Induction of ionic smectic C phases: a systematic study of alkyl-linked guanidinium-based liquid crystals

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ABSTRACT
A series of ionic liquid crystals with an alkoxy biphenyl unit tethered via an alkyl spacer to a guanidinium head group were synthesised and the mesomorphic properties were studied by differential scanning calorimetry, polarising optical microscopy and X-ray diffraction (XRD; WAXS and SAXS). Whereas all symmetrical guanidinium chlorides with the same chain lengths in alkyl tail and spacer displayed enantiotropic SmA1 phases, monotropic SmC2 phases with 1–2 K temperature range were only formed for chain lengths ≥ C10. Shifting the calamitic core more closely to the ionic head group by decreasing the tether length and simultaneously increasing the terminal alkyl chain improved the stability of both SmA and SmC phases considerably and led to enantiotropic SmC phases for the guanidinium chloride with C14 alkyl tail and C6 spacer. An even more pronounced effect was detected during anion exchange. Bromide, iodide, hexafluorophosphate, thiocyanate and triflate suppressed any SmC phase, whereas tetrafluoroborate behaved similar to chloride maintaining the SmC phase. However, acetate stabilised the SmC phase at the expense of the SmA phase. Based on temperature-dependant XRD measurements, a bilayer structure was proposed.

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Introduction
Within the diverse research area of liquid crystals, ionic liquid crystals (ILCs) provide a combination of the beneficial properties of ionic liquids, such as a high thermal stability, low vapour pressure and a wide electrochemical window, with the anisotropic ordered fluidity of thermotropic liquid crystals.[1–3] Therefore, low-molecular-weight ILCs are utilised as self-organised ion conductors,[4,5] biosensors,[6] displays [7] and in several other devices.[2,8,9] For these applications, the physical properties are critical parameters, especially the temperature range as well as the geometry of the mesophase.

For calamitic non-charged liquid crystals with a rod-like cyanobiphenyl core tethered to a terminal halogen via a flexible alkyl spacer, Goodby reported exclusively nematic mesophases.[10,11] Lemieux developed an amphiphilic design, where organosiloxane phenylpyrimidines with a halogen-terminated alkyl chain promoted the formation of lamellar mesophases (SmA and SmC).[12,13] Additionally, alkyl-substituted phenylpyrimidines with a terminal halogen atom and flexible alkyl tether solely displayed SmA phases as described by us previously.[14]

The tendency to form lamellar mesophases is even more pronounced when the terminal halogen atom is replaced by an ionic moiety. Calamitic ILCs prefer lamellar ordering due to a micro-segregation into ionic and non-polar organic domains with the smectic A (SmA) phase being the most common.[8]

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Compared to the vast number of ILCs with a SmA phase, much less ILCs with a SmC phase have been reported. SmC phases are promising hosts for chiral doping experiments resulting in chiral SmC* phases suitable for electro-optical switching devices.[15–18] Previous examples include ammonium salts tethered to azobenzenes,[19,20] pyrroldininium-based biphenyls,[21] pyridinium-based biphenyls,[22] and terphenyls,[23] imidazolium salts with cyanobiphenyl,[24] azobenzene,[25] biphenyl,[26] phenylpyrimidine[27] and hydrogen-bonded units.[28] More recently, bis-cationic imidazolium salts,[29,30] benzimidazolium biphenyl salts,[31] guanidinium biphenyls[32] and triazolium salts[33] were reported.

Motivated by seminal findings reported by Lattermann[22] on pyridinium salts tethered to alkoxybiphenyls 1 that changes in the symmetry and substitution pattern of the cationic head group might lead to the induction of SmC phases (e.g. ortho-substituted 1a vs. para-substituted 1b or unsubstituted 1c in Scheme 1) and our own results on related para- and meta-substituted phenylguanidinium salts para-2 and meta-2, respectively, showing only SmA phases,[32] we initiated a more detailed study on such guanidinium salts. Aiming at ILCs displaying a SmC phase, we decided to particularly focus on derivatives Gua(n,m)X, where the guanidinium head group is directly attached to the alkyl tether and derivative ArGua(10,10)Cl with ortho-substituted aryl guanidinium moiety. This should allow us to access the influence of symmetry and flexibility on the micro-segregation in combination with chain lengths and counterion effects, hopefully providing some useful structure-property guidelines. The results towards this goal are reported below.

