Hunting for smectic C in calamitic azobenzene ionic liquid crystals with different cationic head groups

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Abstract

The tilted smectic C phase is a rather uncommon phase in ionic liquid crystals (ILCs), whereas the orthogonal smectic A phase is the most common phase in ILCs. We now present 2 new groups of mesogens with an azobenzene core that exhibit smectic C as well as smectic A phases. Their phase sequences and tilt angles were studied by polarizing microscopy, and their temperature-dependent layer spacings and orientational order parameters were investigated by X-ray diffraction. We present 1 new amidinium azobenzene mesogen that forms enantiotropic smectic C and A phases and another amidinium as well as 2 new guanidinium azobenzene mesogens that exhibit monotropic smectic C and enantiotropic smectic A phases. With this study, we show that azobenzene is indeed an SmC-promoting group in ILCs. Comparing these results with our earlier results on azobenzenes with an *N*-methylimidazolium head group (N Kapernaum et al, ChemPhysChem 2016, 17, 4116-4123), we show that the aromaticity of the imidazolium head group plays an important role in the formation of smectic C phases.

KEYWORDS

amidinium, de Vries material, guanidinium, imidazolium, ionic liquid crystals, smectic C

1 | INTRODUCTION

Among the huge variety of different low molecular weight compounds forming thermotropic mesophases, the class of ionic liquid crystals (ILCs) has received considerable interest because they combine the unique features of ionic liquids, such as low volatility, adjustable polarity and solubility, and high thermal and electrochemical stability with those of thermotropic liquid crystals and can thus be considered as ordered anisotropic fluid salts.^[1–8] Another remarkable feature of ILCs is that the relative occurrence of various mesophases is not the same as in nonionic thermotropic liquid crystals. For example, the lamellar nontilted SmA phase is the most common mesophase found in ILCs, while tilted SmC phases are much rarer as compared with the corresponding SmA/ SmC ratio in nonionic thermotropic liquid crystals.^[1-8] There are relatively few examples of ILCs with SmC phases described in the literature, most notably calamitic biphenyls,^[9–15] phenylpyrimidines,^[16] and azobenzenes^[17–19] with various cationic head groups. However, general design principles for SmC promoting mesogens are unknown for ILCs in contrast to the guidelines successfully developed by Lemieux for noncharged liquid crystals.^[20–22] From our previous findings that alkoxybiphenyls with tethered guanidinium moiety displayed indeed SmC phases in addition to the SmA phase, when the spacer was sufficiently long,^[23] we concluded that the connection of the cationic head group with a rigid calamitic unit via a flexible tether seems to be a promising design motive for that purpose. In addition, Westphal^[24] and we^[25] independently disclosed that azobenzenes tethered to imidazolium head groups formed tilted mesophases. Moreover, we discovered that these imidazolium salts were the first ILCs with de Vries-like SmA to SmC phase transitions.^[25] The so-called de Vries materials exhibit a very small laver contraction in the tilted SmC phase after the phase transition from the nontilted SmA phase.^[26–29] In conventional, non-de Vries materials, the SmA-to-SmC phase transition is accompanied by a strong contraction of the smectic layer thickness by a factor of $\cos\theta$ depending on the tilt angle θ between the director **n** and the layer normal **k** of the SmC phase. As ILCs with SmC phases are quite rare and show interesting properties like de Vries-type behavior, novel ILCs with SmC phases are highly desirable. Thus, we anticipated that azobenzenes with a flexible spacer connecting the cationic unit might be a promising SmC promoting group. However, the specific role of the head group remained unclear. In the current manuscript, we prepared a dedicated library of tethered azobenzenes with tetramethylguanidinium and dimethylamidinium head group and varying spacer lengths and explored their mesomorphic and physical properties with a special focus on SmA versus SmC phases. These tetramethylguanidinium and dimethylamidinium ILCs were compared with the corresponding known N-methylimidazolium ILCs. The results are reported below.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis of the ionic liquid crystals

The known azobenzene ILCs **MIM(C_n)Br** (n = 4, 6, 8) with *N*-methylimidazolium head group were prepared in 2 steps from 4-dodecyloxy-4'-hydroxyazobenzene **1** according to the previously described method (Scheme 1).^[25] Key intermediate **1** was also used as a precursor for the corresponding guanidinium and amidinium ILCs (Scheme 1).

