison, $N_{\text{hex,slice}}$ and N_{Cub} were also estimated using crystal volume increments and similar values were obtained, see Section 4.1 in the Supporting Information.^[e] The XRD pattern was recorded during the first heating run of a pristine sample. Table 1 lists the onset temperature of the Cub_V-to-Col_{hex} phase transition in the second heating run as 41 °C. Using POM and DSC, we found that, for a pristine sample, the cubic phase can exist until higher temperatures (by up to 20 °C) than for samples that had been previously heated to > 100 °C. We attribute the difference to the presence of small amounts of water that effectively stabilize the microphase-segregated mesophase.^[64, 65] Although all samples were dried before analysis, the uptake of atmospheric moisture could not be avoided. ^[f] ξ : correlation length as

estimated from the Scherrer equation with the shape factor K taken as 0.9. ^[g] The origin of this broad signal centered at about 18 Å (Figure 5(d)) is unclear.

| | Table 3. Sizes | of selected ions | s that are commonly | present in ILCs. |
|--|----------------|------------------|---------------------|------------------|
|--|----------------|------------------|---------------------|------------------|

| Ion ^[a] | Ionic radius, $r_{int}(\text{\AA})^{[b]}$ | $\frac{\text{Ionic}}{V_{\text{ion 1}}}$ | v volume, V_{ion} | (\AA^3) $V_{\text{ion 3}}^{[e]}$ | Projection area, $G_{\rm int} ({\rm \AA}^2)^{[f]}$ |
|--|--|---|-----------------------|--|--|
| | | ' 1011,1 | · 1011,2 | 1011,5 | |
| СН ₃ Н ₃ С- ^{N,} ,СН ₃ СН ₃ | 2.83 [66] | 95 ^[66] | 113 [67] | _ | 25 |
| $C_{2}H_{5}$ $H_{5}C_{2} \sim N_{1}^{+}C_{2}H_{5}$ $C_{2}H_{5}$ | 3.43 [66] | 170 [66] | 199 [67] | _ | 37 |
| H ₃ C∼ _N → N [−] CH ₃ | _ | _ | 129 [68] | _ | - |
| cı⁻ | 1.81 [69] | 25 | 47 [67] | _ | 10 |
| Br ⁻ | 1.96 [69] | 32 | 56 [67] | 42 [70] | 12 |
| r. | 2.20 [69] | 45 | 72 [67] | _ | 15 |
| N ^{EC-N} CN | _ | _ | 89 [68] | 79 ^[70] | _ |
| F I F F | 2.29 [66] | 51 [66] | 73 ^[67] | 69 ^[70] | 16 |
| F, I, F F″I∿F F″I∿F F | 2.54 ^[66] | 69 ^[66] | 109 [67] | 96 [70] | 20 |
| F ₃ C-SO ₃ | _ | 82 [66] | 131 [68] | 112 [70] | _ |
| $\left[F_{3}CO_{2}S^{N}SO_{2}CF_{3}\right]$ | _ | 144 [66] | 232 [68] | 208 [70] | _ |
| [s-c≡n] [¯] | _ | _ | 71 [67] | _ | _ |
| NEC-Ag-CEN | _ | _ | 110 [71] | _ | _ |

