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Influence of the Counteranion on the Ability of 1-Dodecyl-3-methyltriazolium Ionic Liquids to Form Mesophases

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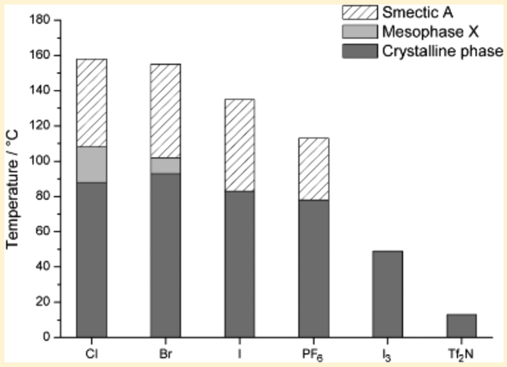
Supporting Information

ABSTRACT: The influence of the counteranion on the ability of the mesogenic cation 1-methyl-3-dodecyl-triazolium to form mesophases is explored. To that avail, salts of the cation with anions of different size, shape, and hydrogen bonding capability such as Cl^-, Br^-, I^-, I_3^-, PF_6^-, and Tf_2N^- [bis(trifluorosulfonyl)amide] were synthesized and characterized. The crystal structures of the bromide, the iodide, and the triiodide reveal that the cations form bilayers with cations oriented in opposite directions featuring interdigitated alkyl tails. Within the layers, the cations are separated by anions. The rod-shaped triiodide anion forces the triazolium cation to align with it in this crystal structure but due to its space requirement reduces the alkyl chain interdigitation which prevents the formation of a mesophase. Rather the compound transforms directly from a crystalline solid to an (ionic) liquid like the analogous bis(trifluorosulfonyl)amide. In contrast, the simple halides and the hexafluorophosphate form liquid crystalline phases. Their clearing points shift with increasing anion radius to lower temperatures.



INTRODUCTION

Ionic liquid crystals (ILCs) combine the research fields of liquid crystals (LCs) and ionic liquids (ILs).[1] ILs, salts with a melting point below 100 °C, show unique properties such as low vapor pressure, wide liquid range, good thermal stability, and ionic conductivity.[2] Due to the ionic composition, ILs are widely tunable by variation of cations and anions. This adjustability is advantageous for several applications and the reason for the name "designer solvents".[3] Initially applied in electrochemistry,[4] they have received considerable attention as alternative solvents in chemical synthesis.[5] With certain structural compositions, ILs may exhibit liquid crystalline phases and thus are then called ionic liquid crystals (ILCs). One of the most important properties of liquid crystals is the anisotropy of their physical and chemical properties.[6] Ionic liquid crystals are promising candidates for electrolytes in dye-sensitized solar cells,[7] self-assembled nanomaterials,[8] as ordered solvents,[9] as switchable fluids,[10] and as soft luminescent and magnetic materials.[11] In recent years, a number of cation types for ionic liquid crystals have been developed,[12] but still by far, the most commonly used are imidazolium cations. For many imidazolium-based salts, the influence of the chain length and of the symmetry of the cation on the phase behavior has been intensively studied.[13] Although it was found that the cation plays a decisive role in determining the phase behavior, it was realized that a variation in the anion also may substantially alter the mesomorphic properties.[11] The role of the anion has been analyzed for different imidazolium-based ILs and ILCs.[14−17] For the 1,3-didodecylimidazolium cation, smectic A phases were observed for the bromide, iodide, tetrafluoroborate, and perchlorate anions,[15,18,19] whereas no liquid crystalline behavior was observed with other anions like triiodide, dicyanamide, hexafluoroantimonate,[15] or bis(trifluorosulfonyl)amide.[20] In the case of the 1,3-di(dodecyl)imidazolium cation, $[C_{12}C_{12}Im]^+$, the anion is able to alter the cation conformation from U-shaped, to rod-shaped or V-shaped. We have made similar observations for the didodecyltriazolium cation.[21] Two totally different conformations were found in the crystal structure of the bromide (U-shaped) and the triiodide (rod-shaped). Even a small change from bromide to iodide affected not only the phase transition temperatures but also the type of the adopted mesophase. Other prominent IL cation systems also show a strong anion-dependent phase behavior.[22]

For that reason, we synthesized and characterized methyl-dodecyltriazolium salts with different anions, which allows us to examine the effect of the anion on the liquid crystalline behavior in detail. Anions of different sizes, symmetry and hydrogen bonding capability were chosen: Cl^-, Br^-, I^-, I_3^-, PF_6^-, and Tf_2N^- (Figure 1). The halide anions Cl^-, Br^-, and I^- are ideally spherically shaped anion of decreasing ion strength

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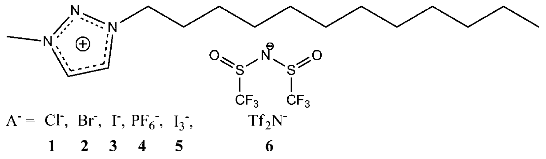