Williamson etherification of the known ω-bromoalkyl-N-phthalimides $2^{[23]}$ provided the azobenzene derivatives $3(C_n)$ with terminal *N*-phthalimido-protecting group. Subsequent hydrazinolysis followed by reaction with tetramethylformamidinium chloride and triethylamine according to the method by Kantlehner^[30] and treatment with HCl or HBr (method A) vielded the guanidinium chlorides $Gua(C_n)Cl$ (n = 4, 6, 8) and bromides $Gua(C_n)Br$ (n = 4, 8), respectively, in 42 to 56%. The bromide with C_6 spacer **Gua(C_6)Br** was obtained via salt metathesis (method B) from the corresponding chloride Gua(C₆)Cl in 99%. For the synthesis of the amidinium salts, N-phthalimides $3(C_n)$ were submitted to hydrazinolysis and the resulting free amines were treated with N.N-dimethylformamide dimethylacetal in DMF at 80°C under microwave conditions followed by reaction with HCl and HBr, respectively, to give the amidinium chloride $Am(C_4)Cl$ in 78% and bromides $Am(C_n)Br$ (n = 4, 6, 8) in 66 to 82%.



SCHEME 1 Synthesis of guanidinium (Gua(C_n)X) and amidinium salts (Am(C_n)X) starting from azobenzene 1

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2.2 | Solid state structures of the ionic liquid crystals

Fortunately, single crystals were obtained for guanidinium chloride $Gua(C_4)Cl$, amidinium chloride $Am(C_4)Cl$, and imidazolium bromide $MIM(C_4)Br$, respectively, which were suitable for X-ray crystal structure determination.^[31] Guanidinium chloride Gua(C₄)Cl crystallizes with 1 molecule in the asymmetric unit, 1 chlorine as counterion, and 2 chloroform solvent molecules in the centrosymmetric space group $P2_1/n$. We found a hydrogen bond with the N-H function of the guanidinium head as donor and the chlorine as acceptor. The hydrogen bond is nearly linear with a N1…Cl1 distance of 3.279(2) Å and a H1…Cl1 distance of 2.45(3) Å and an angle N1-H1…Cl1 of 167(3)°. In addition, a considerable shortening of the O1-C1 distance of 6.1 Å due to folding of the C4 spacer was observed. For comparison, the distance of the linear folded tail atoms C27...C33 is 7.6 Å (Figure 1A).

The guanidinium salt displays a tilted bilayer packing along the *c*-axis with strong interdigitation (Figure 1B). There are 2 types of interdigitating interactions evident. First, there is an interdigitated orientation between 2 molecules with coplanar phenyl moieties. The C33-C11 distance is 3.94 Å, and the lengthening factor is 1.29. Second, there is an interdigitated orientation between 2 molecules with a perpendicular orientation between 2 molecules. The C33-C18 distance is 3.97, and the lengthening factor is 1.51 (Figure 1C).

Derivative $Am(C_4)Cl$ crystallizes with 1 ion pair in the asymmetric unit of the centrosymmetric monoclinic space group P2₁/n (Figure 2A). An intermolecular H bond is evident between the N2-H2 function of the amidinium head group as donor and the Cl counterion as acceptor. The N2…Cl1 distance is 3.11(1) Å and that of H2…Cl1 is 2.27 Å. The N2-H2…Cl1 angle is 159°. The folding of the C4 spacer yields also to a pronounced decrease of the O1…C3 distance (5.34 Å) bringing the amidinium head group closer to the azobenzene. For comparison, the



FIGURE 1 X-ray structure of **Gua(C₄) Cl** in the solid state (A) and packing diagrams (B and C) (H atoms omitted for clarity)





C25···C31 distance of the tail atoms in an extended alltrans conformation is 7.63 Å. In contrast to **Gua(C₄)Cl**, an antiparallel tilted bilayer packing along the *b*-axis without any interdigitation was observed (Figure 2B).

The **MIM(C₄)Br** system crystallizes with 4 independent ion pairs in the asymmetric unit of the centrosymmetric triclinic space group $P\overline{1}$. Additional 4 water molecules co-crystallize in the structure (Figure 3). The structure is stabilized by a complex network of intermolecular hydrogen bond interactions. The H atoms of the water molecules act as donor, where the Br anions work as acceptor. On the imidazolium head group, the C–H groups are also donors of hydrogen bonds, of which the water oxygen atoms and Br anions work alternatively as acceptors. The C4 spacer shows in all conformers no

extended all-*trans* conformation, which yields in a shortened O1-C1 distance to the imidazolium head between 5.71 and 5.83 Å. For comparison, the tail C26····C32 distance is 7.65 Å. In contrast to both **Gua(C₄)Cl** and **Am(C₄)Cl**, the bend spacer of the imidazolium salts resulted in S-shaped dimers forming a tilted bilayer packing along the *c*-axis. As in amidinium salt **Am(C₄)Cl**, an interdigitation of the antiparallel oriented tails of the molecules is not evident (Figure S1).