**Results and discussion**

**Synthesis of aryl guanidinium salt ArGua(10,10)Cl**

The desired aryl-substituted product ArGua(10,10)Cl was synthesised following a previously established procedure (Scheme 2).[32] The synthesis commenced with a Boc-protection of 3 to 4, which was then condensed with 1,10-dibromodecane to yield 5 in 57% over two steps. Subsequent etherification of 5 with 6a provided 7 in 90% yield, followed by an acidic deprotection that was achieved with methanesulfonic acid to form the amine 8. Finally, 8 was treated with chloroformamidinium chloride and NaHCO₃ to afford the desired guanidinium chloride ArGua(10,10)Cl in 95% yield.

**Synthesis of the alkyl guanidinium salts Gua(n,m)X**

The synthetic route used to obtain the alkyl guanidinium chlorides Gua(n,m)Cl followed the same convergent approach as for ArGua(10,10)Cl and is outlined
in Scheme 3. Building blocks 6a–e were synthesised via mono-etherification [35] of 9 with the corresponding n-alkyl bromides. Potassium pthalimide 10 was reacted with dibromoalkane to afford building blocks 11a–e.[36] The condensation [32] of two units 6a–e and 11a–e with similar chain lengths \( n = m = 6–14 \) was found to be convenient, since products 12a–i precipitated from the reaction mixture and could be easily purified by washing the crude product with MeCN followed by an extraction of the product with \( \text{CH}_2\text{Cl}_2 \), r.t., 24 h, 95%.

Unfortunately, the guanidinium chlorides Gua\((n,m)\) Cl could not be synthesised with the procedure described for series ArGua\((10,10)\)Cl. Neither replacing the previously used NaHCO\(_3\) with the stronger base NEt\(_3\).[38] increasing the excess of chloroformamidinium chloride nor extending the reaction time to one week resulted in a full conversion of the starting material 13a–i. The lower solubility of 13a–i compared with 8 is very likely to hinder complete conversion.

Therefore, higher boiling solvents DMF, DMSO and MeCN were examined. In case of DMF and DMSO, no
formation of \textit{Gua}(n,m)\textsubscript{Cl} could be observed by TLC, whereas the use of MeCN successfully afforded the guanidinium chlorides \textit{Gua}(n,m)\textsubscript{Cl} in 32–85%.

Alkyl guanidinium chloride \textit{Gua}(14,6)\textsubscript{Cl} was used for an anion exchange \cite{38} to introduce various inorganic anions X (X = Br, I, OTf, BF\textsubscript{4}, PF\textsubscript{6}, OAc, SCN) summarised in Scheme 3. The products \textit{Gua}(14,6)\textsubscript{X} were formed in high yields by treating \textit{Gua}(14,6)\textsubscript{Cl} with the corresponding sodium or potassium salts.

\textbf{Mesomorphic properties of aryl guanidinium chloride \textit{ArGua}(10,10)\textsubscript{Cl}}

The mesomorphic properties were investigated by differential scanning calorimetry (DSC), polarising optical microscopy (POM) and X-ray diffraction (XRD; WAXS and SAXS). Upon first heating, the DSC curve of the \textit{ortho}-substituted aryl guanidinium chloride \textit{ArGua}(10,10)\textsubscript{Cl} only displayed an endothermal melting transition from the crystalline to the isotropic liquid at 140°C (Figure 1). In the first cooling cycle, crystallisation occurred at 97°C, followed by a crystal to crystal transition at 91°C.

However, the second and third temperature cycles differed from the first cycle. The second heating cycle displayed an additional exothermal recrystallisation peak at 67°C and a clearing transition into the isotropic liquid, which was shifted to 145°C. The subsequent second cooling cycle revealed again exothermal crystallisation and a crystal to crystal transition at 97°C and 91°C, respectively. Compared to the first cooling cycle, the second cycle exhibited an additional crystal to crystal transition at 85°C. The third heating and cooling showed the same behaviour as the second cycle.