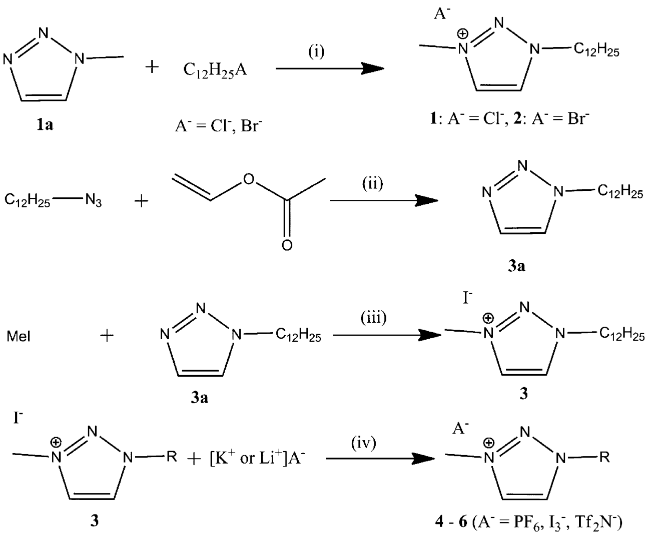
Figure 1. General structures of the synthesized compounds and compound numbering scheme.

and Lewis basicity but are increasingly polarizable. The hexafluorophosphate anion with O_h symmetry is a pseudospherical anion of large size. Triiodide as a rod-shaped anion has a large geometric anisotropy. Tf_2N^- is an anion commonly used in ionic liquids because of its extremely weak coordinating character, comparatively large, low ion strength and its possiblity to adopt multiple conformations which are energetically not too far apart, leading to structural frustration and the inhibition of crystallization. The obtained results of their salts with triazolium cations were compared to the analogous imidazolium ILCs to evaluate the influence of the acidic proton.

■ RESULTS AND DISCUSSION

Synthesis. To obtain the 1-methyl-3-dodecyltriazolium chloride (**1**) and bromide (**2**) methyltriazolium was alkylated with the respective dodecyl halide (Scheme 1). For the iodide (**3**), the synthesis started with the reaction of dodecylazide with an excess of vinyl acetate to obtain the 1-dodecyl-1,2,3-triazole (Scheme 1). (**3a**) was then alkylated at the N-3 position with methyl iodide to yield the desired triazolium iodide (**3**). The compounds **4**–**6** were prepared via anion metathesis with the alkaline salt of the desired anions. All compounds were obtained as white or, in the case of the iodide and triiodide, brown solids. In contrast to the respective imidazolium salts, which are highly hygroscopic,[1,10] astonishingly none of the produced substances is air sensitive or hygroscopic. Thus, no protective atmosphere is required for the synthesis.

Scheme 1. Syntheses of Triazolium Compounds 1–6[a]



[a](i) Acetonitrile, reflux, 3 days; (ii) vinylacetate, 80 °C, 3 days; (iii) acetonitrile, reflux, 3 days; (iv) **4**: CH_2Cl_2, RT, 1 h and **5**-**6**: CH_2Cl_2, RT, 2 days.

Structural Analysis. Single crystals of 1-dodecyl-3-methyl-1,2,3-triazolium bromide [$(C_{12}C_1Tr)Br$, **2**], 1-dodecyl-3-methyl-1,2,3-triazolium iodide [$(C_{12}C_1Tr)I$, **3**] and 1-dodecyl-3-methyl-1,2,3-triazolium triiodide [$(C_{12}C_1Tr)I_3$, **4**] could be grown successfully from dichloromethane solution (Table 1). It was not possible to obtain crystals of the other compounds. Compounds **2** and **3** both crystallize isotypic in the triclinic space group $P\bar{1}$ (no. 2) with two formula units in the unit cell (Figure 2). The cations adopt a rodlike shape with a tilted triazolium head reminind of a crank-handle. The conformation

Table 1. Crystallographic and Refinement Details for Compounds 2 and 3

	$(C_{12}C_1Tr)Br$ (2)	$(C_{12}C_1Tr)I$ (3)	$(C_{12}C_1Tr)I_3$ (4)
empirical formula	$C_{15}H_{30}N_3Br$	$C_{15}H_{30}N_3I$	$C_{15}H_{30}N_3I_3$
formula weight (g/mol)	332.3	379.38	633.1
temperature (K)	170	170	200
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
unit cell dimensions	a = 5.4934(2) Å	a = 5.6056(6) Å	a = 5.4494(1) Å
	b = 8.7114(2) Å	b = 8.9070(1) Å	b = 7.0744(1) Å
	c = 19.5010(5) Å	c = 19.523(3) Å	c = 28.9928(5) Å
	α = 78.910(2)°	α = 79.80(2)°	α = 90.430(2)°
	β = 85.390(3)°	β = 83.50(2)°	β = 92.253(2)°
	γ = 84.046(2)°	γ = 81.78(2)°	γ = 82.929(2)°
volume	909.11(42)	945.6(2)	1108.35(3)
Z	2	2	2
calculated density (g/cm^3)	1.21	1.332	1.9
absorption coefficient (mm^{-1})	2.255	1.69	4.23
Θ-range for data collection	2.4 to 25.00°	2.34 to 25.00°	2.8 to 25.0°
reflections collected/unique	8375/3033	8211/3342	9729/3692
refinement method	full-matrix least-squares on $F2$		
data/parameters	3033/174	3342/173	3692/190
goodness-of-fit on F^2	0.901	0.989	1.149
final R indices [I > 2 sigma(I)]	R_1 = 0.034	R_1 = 0.045	R_1 = 0.104
	wR_2 = 0.076	wR_2 = 0.071	wR_2 = 0.275
R indices (all data)	R_1 = 0.048	R_1 = 0.077	R_1 = 0.151
	wR_2 = 0.080	wR_2 = 0.082	wR_2 = 0.291

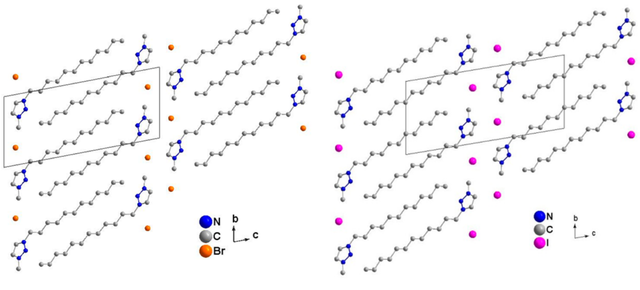


Figure 2. Crystals structures of compounds **2** (left) and **3** (right) viewed along [100].