2.3 | Mesomorphic and physical properties of the ionic liquid crystals

The 3 homologous guanidinium bromides $Gua(C_4)Br$, $Gua(C_6)Br$, and $Gua(C_8)Br$ as well as the 3 amidinium



FIGURE 3 X-ray structure of MIM(C₄)Br in the solid state (packing diagram see Figure S1)

bromides $Am(C_4)Br$, $Am(C_6)Br$, and $Am(C_8)Br$ were investigated to characterize their mesomorphic and physical properties. Polarizing optical microscopy (POM) and differential scanning calorimetry were used to identify the mesophases and to determine the phase transition temperatures and transition enthalpies (Table 1). For the POM investigations, a red band-pass filter with 630 nm was used to prevent the light-induced cis-trans-isomerization of the azo-group.^[32,33] For better comparison of the quanidinium and amidinium mesogens with the mesogens with imidazolium head group,^[25] only the bromides were studied because the imidazolium chlorides $MIM(C_n)Cl$ neither are available via alkylation of the chloroalkyl precursor nor by subsequent salt metathesis of MIM(C_n)Br. Furthermore, the chloride salts are usually more hygroscopic than the bromides.

All 6 mesogens exhibit SmA phases. Furthermore, an SmC phase was observed in both series for the homologs with a spacer length of 6 and 8 carbon atoms, while the 2 homologs with a spacer length of 4 carbon atoms only showed an SmA phase. The mesogen $Am(C_6)Br$ exhibits an enantiotropic SmC phase, while $Gua(C_6)Br$, $Gua(C_8)$ **Br**, and $Am(C_8)Br$ show monotropic SmC phases that only appear on cooling. The phase transition from the SmA to the SmC phase showed small peaks in the differential scanning calorimetry for all 4 mesogens. This indicates weakly first-order phase transitions with transition enthalpies ΔH_{AC} in the range of 0.8 to 1.8 kJ mol⁻¹. These are typical values for ΔH_{AC} as the phase transition of nonionic mesogens are in the same range.^[34,35]

Textures of the SmA and SmC phases under the polarizing microscope are shown in Figures 4 and 5 for **Gua(C₈) Br** and in Figures 6 and 7 for **Am(C₈)Br**. In liquid crystal test cells coated with single side rubbed Nylon **Gua(C₈)** **Br** exhibited a fan-shaped texture in the SmA phase and a broken fan-shaped texture in the SmC phase (Figure 4). $Am(C_8)Br$ showed in the liquid crystal test cell a well aligned planar texture in the SmA phase and a domain texture in the SmC phase (Figure 6). Under homeotropic conditions in the SmA phase, **Gua(C8)Br** (Figure 5, top) showed a black homeotropic texture, while for $Am(C_8)Br$ (Figure 7, top), an oily streak texture is observed. In the SmC phase, both materials exhibit a Schlieren texture under homeotropic conditions (Figures 5 and 7, bottom).

The temperature-dependent smectic layer spacing d(T) of all 6 materials was measured with small-angle Xray scattering. The layer spacing for the guanidinium mesogens is shown in Figure 8A and for the amidinium mesogens in Figure 8B. **Gua(C₄)Br** and **Am(C₄)Br** exhibit only an SmA phase and therefore show a continuously rising layer spacing with decreasing temperature due to increasing orientational order at lower temperatures (small insets in Figure 8A and B).

The layer spacings of $Gua(C_6)Br$, $Gua(C_8)Br$, $Am(C_6)Br$, and $Am(C_8)Br$ increase likewise in the SmA phase until the typical layer shrinkage of the SmC phase takes place. For the enantiotropic SmC phase of $Am(C_6)Br$ as well as for the monotropic SmC phases of Gua(C₆)Br and Gua(C₈)Br, it was possible to measure the layer spacing at least until 10 K below the tilting transition. The monotropic SmC phase of $Am(C_8)Br$ on the contrary crystallized during the X-ray measurements already 3 K below the phase transition from SmA to SmC. The layer shrinkage 10 K below the SmA to SmC phase transition is 12% for Gua(C₆)Br, 12.7% for Gua(C₈)Br, and 7.2% for Am(C6)Br. This indicates that these mesogens are conventional non-de Vries-type materials, which show a regular layer shrinkage below their SmA-to-SmC phase transition.