Under the polarising optical microscope, \textit{ArGua}(10,10)\textsubscript{Cl} displayed crystalline textures upon heating, which melted to the isotropic liquid above 145°C. Upon cooling, no texture appeared while shearing in order to supress homeotropical alignment. At 96°C, a crystalline texture was formed that apparently does not show any changes during further cooling to 70°C.

This result is in contrast to the previously reported analogues \textit{para}-2 and \textit{meta}-2, which both displayed a Sm\textsubscript{A2} phase.\cite{32} Since \textit{ArGua}(10,10)\textsubscript{Cl} is the most bent derivative in this series, presumably the formation of bilayers in the Sm\textsubscript{A2} phase is strongly disfavoured, resulting in the absence of any mesomorphic behaviour. Therefore, no further structural modifications of \textit{ArGua}(10,10)\textsubscript{Cl} regarding chain length or counterions were carried out.

\textbf{Mesomorphic properties of alkyl guanidinium chlorides \textit{Gua}(n,m)\textsubscript{Cl} with \(n = m\)}

A typical DSC curve is shown in Figure 2 for \textit{Gua}(12,12)\textsubscript{Cl} with three endothermal transitions at 93°C, 124°C and 132°C upon first heating and exothermal transitions when first cooling to 133°C, 125°C and 90°C, respectively. Upon second heating, an endothermal crystal to crystal transition was observed at 94°C, followed by a melting transition to the Sm\textsubscript{A} phase at 124°C. Further heating revealed an endothermal clearing transition at 132°C. In the subsequent second cooling cycle, the exothermal transition from the isotropic state to the Sm\textsubscript{A} phase appeared at 94°C, followed by a melting transition to the Sm\textsubscript{A} phase at 124°C. Further heating revealed an endothermal clearing transition at 132°C. In the subsequent second cooling cycle, the exothermal transition from the isotropic state to the Sm\textsubscript{A} phase appeared at 134°C. The transition to the narrow Sm\textsubscript{C} phase was hardly visible on the DSC curve, but could be detected by POM at 126°C upon cooling (Figure 4(b)). The DSC curve only revealed a transition from the liquid crystalline phase presumably to a hexatic or crystalline phase (Cr\textsubscript{x}) at 125°C. For a true crystalline phase, a pronounced hysteresis between heating and cooling would be expected.\cite{39} An additional transition to a crystalline phase (Cr) at 90°C was observed upon further cooling, which indeed showed the expected hysteresis.
Table 1. Phase transitions temperatures/°C (and corresponding enthalpies/kj mol⁻¹) of guanidinium chlorides Gua(n,m)Cl.

|          | Cr⁺ | SmC | SmA | 1 |
|----------|-----|-----|-----|---|
| Gua(6,6)Cl | 73  | –   | 132 | 2nd heat |
|           | 75  | –   | 133 | 2nd cool  |
| Gua(8,8)Cl | 101 | –   | 129 | 2nd heat  |
|           | 101 | –   | 130 | 2nd heat  |
| Gua(10,10)Cl | 113 | –   | 140 | 2nd heat  |
|           | 117 | 118b| 143 | 2nd cool  |
| Gua(12,12)Cl | 124 | –   | 132 | 2nd heat  |
|           | 125 | 126b| 134 | 2nd cool  |
| Gua(14,14)Cl | 124 | –   | 140 | 2nd heat  |
|           | 128 | 129b| 145 | 2nd cool  |

*For additional Cr–Cr transition, see ESI (Table 1); **mesophase indicated by POM textures upon cooling because peaks are not resolved in DSC; Cr: crystalline; SmC: smectic C; SmA: smectic A; I: isotropic; ±: observed; –: not observed; cooling rate: 5 K min⁻¹.

Figure 3. Mesophase ranges of Gua(n,m)Cl with increasing chain and spacer lengths n and m, respectively.

Since the first heating and cooling cycles often slightly differ from the second and third, the second temperature cycle was used to determine phase transitions and judge reproducibility by comparison with the third cycle.