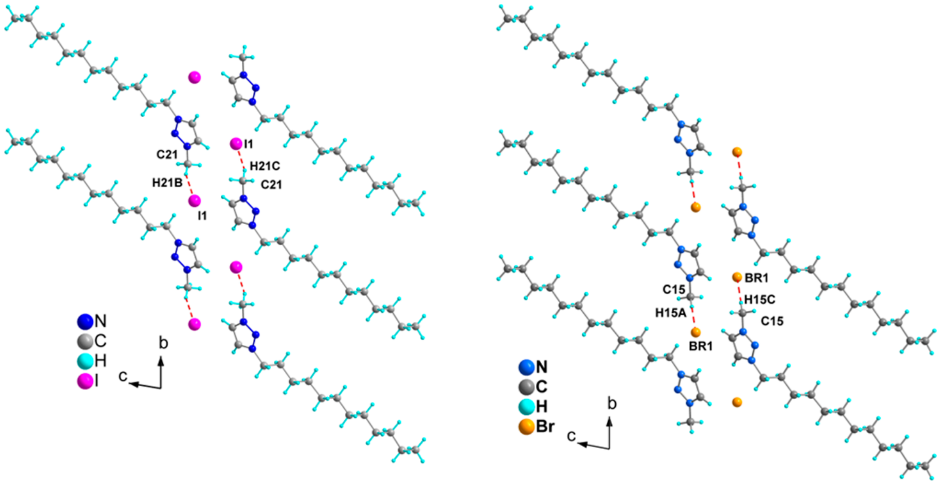


Figure 3. Hydrogen-bonding interactions in detail for compounds **2** and **3**.

of the alkyl chain is all trans. The rod-shaped cations form an interdigitated bilayer structure with the triazolium cations not facing each other directly but alternating with the bromide anions (Figure 3). The hydrophobic alkyl tails of the triazolium cation form apolar regions, which are clearly separated from the charged, polar domains built up by the triazolium headgroup and the hydrogen-bonded bromide anions. Hydrogen bonds are formed between the bromide/iodide and one hydrogen of the methyl groups (Figure 3).

1-Dodecyl-3-methyl-1,2,3-triazolium triiodide [$(C_{12}C_1Tr)I_3$, **4**] also crystallizes in the triclinic space group $P\overline{1}$ (no. 2) with two formula units in the unit cell (Figure 4). The triiodide anion lines up in the crystal structure with the triazolium cation. The linear form of the triiodide anion forces the triazolium cation to adopt a totally linear shape with an all trans conformation of the alkyl chain and the alkyl chain is in the plane of the triazolium ring (Figure 4). No significant hydrogen bonds to the anion can be found. The cations form interdigitated bilayers similar to those of compounds **2** and **3** but feature a lower degree of alkyl tail interdigitation due to the space requirements of the triiodide anion. However, the interdigitated alkyl chains are much closer to each other than in the halide salts, as the cations are strictly linear and the imidazolium head not tilted with respect to the alkyl tail of the cations as in **2** and **3**.

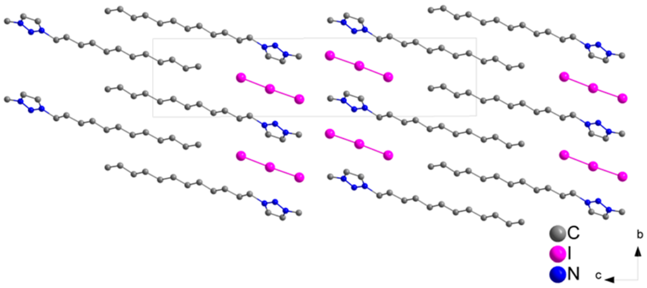


Figure 4. Crystal structure of compound **4** viewed along [100].

Table 2. Phase Transition Temperatures of Compounds 1 to 6

$(C_1C_{12}Tr)Cl$ (**1**)	$\mathrm{Cr} \xrightarrow{88.6\,^\circ\mathrm{C}(10.82)} \mathrm{X} \xrightarrow{107.5\,^\circ\mathrm{C}(9.96)} \mathrm{SmA} \xrightarrow{159.1\,^\circ\mathrm{C}(1.06)} \mathrm{L}$
$(C_1C_{12}Tr)Br$ (**2**)	$\mathrm{Cr} \xrightleftharpoons[53.7\,^\circ\mathrm{C}(-)]{93.2\,^\circ\mathrm{C}(14.86)} \mathrm{X} \xrightleftharpoons[59.1\,^\circ\mathrm{C}(44.89)]{102.3\,^\circ\mathrm{C}(17.03)} \mathrm{SmA} \xrightleftharpoons[149.8\,^\circ\mathrm{C}(1.48)]{155.1\,^\circ\mathrm{C}(0.96)} \mathrm{L}$
$(C_1C_{12}Tr)I$ (**3**)	$\mathrm{Cr} \xrightleftharpoons[30.0\,^\circ\mathrm{C}(40.04)]{83.1\,^\circ\mathrm{C}(39.43)} \mathrm{SmA} \xrightleftharpoons[126.6\,^\circ\mathrm{C}(1.05)]{135.3\,^\circ\mathrm{C}(1.03)} \mathrm{L}$
$(C_1C_{12}Tr)PF_6$ (**4**)	$\mathrm{Cr} \xrightleftharpoons[26.3\,^\circ\mathrm{C}(0.19)]{60.8\,^\circ\mathrm{C}(1.31)} \mathrm{Cr'} \xrightleftharpoons[33.9\,^\circ\mathrm{C}(39.3)]{78.1\,^\circ\mathrm{C}(24.2)} \mathrm{SmA} \xrightleftharpoons[110.1\,^\circ\mathrm{C}(0.84)]{113.1\,^\circ\mathrm{C}(0.8)} \mathrm{L}$
$(C_1C_{12}Tr)I_3$ (**5**)	$\mathrm{Cr} \xrightleftharpoons[32.1\,^\circ\mathrm{C}(50.63)]{48.9\,^\circ\mathrm{C}(52.32)} \mathrm{L}$
$(C_1C_{12}Tr)Tf_2N$ (**6**)	$\mathrm{Cr} \xrightleftharpoons[-10.6\,^\circ\mathrm{C}(41.49)]{13.3\,^\circ\mathrm{C}(46.79)} \mathrm{L}$