^[a] Only one canonical resonance structure is shown for $[N(CN)_2]^-$ and $[SCN]^-$. ^[b] Listed for (pseudo)spherical ions. Cl⁻, Br⁻, I[:] r_{ion} as found in ionic crystals.^[69] $[N(CH_3)_4]^+$, $[N(C_2H_5)_4]^+$, $[BF_4]^-$, $[PF_6]^-$: r_{ion} as estimated by Ue.^{[66] [c]} $V_{ion,1}$: calculated as $(4/3) \cdot \pi \cdot r_{ion}^{-3}$. Cl⁻, Br⁻, I[:] based on the value for r_{ion} in the second column of the table. $[N(CH_3)_4]^+$, $[N(C_2H_5)_4]^+$, $[N(C_2H_5)_4]^+$, $[N(C_2H_5)_4]^+$, $[BF_4]^-$, $[PF_6]^-$, $[OTf]^-$, $[NTf_2]^-$: values reported by Ue.^{[66] [d]} $V_{ion,2}$: 'effective close-packing ion volume' in ionic crystals as reported by Jenkins, Glasser, Passmore and Marcus.^[67, 68, 71, 72] The values that were selected for $[N(CN)_2]^-$, $[OTf]^-$ and $[NTf_2]^-$ in ref. 68 came from ref. 73. ^[e] $V_{ion,3}$: ion volume as determined by AIM partitioning of electron density distributions that were reconstructed from the single-crystal XRD data recorded for $[C_{14}mim][X]$ salts, as reported by Nelyubina et al.^{[70] [f]} Estimated for ions whose shape can be approximated as a sphere using the equation: $\sigma_{ion} = \pi \cdot r_{ion}^2$ (where the value of r_{ion} is that listed in the second column of the table).



Figure 4. Polarized light optical microscopy images as viewed through crossed polarizers and their respective descriptions: (a) focal conic texture of the SmA phase of **1** at 97 °C; (b) fan-like texture of the Col_{hex} phase of **6** at 105 °C after cooling from its isotropic liquid state; (c) pseudo-focal conic fan-shaped texture of the Col_{hex} phase of **3** at 140 °C; (d) fan-shaped texture of the Col_{hex} phase of **3** at 140 °C; (e) Col_{hex} phase and (f) cubic phase of **4** at 70 °C and at 40 °C, respectively, after cooling (the texture in (f) at the edge of the sample originates from a small region of remaining Col_{hex} phase). Additional POM images can be found in the Supporting Information.



Figure 5. (a) X-ray diffraction profile of **2** recorded at 92 °C (SmA phase). (b) X-ray diffraction profile of **3** recorded at 83 °C (Col_{hex} phase). (c) X-ray diffraction profile of **6** recorded at 92 °C (Col_{hex} phase). (d) Small-angle X-ray diffraction profile of **4** recorded at 45 °C ($Cub_V(Ia\bar{3}d)$ phase) (see also Figure S20). In all cases, the X-ray wavelength used was 1.00 Å.



Figure 6. (a) Evolution of the layer thickness, *d*, and of the "molecular area", A_M , as a function of temperature for the SmA phases adopted by **1** and **2**. The clearing points T_c of **1** and **2** are indicated by vertical dashed lines. (b) Evolution of the hexagonal lattice parameter, a_{hex} , and of the number of molecules within one hypothetical slice of a column, $N_{hex,slice}$, as a function of temperature for the Col_{hex} phases adopted by **3**, **5** and **6**. The clearing points T_c of **3**, **5** and **6** are indicated by vertical dashed lines. (c) Evolution of the cubic lattice parameter, a_{Cub} , and of the number of molecules within the cubic cell, N_{Cub} , as a function of temperature for the Cub_V($Ia\bar{3}d$) phase adopted by **4** during the first heating run of a pristine sample (see text).



Figure 7. (a) Structural model of the SmA phases adopted by dicyanamide salts 1 and 2. Undulation of the central ionic sublayers (represented here as a wavy ribbon) may occur to a greater extent for compound 2, which features a relatively bulky benzyltriethylammonium cationic headgroup (see text). (b) Structural model for the Col_{hex} phase adopted by dicyanamide salt 4. The outer, solid circle delineates the cross-section of one supramolecular column in the columnar phase. The inner, dashed circle may reflect a non-aliphatic column center that is composed of the cationic benzyltrialkylammonium headgroups and the $[N(CN)_2]^-$ anions. Efficient space-filling is ensured by interdigitation of alkyl chains from neighboring columns. The column cross-sections may be elliptical as the 2D *p6mm* symmetry was inferred from space- and time-averaged XRD data. The model is an approximation as discrete columnar slices are unlikely to exist in highly dynamic Col_{hex} phases formed by flexible amphiphilic salts. It can be assumed that the minicylinders in between ternary junctions in the Cub_V phase of **4** show a similar local molecular arrangement. Comparable conclusions may be drawn for the structures of the Col_{hex} phases adopted by salts **3**, **5** and **6**.