The DSC results of alkyl guanidinium chlorides Gua(n,m)Cl are summarised in Table 1 and visualised in Figure 3. Figure 3 reveals an increase of melting points with increasing chain length of both spacer and terminal chain, whereas clearing points showed a trend which somehow reminds of an odd–even effect (despite the presence of only even chain lengths). That means, derivatives Gua(8,8)Cl and Gua(12,12)Cl have lower clearing points compared to Gua(6,6)Cl and Gua(10,10)Cl, respectively. Moreover, a second mesophase appeared for derivatives with longer alkyl chains (n ≥ 10) of only 1–2 K. This mesophase could not be resolved in the DSC curve, but was detected by its characteristic POM textures, as discussed below.

Under the POM, upon cooling from the isotropic phase, compounds Gua(n,m)Cl displayed bâtonnet textures, as shown in Figure 4(a) for Gua(12,12)Cl. In some cases, strong homeotropically aligned textures with maltese crosses were observed. These textures indicate the presence of a SmA phase. Upon cooling, derivatives Gua(n,m)Cl with longer alkyl chains (n ≥ 10) showed additional schlieren textures characteristic for SmC phases within a temperature range of 1–2 K. For Gua(12,12)Cl, the schlieren texture could be observed between 126°C and 125°C (Figure 4(b)), followed by crystallisation at 125°C. As already mentioned, due to the small SmC phase ranges, derivatives Gua(10,10)Cl–Gua(14,14)Cl exhibited no well-resolved SmA-SmC transition in the DSC.

Furthermore, XRD studies were carried out to confirm the mesophase assignments. As shown for the WAXS measurement in Figure 5, compound Gua(12,12)Cl displayed a first order (001) and second order (002) diffraction peak as well as a diffuse halo scattering in the SmA phase at 131°C.

The relatively strong intensity of the second order diffraction peak compared to the first order peak could be explained by multiple scattering. The beam originating from two successive 001 scatterings, for example, at different domains leads to the same scattering angle as the second order peak and therefore increases the relative intensity of the first compared to the second-order diffraction peak.[40] After cooling to 104°C, an additional peak at a wide angle could be observed. The absence of further sharp reflexes in the wide angle section suggests that the SmA phase of Gua(12,12)Cl converts either into a hexatic or crystalline smectic phase upon cooling to 104°C.[41]

Temperature-dependant SAXS measurements were carried out for derivatives Gua(6,6)Cl, Gua(10,10)Cl and Gua(14,14)Cl to fit the fundamental peak (001) with a Gaussian distribution. The resulting d₀₀₁ values are given in Figure 6. All compounds showed a decrease of the SmA layer spacing upon heating. This decrease can be explained by a loss of orientational order [42,43] and is in agreement with reports on ILCs exhibiting bilayered SmA₂ phases.[27,44–46] Unfortunately, no SmC XRD pattern of Gua(10,10) Cl, Gua(12,12)Cl and Gua(14,14)Cl could be obtained due to the small SmC temperature range of 1–2 K.
Mesomorphic properties of alkyl guanidinium chlorides \( \text{Gua}(n,m)\text{Cl} \) with \( n \neq m \)

Although the increase of molecular flexibility by replacing the more rigid anchoring of the guanidinium head group in the previously studied ILCs \( \text{Gua}(n,m)\text{Cl} \) indeed resulted in the formation of SmC phases, the phase width was still rather small. In order to improve the temperature range, the effect of spacer lengths versus terminal chain lengths was studied. Therefore, a series of ILCs \( \text{Gua}(n,m)\text{Cl} \) with a total alkyl chain length of 20 carbon atoms \( (n + m = 20) \) was investigated to determine the effect of the biphenyl core being closer or farther away from the ionic head group. Gratifyingly, this approach turned out to be successful as can be seen from the DSC results in Table 2 and Figure 7.