Thermal Behavior. The thermal properties of all compounds were examined by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The transition temperatures, enthalpies, and phase transition assignments are listed in Table 2. Figure 5 shows the heating traces of the three monohalide salts. For the chloride (**1**) and the bromide compound (**2**), three phase transitions could be observed, whereas the iodide (**3**) shows only two thermal events (Figure 5). In compound **3**, temperature-dependent POM identifies the first transition to be the flow point (S → LC) and the second one belongs to the clearing point (LC → L_{ISO}). Compound **2** exhibits a liquid crystalline phase above 102 °C and clears at 155 °C. The first transition at 93 °C is proposed to correspond to a change from crystalline to another liquid crystalline phase, but this phase could not be clearly identified and thus is named X here. All these transitions are reversible and reappear during cooling, albeit at slightly lower temperatures (Table 2). Compound **1** shows similar behavior to **2** with a mesophase existing between 108 and 158 °C. Additionally, solid−solid phase transitions occur at around 40 and 50 °C (Figure 5). As the related enthalpies are small, they should correspond to minor structural changes. From 150 °C on, the baseline of the DSC heating trace of compound **1** increases, which indicates a decomposition. Thus, no transition temperatures are listed for the subsequent cooling cycle. The mesophases of compounds **1**−**3** were identified on the basis of their optical defect textures: in all cases oily streak textures were observed by POM, indicating smectic A phases (Figure 5, panels b and c).

The hexafluorophosphate salt **4** features three endothermic events upon heating (Figure 6). The first thermal change around 60 °C is due to a solid−solid phase transition, which is directly followed by the transition to a liquid crystalline phase

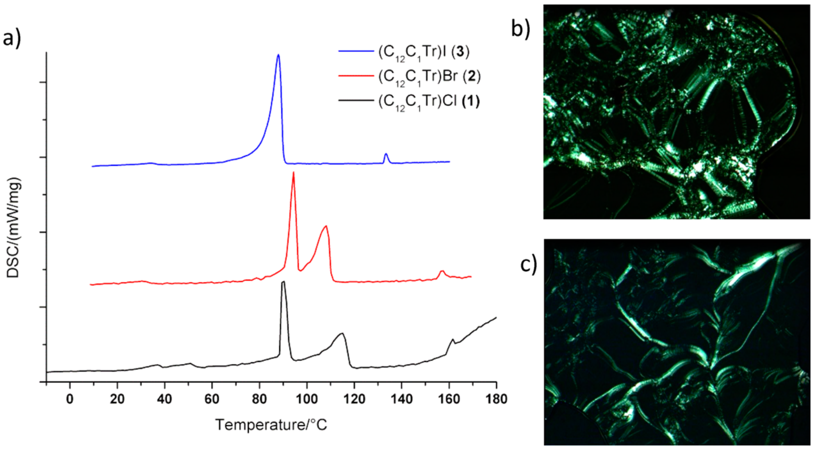


Figure 5. (a) DSC-heating-traces of compounds **1**, **2**, and **3** and POM pictures of (b) compound **1** during heating at 144.9 °C and (c) compound **2** during cooling at 87.2 °C.

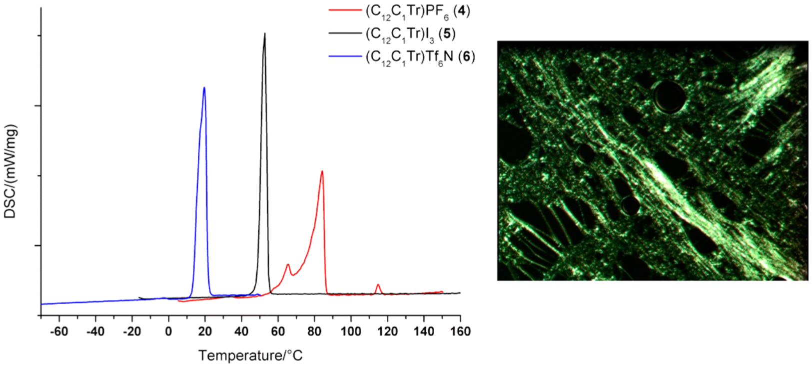


Figure 6. DSC-thermograms of compounds **4**–**6** (left) and POM-picture of compound **5** at 103.4 °C (right).