Discussion

The evolution from the lamellar phases adopted by **1** and **2** through the bicontinuous cubic and columnar phases of **3** and **4** to the exclusively columnar mesomorphism exhibited by **5** and **6** results from a progressively increasing curvature of the interface between the incompatible molecular segments. Such mesophase behavior can be explained by the Israelachvili theory of self-assembling hydrocarbon amphiphiles.^[74] Similar phase sequences have been observed for other thermotropic LC amphiphiles, and analogies to lyotropic systems have been drawn.^[35, 53] It should be noted that we did not find a micellar cubic phase, Cub_I, for salts **5** and **6** upon heating; rather, in both cases, the Col_{hex} phase cleared directly to the isotropic liquid state. Cheng et al. observed Cub_I($Pm\bar{3}n$) phases for some taper-shaped imidazolium-based mesogens with three long alkyl chains and a short *N*-terminal chain (ethyl or *n*-propyl) on the imidazolium cations.^[75, 76] The taper angles of compounds **5** and **6** are presumably not appropriate to form a stable micellar cubic phase. We surmise that the trialkylammonium headgroups also hinder close packing in micelles with polar cores. Dendromesogens with trialkylammonium chloride apices, reported by Percec and co-workers, also did not show micellar cubic phases, although analogues with imidazolium or pyridinium headgroups did exhibit $\text{Cub}_1(Pm\bar{3}n)$ phases.^[77]

The appearance of a cubic phase for salt 4 and its apparent absence for the structurally similar compound **3** merit further comment. The importance of the triethylammonium motif in bicontinuous cubic LC materials was discovered by Kato and co-workers, who semiquantitatively explained the key contributors to mesophase formation in terms of molecular geometry.^[14] Theoretical dV/dr profiles showing the average radial distribution of volume for an optimal molecular packing were constructed by Ungar and co-workers for a variety of mesophases, including Col_{hex} , $\operatorname{Cub}_V(Ia\overline{3}d(G))$, $\operatorname{Cub}_V(Im\overline{3}m(P))$, $\operatorname{Cub}_V(Im\overline{3}m(I))$ and $\operatorname{Cub}_{V}(Pn\overline{3}m(D))$ phases.^[57, 78, 79] Close to the central axis of the cylindrical columns or network segments that are present in such phases, i.e. for small values of r, the profiles are similar but not identical. Benzyltriethylammonium salts with three chains of appropriate size and with suitable anions display cross-sectional area profiles, A(r), that match those of bicontinuous cubic phases (i.c., the double gyroid phase) due to the three additional methylene groups near their apices in comparison to the corresponding trimethylammonium salts. Similarly, it had previously been demonstrated that alkali metal dihexadecylphosphates, which all show a Col_{hex} phase, exhibit an additional $\operatorname{Cub}_{V}(Ia\overline{3}d)$ phase when matched with larger alkali metal cations (i.e., K^+ , Rb^+ and Cs^+).^[80] The enantiotropic Cub_V($Ia\overline{3}d$) phase at low temperatures that was previously reported for benzyltriethylammonium salts with either $[BF_4]$ or $[PF_6]$ anions^[12-14] is also found for dicyanamide salt **4**.