While guanidinium chloride \( \text{Gua}(6,14)\text{Cl} \) with short side chain and long tether showed an enantiotropic SmA phase with decreased width (20 K) and no SmC phase as compared to symmetrical derivative \( \text{Gua}(10,10)\text{Cl} \), mesomorphism was completely lost for guanidinium chloride \( \text{Gua}(8,12)\text{Cl} \). However, when the reversed combination was studied, that is, \( \text{Gua}(12,8)\text{Cl} \), not only the stability of the SmA phase could be improved with an increased temperature range of 55 K but also the SmC phase turned out to be enantiotropic with a phase width of 14 K. This trend was even more pronounced, when the terminal chain became longer and the spacer was shortened. Thus, ILC \( \text{Gua}(14,6)\text{Cl} \) displayed a melting transition to the SmC phase at 65°C, an endothermic SmC\( \rightarrow \)SmA transition at 84°C and a clearing transition at 193°C upon heating and the corresponding phase transitions at 194°C, 93°C and 66°C, respectively, in the cooling cycle (Figure 8), resulting in a temperature range of 27 K for SmC and 101 K for SmA as compared to 1 K and 26 K for the symmetrical compound \( \text{Gua}(10,10)\text{Cl} \). For each sequential heating and cooling cycle of \( \text{Gua}(14,6)\text{Cl} \), both melting and clearing points shifted to lower temperatures, indicating thermal decomposition in the isotropic phase (arrows in Figure 8). The decomposition of \( \text{Gua}(14,6)\text{Cl} \) can be caused by a high clearing temperature of 193°C.

Figure 4. (colour online) POM image of \( \text{Gua}(12,12)\text{Cl} \) (a) bâtonnet texture of SmA at 130°C; (b) schlieren texture of SmC at 126°C upon cooling from the isotropic liquid (magnification \( \times 200 \), cooling rate 5 K min\(^{-1}\)).

Figure 5. (colour online) WAXS diffraction pattern of \( \text{Gua}(12,12)\text{Cl} \) of the SmA phase at 131°C (solid line and image) and of the hexatic or crystalline smectic phase at 104°C (dashed line).

Figure 6. Temperature-dependant layer spacing for \( \text{Gua}(6,6)\text{Cl} \)–\( \text{Gua}(14,14)\text{Cl} \) in the SmA phase.

Mesomorphic properties of alkyl guanidinium chlorides \( \text{Gua}(n,m)\text{Cl} \) with \( n \neq m \)

Although the increase of molecular flexibility by replacing the more rigid anchoring of the guanidinium head...
Under the POM, compounds Gua(6,14)Cl, Gua(12,8)Cl and Gua(14,6)Cl displayed homeotropic textures with maltese crosses and focal conic textures in the SmA phase during cooling from the isotropic phase. Additionally, compounds Gua(12,8)Cl and Gua(14,6)Cl displayed schlieren textures (Figure 9).

Temperature-dependant SAXS measurements for Gua(14,6)Cl were carried out to determine $d_{001}$. As shown in Figure 10, the incorporated layer spacing and DSC curve of Gua(14,6)Cl displayed a clear correlation regarding the SmA/SmC transition at the temperature $T_{AC}$. As previously reported, layer spacing increased in the SmC phase with increasing temperature [27] due to a decrease of the SmC tilt angle.[47,48] During further heating, the SmA layer spacing decreased as described above for Gua(n,m)Cl. The derivative Gua(12,8)Cl with shorter alkyl tail exhibited the same correlation and temperature-dependant behaviour as Gua(14,6)Cl, which is shown in the ESI.

**Mesomorphic properties of alkyl guanidinium salts Gua(14,6)X with different anions X**

Motivated by these results, the guanidinium chloride Gua(14,6)Cl with the most promising mesophase properties was submitted to salt metathesis and a series of ILCs with different anions Gua(14,6)X (X = Br, I, OTf, BF$_4$, PF$_6$, OAc, SCN) were prepared to further improve the mesophase broadness and thermal stability (Scheme 3). From the DSC results in Table 3 and Figure 11, it is immediately evident, that the anion plays a critical role in the mesophase behaviour. For example, replacement of the chloride by bromide or iodide resulted in complete disappearance of the SmC phase while the stability of the SmA phase was further improved. Similar results were found for the hexafluorophosphate and thiocyanate derivatives Gua(14,6)PF$_6$ and Gua(14,6)SCN, respectively. Exchanging chloride by triflate decreased the stability of the SmA phase considerably, while no indication for SmC was found. In contrast, the guanidinium tetrafluoroborate Gua(14,6)BF$_4$ showed very similar phase behaviour as compared to the parent chloride Gua(14,6)Cl except for the fact that the monotropic SmC phase occurred only in the cooling cycle of Gua(14,6)BF$_4$.