(78 °C). An oily streak texture was observed under polarized light (Figure 6, right). This indicates a smectic A phase. Compound **4** clears to an isotropic liquid at 113 °C. Compounds **5** and **6** do not exhibit a mesophase but directly melt into isotropic liquids at 13 and 49 °C, respectively (Figure 6).

Comparison of the phase transition temperatures of all compounds illustrates the dependency of the mesophase formation on the anion (Figure 7). With increasing size of the anion, the clearing point temperature decreases. The mesophase temperature window has the same size for the three halides (**1**–**3**): with increasing anion sizes both the formation temperature and the clearing temperature for the smectic A phase decrease simultaneously (Figure 7). The interactions of the positively charged headgroups of the cations with the anions are more efficient for smaller anions. This leads to formation of another more highly ordered mesophase for the chloride (**1**) and the bromide (**2**) before the smectic A phase is formed. The hexafluorophosphate salt (**4**) exhibits the smectic A phase at an even lower temperature (60 °C) and melts into an isotropic liquid at 118 °C. Thus, compound **4** has the narrowest mesophase temperature window, as expected for a larger anion with weaker hydrogen bonds. The smaller Coulombic interaction with the cation leads presumably to a lowering of the phase transition temperatures, but at the same time, the large anion is not able to stabilize the order of the mesophase as well as the smaller halide anions. For the largest and less symmetric anions, triiode and bis(trifluorosulfonyl)-amide, no mesophase was observed. The triiodide (**5**) melts around 50 °C and the bis(trifluorosulfonyl)amide (**6**) is even liquid at room temperature, which is expected since it is the largest, least weakly coordinating anion among the investigated. All triazolium salts show different thermal behavior compared to the analogous imidazolium compounds (Table 3). The imidazolium halides exhibit the smectic A phase at much lower temperatures and also melt at lower temperatures. The mesophase temperature window range of the triazolium chloride is much narrower than that of the corresponding imidazolium salt (Tri: 52 °C vs Im: 102 °C), whereas the mesophase temperature windows of the bromides are just slightly different: Tri: 53 °C versus Im: 58 °C but shifted to

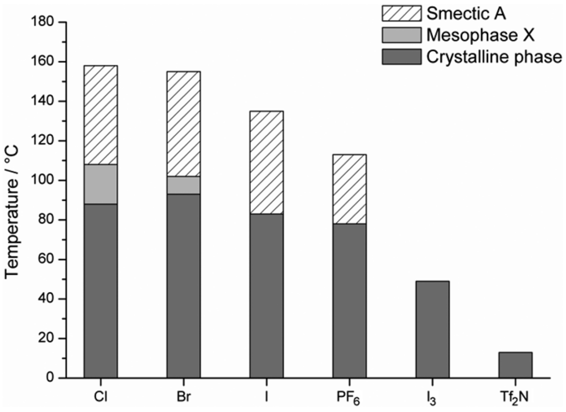


Figure 7. Phase transition temperatures of compounds **1**–**6**.

Table 3. Comparison of DSC-Data of Triazolium and Imidazolium Salts

	Cr/SmC → SmA [T (°C)]			SmA → L_{iso} [T (°C)]			Cr → L_{iso} [T (°C)]	
	($C_1C_{12}Tr$)	($C_1C_{12}Im$)	($C_1C_1C_{12}Im$)	($C_1C_{12}Tr$)	($C_1C_{12}Im$)	($C_1C_1C_{12}Im$)	($C_1C_{12}Tr$)	($C_1C_{12}Im$)
Cl	107.5	−2.8[23]	–[a]	159.1	104.4[1]	–[a]		
Br	102.3	42.0[24]	74.8[25]	155.1	100.2[2]	140.9[23]		
I	88.1	26.4[26]	–[a]	135.3	68.0[3]	–[a]		
PF_6	78.1	–	85.1	113.1	–	123.3	–	60[27]
I_3							48.9	–[a]
Tf_2N							13.3	16.7[1]

[a] No literature available; C1C12Im = 1,2-dimethyl-3-dodecylimidazolium.

higher temperatures with the triazolium cation (Table 3). The mesophase temperature range of the iodides is approximately the same size (47 °C vs 42 °C) but shifted to higher temperatures for the triazolium compound. 1-Methyl-3-alkyl-imidazolium hexafluorophosphate salts with an alkyl chain length of at least 14 carbons exhibit a smectic A phase.[23] In contrast to compound **4**, which exhibits a smectic A phase from 78 until 113 °C, the 1-methyl-3-dodecyl-imidazolium hexafluorophosphate does not show a mesophase and melts at 60 °C. Both salts with bis(trifluoromethanesulfonyl)amide-anion do not form a mesophase and melt slightly below room temperature (Tr:13.3 °C vs Im: 16.7 °C).

Powder X-ray Diffraction. To identify the mesophase and to comprehend the molecular arrangement of the triazolium salts, temperature-dependent powder-XRD measurements in the low to wide angle region were carried out. The X-ray powder pattern of compound **1** is displayed in Figure 8.

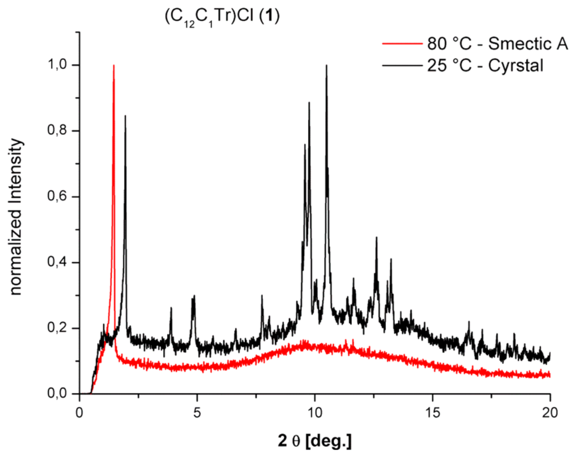


Figure 8. Temperature-dependent powder X-ray pattern of compound **1**.