As mentioned above, the volume of $[N(CN)_2]^-$ is intermediate that of $[BF_4]^-$ and $[PF_6]^-$ (Table 3), but its shape is different. The difference may be important in thermotropic LCs as efficient space-filling needs to be achieved in the LC state. The latter is less important in conventional lyotropic LC systems, where water molecules can fill gaps of any shape. To the best of our knowledge, the only other examples of ILCs containing relatively small, nonmesogenic, V-shaped anions are the $[C_n mim][F(HF)_2]$ and $[C_n mpyrr][F(HF)_2]$ ($[C_n mpyrr]^+ =$ *N*-alkyl-*N*-methylpyrrolidinium) salts that were reported by Xu et al. and which show only SmA phases.^[81-83] Our results demonstrate that the thermotropic Cub_V($Ia\overline{3}d$) structure adopted by taper-shaped ionic amphiphiles, such as **4**, is apparently compatible with different anion shapes, at least for moderately sized anions. Bulky $[NTf_2]^-$ anions (which are conformationally flexible but can also adopt a bent shape) have already been incorporated in bicontinuous cubic mesophases formed by low molar mass ionic and zwitterionic LCs but, in those cases, the anions were located primarily on an infinite periodic minimal surface (IPMS), where the steric restrictions are less severe than inside the polar channels of an inverted-type Cub_V phase.^[84-90]

We also note that thiocyanate salt **9** exhibits only a Col_{hex} phase. Samples of compound **9** were heated and cooled at different rates (down to 1 °C min⁻¹) but, in all cases, evidence for a cubic phase was not observed by POM or XRD. Since the [SCN]⁻ ion is similar in volume to [BF₄]⁻ (Table 3), the result may be due to a shape effect as linear counterions may not be compatible with thermotropic, inverted-type $\operatorname{Cub}_V(Ia\overline{3}d)$ phases. Presumably linear anions cannot efficiently fill the space in the junction regions where three channel segments in the cubic phase come together.

Inspection of the comparative LC data presented in Table S4 revealed the following structure-property relationships for ILCs with N,N,N-triethyl-N-(3,4,5-tris(ndodecyloxy)benzyl)ammonium cations and $[SCN]^2$, $[BF_4]^2$, $[N(CN)_2]^2$, $[PF_6]^2$ or $[OTf]^2$ anions: (i) a bicontinuous cubic phase is only found for the salts featuring moderately sized and pseudospherical or V-shaped $[BF_4]^-$, $[N(CN)_2]^-$ or $[PF_6]^-$ anions, and not for derivatives with linear [SCN]⁻ or [OTf]⁻ anions; (ii) a Col_{hex} phase is observed for the [SCN]⁻ salt but the mesomorphic properties vanish for the [OTf]⁻ derivative; (iii) the melting as well as the clearing point of the $[N(CN)_2]^{-1}$ salt are lower than those of the $[BF_4]^{-1}$ salt, which appears to be in line with the generally observed evolution of phase transition temperatures with increasing anion size,^[1] although the [SCN]⁻, $[PF_6]^-$ and $[OTf]^-$ salts deviate from this behavior. Given the fact that the benzyltriethylammonium [OTf]⁻ salts that are listed in Table S4 are not LC, it may be expected that the corresponding salts with an even bulkier $[NTf_2]^-$ anion may also not exhibit mesomorphic characteristics. Structurally related ILCs with a 1-methylimidazolium headgroup and $[OTf]^{-}$ or $[NTf_2]^{-}$ anions only adopt enantiotropic Col_{hex} phases when three very long alkyl chains are attached to the cation (i.e., *n*-hexadecyl or *n*-octadecyl).^[91]

When comparing the phase transition temperatures of salts 1 and 2 with those of 7 and 8, the benzylammonium-based molecular architecture with two alkyl chains facilitated the formation of SmA phases with higher clearing points (i.e., they exhibited higher thermodynamic stabilities) than those adopted by other alkyl-substituted salts. To the best of our knowledge, N,N,N-trialkyl-N-[3,4-bis(alkyloxy)benzyl]ammonium cations have not yet been used to prepare ionic mesogens.