Within the series of different anions, derivatives Gua(14,6)X (X = Cl, Br, I, BF$_4$ and SCN) showed thermal decomposition due to high clearing points $> 170^\circ$C, which could be deduced from decreasing clearing temperatures upon successive heating and

| Compound | SmC | SmA | I |
|----------|-----|-----|---|
| Gua(6,14)Cl | 130 (−7.5) | – | 142 (−6.6) |
| Gua(8,12)Cl | 142 (−27.4) | – | 151 (6.5) |
| Gua(10,10)Cl | 113 (−4.8) | – | 140 (−5.4) |
| Gua(12,8)Cl | 86 (−21.8) | 103 (−1.1) | 143 (5.7) |
| Gua(14,6)Cl | 87 (22.0) | 84 (−2.8) | 193 (1.0) |

*For additional Cr–Cr transition, see ESI (Table 2); mesophase indicated by POM textures upon cooling; clearing transitions decreased upon successive heating and cooling cycles; Cr: crystalline; SmC: smectic C; SmA: smectic A; I: isotropic; < observed; –: not observed; cooling rate: 5 K min$^{-1}$.*

**Table 2. Phase transitions temperatures/°C (and corresponding enthalpies/kJ mol$^{-1}$) of guanidinium chlorides Gua(n,m)Cl.**

![Figure 7. Mesophase ranges of Gua(n,m)Cl with various chain (n) and spacer lengths (m), respectively.](image)

![Figure 8. DSC curve of Gua(6,14)Cl (2$^{nd}$ and 3$^{rd}$ heating and cooling cycles; rates 5 K min$^{-1}$).](image)
cooling cycles. In contrast, Gua(14,6)OTf showed lower clearing points and therefore stable mesophases. Most surprisingly, replacement of chloride by acetate significantly increased the stability of the SmC phase at the expense of the SmA phase. Thus, upon second heating of Gua(14,6)OAc, an endothermic melting transition at 72°C followed by an endothermal SmC to SmA transition (90°C) and a clearing transition at 139°C were observed. The reproducible clearing points of Gua(14,6)OAc indicated thermal stability due to a lowered clearing point of Gua(14,6)OAc compared with Gua(14,6)Cl. In the subsequent cooling cycle, the corresponding transitions were found at 142°C, 110°C and 62°C indicating a small hysteresis. The incorporated layer spacing of Gua(14,6)OAc (Figure 12 top) exhibits the same correlation with the DSC curve as Gua(14,6)Cl (Figure 10). Additionally, thermally stable Gua(14,6)PF₆ displayed reproducible clearing points in consecutive DSC measurements even though a clearing point > 170°C was present (Figure 12 bottom). The thermal stability of Gua(14,6)PF₆ was confirmed by TGA and DSC measurements (see Electronic Supporting Information).

Table 3. Phase transitions temperatures/°C (and corresponding enthalpies/kJ mol⁻¹) of guanidinium salts Gua(14,6)X with different anions.

| Gua(14,6)X | Cr | SmC | SmA | I |
|------------|----|----|----|----|
| Cl         | 65 | 84 | 193| 2nd heat |
| Br         | 74 | 93 | 194| 2nd cool |
| I          | 112| 80 | 187| 2nd cool |
| OTf        | 71 | 60 | 127| 2nd heat |
| BF₄        | 87 | 40.1| 70.1| 2nd heat |
| PF₆        | 62 | 89 | 183| 2nd cool |
| OAc        | 72 | 70 | 178| 2nd cool |
| SCN        | 67 | 110| 173| 2nd heat |
|            | 57 | 23.4| 173| 2nd cool |