Table 4. Layer Spacing (d, Å) of the Triazolium Salts in the Different Phases

no.	formula	crystal	smectic A
1	**($C_1C_{12}Tr$)Cl (1)**	20.9	28.0
2	**($C_1C_{12}Tr$)Br (2)**	19.0	28.8
3	**($C_1C_{12}Tr$)I (3)**	19.0	27.8
4	**($C_1C_{12}Tr$)PF_6 (4)**	20.4	27.7
5	**($C_1C_{12}Tr$)I_3 (5)**	28.6	
6	**($C_1C_{12}Tr$)Tf_2N (6)**	–[a]	–[a]

[a] Not measured due to the low crystallization temperature.

Compounds **1**–**4** show similar patterns with several sharp peaks in the small angle region as well as in the wide angle region (Figure 7). The layer distances, calculated from Bragg's law are listed in Table 4. The halide salts (**1**, **2**, and **3**) and the hexafluorophosphate (**4**) have a layer distance of 19–20 Å in the crystalline state. Comparing to the SXRD studies, this distance corresponds to the interlayer distance, as shown in Figure 2. The layer distance in the smectic A phase is much larger for all four compounds (Table 4: 27.7–28.8 Å). The increase in layer spacing can be attributed to partial melting of the alkyl chain melting and simultaneous decrease of interdigitation. The triiodide, which does not show a liquid crystalline phase features a quite large layer distance in the crystalline state compared to the halides (Table 4: 28.6 vs 19–20 Å). Apparently, the degree of alkylchain interdigitation in 5 is too low to allow for a stabilization of a mesophase, and rather, a direct transition from the crystalline to the liquid crystalline state is observed.

■ CONCLUSION

Salts of 1-methyl-3-dodecyl-triazolium cation with anions of different size and shape: Cl^-, Br^-, I^-, I_3^-, PF_6^-, and Tf_2N^- were synthesized and characterized with the aim of studying the influence of the anion on the mesophase formation of these ionic liquids. The three halide salts and the hexafluorophosphate salt exhibit a smectic A phase before melting to the isotropic liquid. The triiodide is an ionic liquid, due to the melting point at 49 °C but does not form a mesophase. Neither does the bis(trifluormethylsulfonyl)amide form a mesophase. This room temperature ionic liquid melts at 13 °C. For the three simple halide salts, the clearing point temperature decreases with increasing size of the anion (Cl^-, 158 °C; Br^-, 155 °C; and I^-, 135 °C). Due to a similar decrease in the flow point temperature, the mesophase temperature range does not change significantly. In the hexafluorophosphate salt, the transition temperatures are even lower due to the increased anion size (the compound exhibits the smectic A phase at 78 °C and melts into an isotropic liquid at 113 °C), but the mesophase temperature window is narrower (35 °C compared to 50 °C for the halides).

In summary, it is observed that the thermal behavior of the 1-methyl-3-dodecyl-triazolium salts strongly depends on the anion and some trends could be noticed: with highly symmetric anions mesophase formation can be observed. The larger the anion, the lower the phase transition temperatures and the less stable the mesophase. With the nonspherical and large anions triiodide and Tf_2N, no formation of a liquid crystalline phase was observed; instead low melting ionic liquids formed.

Compared to the respective analogous imidazolium compounds mesophases of the triazolium halides form at higher temperatures. In contrast to the imidazolium hexafluorophsophate salt, which directly melts into an isotropic liquid, the respective triazolium compound exhibits a smectic A phase. For the extremely low melting Tf_2N salts, no mesophase formation was observed for the 1-methyl-3-dodecylimidazolium as well as the 1-methyl-3-dodecyltriazolium cation. Nevertheless, it appears that mesophase formation is favored for triazolium salts compared to imidazolium salts, an observation which we already have made for symmetric 1,3-dodecyl salts.[19]

EXPERIMENTAL SECTION

Synthesis. Dodecylazide was synthesized according to a common literature method.[28] All other starting materials and solvents were purchased from standard commercial sources and were used without further purification. No protective atmosphere was required during synthesis.

Preparation of 1-Methyl-1,2,3-triazole (1a). Four milliliters of (68 mmol) 1-H-1,2,3-triazol and 19.05 g (137.75 mmol) of potassium carbonate were dissolved in 75 mL of tetrahydrofuran. 6.46 mL (103 mmol) of methyl iodide was added, and the mixture was stirred for 3 h at room temperature. After filtration, the solution was concentrated and the residue dried in dynamic vacuum to receive the 1-methyl-1,2,3-triazole.

Yield: 4.79 g (83.7%), ^{1}H NMR (200 MHz, $CDCl_3$): δ [ppm] = 7.68 (s, 1H), 7.53 (s, 1H), 4.11 (s, 3H).

General Procedure for the Preparation of 1-Methyl-3-dodecyl-1,2,3-triazolium chloride/bromide (1/2). Twelve mmol (1 g) 1-methyl-1,2,3-triazole were dissolved in acetonitrile, and 27 mmol of the respective dodecylhalide were added. The solution was heated under reflux for 3 days and then poured into cold ethyl acetate and stored at −40 °C for 20 h. The white precipitate was filtered off and dried under dynamic vacuum at room temperature to give the products in good yields and purity.