TABLE 1	Phase sequences on heating (top row) and cooling (bottom row) determined by polarizing optical microscopy (POM) and tran-
sition enthal	lpies ΔH_{AC} of the SmA-to-SmC phase transition determined by differential scanning calorimetry (DSC) of guanidinium and
amidinium l	bromides

Mesogen	Phase Sequence	$\Delta H_{\rm AC}$
Gua(C ₄)Br	Cr 141°C SmA 217°C Iso Iso 213°C SmA 121°C Cr	
Gua(C ₆)Br	Cr 124°C SmA 166°C Iso Iso 163°C SmA 102°C (SmC) 63°C Cr	-0.8 kJ mol^{-1}
Gua(C ₈)Br	Cr 124°C SmA 167°C Iso Iso 166°C SmA 118°C (SmC) 83°C Cr	-1.4 kJ mol^{-1}
Am(C ₄)Br	Cr 155°C SmA 226°C Iso Iso 225°C SmA 150°C Cr	
Am(C ₆)Br	Cr 135°C SmC 146°C SmA 214°C Iso Iso 213°C SmA 145°C SmC 110°C Cr	+1.2 kJ mol ⁻¹ -1.6 kJ mol ⁻¹
Am(C ₈)Br	Cr 153°C SmA 178°C Iso Iso 178°C SmA 148°C (SmC) 136°C Cr	-1.8 kJ mol^{-1}



FIGURE 4 Planar textures of **Gua**(C_8)**Br** in liquid crystal test cells coated with single-side rubbed nylon with a cell gap of 1.8 µm under the polarizing microscope. Top: fan-shaped texture of the SmA phase at 130°C. Bottom: broken fan-shaped texture of the SmC phase at 105°C

The optical tilt angles θ were measured for all 4 SmC mesogens with the polarizing microscope (Figure 9). The 2 guanidinium mesogens showed higher tilt angles than the amidinium compounds. The highest tilt angles of about 38° were found for **Gua(C₈)Br**, while the tilt angles of the shorter homolog **Gua(C₆)Br** reached only 27°. The 2 amidinium compounds **Am(C₆)Br** and **Am(C₈)Br** exhibit similar values of their tilt angles with a maximum tilt of approximately 23°.

The optical tilt angles θ were compared with the tilt angles θ_{Xray} calculated from the layer shrinkage in the small-angle X-ray scattering measurements for **Gua(C6) Br**, **Gua(C8)Br**, and **Am(C₆)Br** 10 K below the SmA-to-SmC phase transition to check whether these compounds exhibit de Vries-type behavior (Table 2). The X-ray tilt angles θ_{Xray} were calculated according to Equation 1:

$$\theta_{\rm Xray} = \cos^{-1}(d_{\rm C}/d_{\rm A}). \tag{1}$$

where d_A denotes the maximum layer spacing in the SmA phase and d_C the layer spacing in the SmC phase 10 K below the SmA-to-SmC phase transition. These X-ray tilt angles θ_{Xray} were compared with the optical tilt angles θ at $T - T_{AC} = -10$ K to receive the figure of merit *R* (Equation 2)^[36,37]



FIGURE 5 Homeotropic textures of $Gua(C_8)Br$ between 2 plain glass plates under the polarizing microscope. Top: black homeotropic texture of the SmA phase with few defects at 150°C. Bottom: Schlieren texture of the SmC phase at 84°C

$$R = \theta_{\rm Xray} / \theta. \tag{2}$$

In the case of conventional behavior, R is 1, while it is 0 for perfect de Vries behavior. The best de Vries materials known show R values in the range of 0.17.^[38] The mesogens **Gua(C₆)Br** and **Am(C₆)Br** have R values of 1 or even higher, which means that they do not show de Vries behavior and behave completely conventional. **Gua(C₈)Br** has an R value of 0.78. This shows that its X-ray layer shrinkage is a little bit smaller than what is expected from the optical tilt angles but still exhibits a huge layer shrinkage and is thus also a conventional non-de Vries-type material.