Clearing transitions decreased upon successive heating and cooling cycles for anions X = Cl, Br, I, BF₄ and SCN; “for additional Cr–Cr transition, see ESI (Table 3); Cr: crystalline; SmC: smectic C; SmA: smectic A; I: isotropic; •: observed; –: not observed; cooling rate: 5 K min⁻¹.
In addition to \( \text{Gua}(14,6)\text{Cl} \), XRD measurements were carried out for guanidinium salts \( \text{Gua}(14,6)\text{OAc} \) and \( \text{Gua}(14,6)\text{BF}_4 \) with a SmC phase in order to obtain temperature-dependant \( d_{001} \) values (Figure 13). As described above (see Figures 6 and 10), \( d_{001} \) values for all guanidinium salts \( \text{Gua}(14,6)\text{X} \) (\( \text{X} = \text{BF}_4, \text{OAc} \) and \( \text{Cl} \)) increased within the SmA phase with decreasing temperature. After passing the SmA→SmC transition at 90–95°C, the layer spacing decreased upon further cooling of the SmC phase.

These results clearly show that the anion plays a critical role with respect to the mesogenic temperature range and mesophase type. Since the anions and organic cations often assemble in separate layers,[2] the proper choice of the anion might be as important as the shape of the organic cation. For derivatives \( \text{Gua}(14,6)\text{X} \), halide ions Cl, Br and I, BF\(_4\) and PF\(_6\) as well as SCN maintained broad mesophases with high clearing points \( > 170°C \) and melting points \( \leq 80°C \). In case of triflate and acetate, clearing points were lowered compared with \( \text{Gua}(14,6)\text{Cl} \). Smectic polymorphism was present for compounds \( \text{Gua}(14,6)\text{Cl} \), \( \text{Gua}(14,6)\text{BF}_4 \) and \( \text{Gua}(14,6)\text{OAc} \), which showed a SmA phase and a SmC phase at lower temperatures.

Among several theories for the molecular order within the SmC phase,[49] the zigzag model of Wulf[50] and Bartolino,[51] where the aromatic core is more tilted than the aliphatic chains, is widely accepted. Therefore, the zigzag model has been implemented in the boulder model by Walba and Clark,[52–54] which is a useful tool to predict the polarisation properties of ferroelectric liquid crystals such as fluorenones[55] and phenylpyrimidines.[56] Further studies such as XRD measurements by Böffel[57] and infrared dichroism experiments by Clark[58] confirmed that only the rigid core and a small adjacent part of the alkyl is tilted strongly within the SmC phase.

To improve the understanding of the mesophases of \( \text{Gua}(14,6)\text{X} \) on a molecular level, \( d_{001} \) values were extrapolated linearly to 0.95 \( T_c \) (clearing temperature), 0.95 \( T_{A/C} \) (SmA→SmC transition temperature) as well as 1.05 \( T_{A/C} \) and compared with the all-trans molecular length \( L_{\text{calc}} \) calculated with Chem3D (Table 4). The resulting ratio \( d_{001}/L_{\text{calc}} \) ranged from 1.8 to 1.3 for SmA phases. Regarding the symmetrically substituted series \( \text{Gua}(6,6)\text{Cl} \), \( \text{Gua}(10,10)\text{Cl} \) and \( \text{Gua}(14,14)\text{Cl} \), these ratios are in good agreement with the theoretical
ratio \((d_{\text{calc}}/L_{\text{calc}})\) which is based upon the layer thickness \(d_{\text{calc}}\) (Chem3D) of a bilayer structure with complete terminal interdigitation. Therefore, a smectic bilayer structure as shown in Figure 14 can be assumed.

The extrapolated ratio of 1.3 at 0.95 \(T_c\) might be due to the high clearing point of Gua(14,6)Cl compared with all other chlorides Gua(n,m)Cl which leads to an increased interlayer fluctuation resulting in a smaller \(d_{001}/L_{\text{calc}}\). An interpolation to 1.05 \(T_{A/C}\) as well as 0.95 \(T_{A/C}\) leads to ratios of 2.0 and implies a bilayer structure with some terminal interdigitation, since \(L_{\text{calc}}\) neglects the anion layer thickness completely. Due to structural similarities, we propose this molecular model for all guanidinium salts Gua(n,m)X with a zigzag shape in the SmC phase.