1-Methyl-3-dodecyl-1,2,3-triazolium chloride (1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.90 (s, 1H), 9.71 (s, 1H), 4.72 (t, J = 7.4 Hz, 2H), 4.53 (s, 3H), 2.02 (d, J = 6.9 Hz, 2H), 1.37−1.14 (m, 18H), 0.87 (t, J = 6.4 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 132.8, 131.9, 54.2, 40.5, 32.0, 29.7, 29.7, 29.6, 29.4, 28.9, 26.3, 22.8, 14.2. MS (FAB$^+$): m/z = 84 (15%, K$^+$-$C_{12}H_{24}$), 252 (100%, K$^+$), 539 (6%, 2*K$^+$ + Cl$^-$). Elemental analysis (%) calcd for ($C_{15}H_{30}N_3Cl$): C, 65.36; H, 8.35; N, 8.92. Found: C, 65.44; H, 7.91; N, 9.19.

1-Methyl-3-dodecyl-1,2,3-triazolium bromide (2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.77 (d, J = 1.2 Hz, 1H), 9.61 (d, J = 1.3 Hz, 1H), 4.74 (t, J = 7.4 Hz, 2H), 4.54 (s, 3H), 2.04 (t, J = 7.2 Hz, 2H), 1.37−1.21 (m, 18H), 0.87 (t, J = 6.4 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 132.6, 131.7, 54.3, 40.7, 31.9, 29.8, 29.7, 29.6, 29.4, 28.9, 26.2, 22.8, 14.2. MS (FAB$^+$): m/z = 84 (14%, K$^+$-$C_{12}H_{24}$), 252 (100%, K$^+$), 406 (1.3%, K$^+$-CH_3 + $C_{12}H_{25}$), 583 (22%, 2*K$^+$ + Br$^-$). Elemental analysis (%) calcd for ($C_{15}H_{30}N_3Br$): C, 54.12; H, 9.1; N, 12.64. Found: C, 53.06; H, 10.01; N, 12.24.

Preparation of 1-Dodecyl-1,2,3-triazole (3a). 5 g of Dodecylazide (23.7 mmol) and 10 mL vinyl acetate were heated in a closed glass tube for 3 days. After addition of 200 mL *n*-hexane, the suspension was filtered and the solution cooled to −40 °C for 24 h. The precipitated product was filtered off and dried overnight under a dynamic vacuum at room temperature.

Yield: 3.98 g (71%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.69 (s, 1H), 7.52 (s, 1H), 4.38 (t, J = 7.2 Hz, 2H), 1.92 (dd, J = 12.4, 5.7 Hz, 2H), 1.25 (s, 18H), 0.88 (t, J = 6.3 Hz, 4H).

Preparation of 1-Methyl-3-dodecyl-1,2,3-triazolium iodide (3). 1.27 g (5.35 mmol) of 1-dodecyl-1,2,3-triazole and 3 eq of methyl iodide (1 mL) were added to 50 mL of acetonitrile and heated under reflux for 72 h. After cooling down to room temperature, ethyl acetate was added, and the resulting solution was stored at −40 °C for 24 h. The precipitated product was filtered off and dried overnight under dynamic vacuum at room temperature.

Yield: 1.47 g (72%), ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.50 (d, J = 1.3 Hz, 1H), 9.34 (d, J = 1.4 Hz, 1H), 4.80−4.66 (m, 2H), 4.53 (s, 3H), 2.12−1.99 (m, 2H), 1.25 (s, 18H), 0.88 (t, J = 6.5 Hz, 4H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 132.6, 131.6, 54.6, 41.2, 31.9, 29.6, 28.9, 26.2, 22.8, 14.2. MS (FAB$^+$): m/z = 84 (11%, K$^+$-$C_{12}H_{24}$), 252 (100%, K$^+$), 631 (6%, 2*K$^+$ + I$^-$). Elemental analysis (%) calcd for ($C_{15}H_{30}N_3I$): C, 47.5; H, 7.97; N, 11.08. Found: C, 47.61; H, 7.38; N, 11.16.

Preparation of 1-Methyl-3-dodecyl-1,2,3-triazolium triiodide (4). To a solution of 500 mg (1.32 mmol) of 1-methyl-3-dodecyl-1,2,3-triazolium iodide (**3**) in dichloromethane, 1 eq (330 mg, 1.32 mmol) iodide was added and stirred for 1 h. The solvent was evaporated, and *n*-pentane was added to the residue. The precipitated product was filtered off and washed with *n*-pentane. The product was dried at RT in dynamic vacuum to give a golden brown solid.

Yield: 0.67 g, (81%). ^{1}H NMR (200 MHz, $CDCl_3$): δ [ppm] = 8.76 (s, 1H), 8.63 (s, 1H), 4.75−4.64 (m, 2H), 4.52 (s, 3H), 2.21−2.02 (m, 2H), 1.48−1.17 (m, 18H), 0.88 (t, J = 6.4 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 132.6, 131.4, 55.5, 32.0, 29.7, 29.6, 29.6, 29.5, 29.0, 26.5, 22.8, 14.3. MS (FAB$^+$): m/z = 84 (12%, K$^+$-$C_{12}H_{24}$), 252 (100%, K$^+$). Elemental analysis (%) calcd for ($C_{15}H_{30}N_3I_3$): C, 28.46; H, 4.78; N, 6.64. Found: C, 28.55; H, 4.76; N, 6.62.