The analogue of compound **8** with relatively bulky $[NTf_2]^-$ anions, i.e. $[C_{16}mim][NTf_2]$, is not LC.^[44] Although 1,3-bis(*n*-dodecyl)-1,2,3-triazolium dicyanamide shows a smectic phase between 82 °C and 102 °C,^[7] and the 1,3-bis(*n*-dodecyl)imidazolium salts with Γ , $[BF_4]^-$ or $[ClO_4]^-$ counterions exhibit SmA phases,^[92, 93] 1,3-bis(*n*-dodecyl)imidazolium dicyanamide does not exhibit LC properties.^[93] $[C_{14}mim][N(CN)_2]$ is also not LC,^[70] while the corresponding $[NO_3]^-$, $[BF_4]^-$, $[PF_6]^-$ and $[ClO_4]^-$ salts are mesomorphic.^[1] We report here that salt **8**, with a slightly longer alkyl chain than $[C_{14}mim][N(CN)_2]$, shows a SmA phase. The fact that mesomorphism was observed for a chain length of 14 carbon atoms in the series $[C_nmim][PF_6]$ and that a longer alkyl chain is required in the series $[C_nmim][N(CN)_2]$, despite the smaller volume of the $[N(CN)_2]^-$ anion (Table 3), indicates that not only the size of the counterion^[94] but also its shape should be considered in the design of an ILC.

Finally, it is important to note that salt **7** shows a SmA phase, which lacks long-range intralayer ordering, whereas its bromide salt precursor is known to form a crystal smectic T phase with 2D square ordering of the polar headgroups within the ionic sublayers.^[95] Much in the same way as a linear [SCN]⁻ anion was found to be incompatible with such a tight packing arrangement (in contrast to Br⁻, $[BF_4]^-$ and $[PF_6]^-$),^[46] the $[N(CN)_2]^-$ anions may disrupt intralayer ordering and cause the appearance of a SmA phase instead.

Conclusions

We describe the first series of ionic mesogens outfitted with halogen-free dicyanamide anions that adopt smectic, columnar or bicontinuous cubic thermotropic LC mesophases depending on their structures and compositions. These compounds cover the most common, microphase-segregated mesophase morphologies displayed by thermotropic LC amphiphiles, with the exception of micellar cubic phases. Synchrotron XRD experiments facilitated elucidation of the molecular packing arrangements in the different types of mesophases.

The dicyanamide-based ILCs represent rare examples of LC salts with *V-shaped* anions. The bent shape was found to influence the presence, stability range, and intralayer structural order of lamellar phases. For example, salt **7** shows a SmA phase instead of the ordered crystal smectic T phase adopted by its bromide analogue. On the other hand, the V-shaped anions appeared to be compatible with the inverted-type columnar and bicontinuous cubic mesophases adopted by the taper-shaped benzylammonium dicyanamide salts **3–6**. For comparison, cubic phases were not observed for salt **9**, which features a *linear* thiocyanate

anion. Our results reveal the importance of the *shapes* of anions in ionic mesogens, in addition to their *size* (volume).

To the best of our knowledge, this is also the first study addressing the thermal stability of N,N,N-trialkyl-N-benzylammonium dicyanamide salts.^[96] Data from TGA and TGA-MS measurements indicated that the initial stage of thermal degradation (below 300 °C) of compounds **1**–**6** is specific to the benzylammonium motif and involves the expulsion of tri(m)ethylamine as well as further reaction of the cyano groups present in the dicyanamide moieties.

We are currently exploring ways to induce polymerization of the $[N(CN)_2]^-$ anions within the temperature ranges of the different mesophases, in order to obtain templated, nitrogen-rich carbon materials. The Lewis basicity of the $[N(CN)_2]^-$ anions could also be exploited when these ILCs are used as organized media to facilitate selective, base-catalyzed chemistry.

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TOC Graphic and Text



Ionic liquid crystals with "V-shaped" anions: A series of halogenfree, amphiphilic dicyanamide (i.e., $[N(CN)_2]$) salts were found to adopt smectic, columnar as well as bicontinuous cubic thermotropic liquid-crystalline mesophases, even at room temperature in some cases. The results show that not only the size of the anions, but also their shape play important roles in determining the thermal phase characteristics displayed by ILCs, a design parameter that is often neglected. The thermal decomposition pathways of the dicyanamide salts were also studied.

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