For compounds Gua(n,m)Cl, a long terminal alkyl chain \((n > 10)\) is a prerequisite for the formation of the ionic SmC phase, since only Gua(10,10)Cl–Gua(14,14)Cl and Gua(10,10)Cl–Gua(14,6)Cl showed this phase geometry. This seems to be a general tendency because most reported ILCs with SmC phases have terminal chain lengths \(n > 10\).[21–23,26,27,30] The preferred appearance of SmC phase upon increasing length of the terminal chain is well known for neutral liquid crystals and in accordance with the zigzag model of Wulf.[39]

**Conclusion**

A series of liquid crystalline guanidinium chlorides Gua(n,m)X containing an alkoxy biphenyl unit tethered via a flexible alkyl spacer to a guanidinium head group has been prepared, in order to identify the parameters which might be beneficial for the SmC phases, being much rarer in ILCs than the more common SmA phase. First of all, comparison with the corresponding para- and meta-substituted phenylguanidinium chlorides 2 reported earlier [32] and the ortho-substituted phenylguanidinium chloride ArGua(10,10)Cl revealed that flexibility is a prerequisite for SmC. Whereas ArGua(10,10)Cl was non-mesomorphic, para-2 and meta-2 showed only SmA phases and no evidence for SmC phases. In contrast, small SmC phases of 1–2 K for salts with flexible tether Gua(n,m)Cl were found for chain lengths \(n \geq C_{10}\). Thus longer terminal chain lengths seem to be beneficial for SmC mesomorphism.

However, the ratio of terminal alkyl chain versus spacer length seems to be a more important parameter. In other words, moving the calamitic unit closer to the head group while simultaneously extending the alkyl tail strongly improved both SmA and SmC phase stability as was seen for Gua (14,6)Cl. The second parameter which drives

| Phase type | \(d_{001}/Å\) | \(L_{\text{calc}}/Å\) | \(d_{001}/L_{\text{calc}}\) | \(d_{\text{calc}}/Å\) |
|-----------|-------------|-----------------|-----------------|-----------------|
| Gua(6,6)Cl | SmA\(_2\) | 49.6 | 27.4 | 1.8 | 48.6 | 1.77 |
| Gua(10,10)Cl | SmA\(_2\) | 62.2 | 36.6 | 1.7 | 63.4 | 1.73 |
| Gua(14,14)Cl | SmA\(_2\) | 72.9 | 45.8 | 1.6 | 80.4 | 1.76 |
| Gua(14,6)Cl | SmA\(_2\) | 47.4 | 37.4 | 1.3 | 58.7 | 1.57 |
| Gua(14,6)Cl | SmC\(_2\) | 76.3\(^{3}\) | 37.4 | 2.0 | 58.7 | 1.57 |
| Gua(14,6)BF\(_4\) | SmA\(_2\) | 54.0 | 37.4 | 1.4 | 58.7 | 1.57 |
| Gua(14,6)OAc | SmA\(_2\) | 59.4 | 37.4 | 1.6 | 58.7 | 1.57 |

\(^{3}\)Proposed bilayered mesophase; \(^{1}\)linear extrapolation to 0.95 \(T_c\); \(^{2}\)All-trans molecular length calculated with Chem3D; \(^{4}\)calculated \(d_{\text{calc}}\) with complete terminal interdigitation (Chem3D); \(^{5}\)linear interpolation to 1.05 \(T_{A/C}\); \(^{6}\)linear interpolation to 0.95 \(T_{A/C}\).

**Figure 14.** (colour online) Proposed SmA\(_2\) phase consisting of bilayers with terminal interdigitation and model of the SmC\(_2\) phase.
mesomorphism was found to be the anion. Within series Gua(14,6)X X = Br, I, OTf, PF6, SCN completely suppressed the formation of SmC, whereas X = Cl and X = BF4 induced an enantiotropic or monotropic SmC phase of ~27 K and still keeping a broad enantiotropic SmA phase of ~100 K. Surprisingly, acetate significantly increased the stability of the enantiotropic SmC to 48 K while decreasing the stability of enantiotropic SmA phase. Thus anions such as chloride, tetrafluoroborate and acetate might be considered as SmC promoting. XRD studies resulted in the proposal of a bilayer type structural model. The above mentioned structural parameters might be useful in the tailoring of other ILC families as well and should ultimately lead to increase the number of SmC ILCs suitable for applications.

Disclosure statement

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