Preparation of 1-Methyl-3-dodecyl-1,2,3-triazolium hexafluorophosphate (5). 0.27 g (1.45 mmol) of Potassium hexafluorophosphate was added to a solution of 0.5 g (1.32 mmol) of 1-methyl-3-dodecyl-1,2,3-triazolium iodide (**3**) in dichloromethane and stirred for 3 days at room temperature. The white precipitate was filtered off. The organic phase was washed with small volumes of water until no precipitation of AgCl occurred in the aqueous phase upon addition of $AgNO_3$ solution. The organic phase was dried over Na_2SO_4, filtered, the solvent was removed, and the residue dried under dynamic vacuum to give a colorless product.

Yield: 3.23 g, (71%), ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.30 (d, J = 1.2 Hz, 1H), 9.05 (d, J = 1.3 Hz, 1H), 4.73−4.61 (m, 2H), 4.50 (s, 3H), 2.04 (d, J = 7.3 Hz, 2H), 1.38−1.20 (m, 18H), 0.88 (t, J = 6.5 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 132.5, 131.4, 54.6, 40.9, 32.0, 29.7, 29.7, 29.6, 29.5, 29.4, 28.9, 26.3, 22.8, 14.3. MS (FAB$^+$): m/z = 84 (15%, K$^+$-$C_{12}H_{24}$), 252 (100%, K$^+$), 649 (2%, 2*K$^+$ + PF_6^-). Elemental analysis (%) calcd for ($C_{15}H_{30}N_3PF_6$): C, 45.34; H, 7.61; N, 10.57. Found: C, 47.11; H, 7.68; N, 10.89.

Preparation of 1-Methyl-3-dodecyl-1,2,3-triazolium bis(trifluormethylsulfonyl)amide (6). This compound was synthesized by the same procedure described for the synthesis of compound **5**. From 0.42 g (1.45 mmol) of lithium bis(trifluormethylsulfonyl)amide and 0.5 g (1.32 mmol) of 1-methyl-3-dodecyl-1,2,3-triazolium iodide (**3**), 1-methyl-3-dodecyl-1,2,3-triazolium bis(trifluormethylsulfonyl)amide was obtained as a highly viscous oil.

Yield: 0.55 g, (78%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.43 (d, J = 1.1 Hz, 1H), 4.57 (t, J = 7.5 Hz, 2H), 4.36 (s, 3H), 2.09−1.93 (m, 2H), 1.38−1.21 (m, 18H), 0.87 (t, J = 6.3 Hz, 3H). ^{13}C, MS (FAB$^+$): m/z = 84 (13%, K$^+$-$C_{12}H_{24}$), 252 (100%, K$^+$), 784 (0.6%, 2*K$^+$ + Tf_2N^-). Elemental analysis (%) calcd for ($C_{17}F_6H_{30}N_4O_4S_2$): C, 38.34; H, 5.68; N, 10.52; S, 12.04. Found: C, 38.26; H, 5.50; N, 10.71; S, 12.01.

Instrumentation. Differential scanning calorimetry (DSC) was performed with a computer-controlled PhoenixDSC 204 F1 thermal analyzer (Netzsch, Selb, Germany). Measurements were carried out at a heating rate of 5 °C/min in sealed aluminum crucible with an argon flow rate of 20 mL/min. The samples were placed in aluminum pans which were cold-sealed. Given temperatures correspond to the onset of the respective thermal processes.

Optical analyses were made by heated-stage polarized optical microscopy (POM) with an Axio Imager A1 microscope (Carl Zeiss MicroImaging GmbH,Göttingen, D) equipped with a hot stage, THMS600 (Linkam ScientificInstruments Ltd., Surrey, U.K.), and Linkam TMS 94 temperature controller (Linkam Scientific Instruments Ltd., Surrey, U.K.). Images were recorded at a magnification of 100× as a video with a digital camera during heating and cooling the sample which was placed between two coverslips. Heating and cooling rates were 5 K/min^{-1}.

Mass spectrometric analysis was carried out on a VG Autospec mass spectrometer with EBEE geometry (VG instruments). Fast atom bombardment (FAB) was used to ionize the samples.

Elemental analysis was conducted with a Vario EL C, H, N, S analyzer of the company Elmentar (Hanau, Germany).

Nuclear magnetic resonance measurements (^{1}H NMR and ^{13}C NMR) were made using a Bruker Advance DPX 200 spectrometer (Karlsruhe, Germany). The frequencies used were 200 and 50 MHz. Deuterated chloroform (Deutero GmbH) was used as the solvent. The chemical shift δ is given in ppm. The peak multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

Powder diffraction X-ray experiments were carried out with a D8 Advanced diffractometer (Bruker) at the Institute of Crystallography of the Ruhr-Universität Bochum.

Single crystals of 1-dodecyl-3-methyl-1,2,3-triazolium bromide [$(C_{12}C_1Tr)Br$, **2**], 1-dodecyl-3-methyl-1,2,3-triazolium iodide [$(C_{12}C_1Tr)I$, **3**], and 1-dodecyl-3-methyl-1,2,3-triazolium triiodide [$(C_{12}C_1Tr)I_3$, **4**] could be grown successfully from a dichloromethane solution. Measurements were carried out on a Stoe IPDS-I single-crystal X-ray diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å at 100 K). Crystal structure solution by direct methods using SIR 92[29] yielded the heavy atom positions. Refinement with SHELXL-97[30] allowed for the localization of the remaining atom positions. Hydrogen atoms were added and treated with the riding atom mode. Data reduction was performed with the program package X-Red,[31] and numerical absorption correction was carried out with the program X-Shape.[32] To illustrate the crystal structures, the program Diamond[33] was used.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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