For the 2 mesogens $Gua(C_6)Br$ and $Am(C_8)Br$, the orientational order parameters S_2 of the SmA phases were determined by X-ray measurements on cooling from the isotropic phase (Figure 10). The orientational order parameter measures the quality of the parallel orientation of the long axes of the rod-like mesogens with respect to the director. Experimental values of S_2 are obtained from the directional intensity profile of the diffuse wide-angle scattering arcs of aligned monodomain samples according to the procedure by Davidson and Levelut.^[39]

The orientational order parameters of the SmA phases were in the range of 0.5 for both mesogens and nearly



FIGURE 6 Planar textures of $Am(C_8)Br$ in liquid crystal test cells coated with single-side rubbed nylon with a cell gap of 1.8 µm under the polarizing microscope. Top: aligned planar texture of the SmA phase at 155°C. Bottom: planar domain texture of the SmC phase at 140°C

independent of temperature. In the SmA phases of nonionic thermotropic liquid crystals, S_2 usually exhibits values of about 0.7.^[40] The values for S_2 for **Gua(C₆)Br** and **Am(C₈)Br** are thus substantially smaller, but these low values are typical for ILCs.^[25,33] In the case of ILCs, the driving force for the formation of liquid crystal phases is the nanosegregation between the ionic and the nonionic parts of the molecule, which leads to a strong layering.^[41,42] The orientational order is thus only a secondary order parameter and often remains quite low and shows only a weak temperature dependence.

With all the data collected so far, we will now present a structure model for these smectic ILCs by using the example of **Gua(C₆)Br** for the guanidinium series and **Am(C₈)Br** for the amidinium series; as for these 2 mesogens, the values of their orientational order parameters are known. The molecular lengths *L* of both molecules are calculated by molecular modeling. It is 36.9 Å for **Gua(C₆)Br** and 41.3 Å for **Am(C₈)Br**. These values for the molecular length are compared with the layer spacing *d* of the smectic A phase of the 2 mesogens, and we receive for both mesogens a ratio of approximately *d/* $L \approx 1.8$. This means that the smectic A phases of the guanidinium and the amidinium mesogens investigated in this study are SmA₂ phases, which are built of double



FIGURE 7 Homeotropic textures of $Am(C_8)Br$ between 2 plain glass plates under the polarizing microscope. Top: oily streak texture of the SmA phase at 155°C. Bottom: Schlieren texture of the SmC phase at 138°C

layers like most smectic A phases of ILCs. The ratio of 1.8 seems to indicate that the SmA₂ phase is built of partially interdigitated double layers. Nevertheless, for this simple calculation, the orientational order was not taken into account. For these ILCs, S_2 is in the range of 0.5 (see Figure 10). The orientational order parameter measures the quality of the orientational order of the long axes of the mesogens with respect to the director. The value of 0.5 indicates that most mesogens are randomly tilted with respect to the director in all possible directions, and this involves a contraction of the smectic layers. To take this impact of the orientational order on the layer spacing d into account the effective molecular length, L_{eff} is needed. The effective molecular length can be interpreted as the layer spacing at a certain temperature if the rod-like mesogens had perfect orientational order. It is calculated after (Equation 3):^[43,44]

$$L_{\text{eff}} = \frac{3 \cdot d(T)}{S_2(T) + 2}.$$
(3)

where L_{eff} is determined for all temperatures where the orientational order parameter S_2 is known (Figure 10). The averaged values for the effective molecular length are $L_{\text{eff}} = 80.6$ Å for **Am(C₈)Br** and $L_{\text{eff}} = 77.5$ Å for **Gua(C₆)Br**. By comparing these values with the



FIGURE 8 Layer spacing *d* versus temperature *T* relative to the SmA-SmC transition temperature T_{AC} for (A) the 3 guanidinium mesogens **Gua(C₄)Br**, **Gua(C₆)Br**, and **Gua(C₈)Br** and (B) the 3 amidinium mesogens **Am(C₄)Br**, **Am(C₆)Br**, and **Am(C₈)Br**

calculated molecular length *L*, we get a ratio L_{eff}/L of 1.95 for **Am(C₈)Br** and of 2.1 for **Gua(C₆)Br**. This indicates that the smectic A₂ phases of these ILCs are within experimental error built of full double layers without any considerable degree of interdigitation.

2.4 | Comparison of the mesomorphic properties with our earlier results on imidazolium azobenzenes^[25]

The results on our azobenzene bromides with guanidinium or amidinium head groups are compared with our previous results on the same azobenzene bromides but with imidazolium head groups **MIM(C_n)Br** (n = 4, 6, 8) (Scheme 1 and Kapernaum et al^[25]). The phase transition temperatures for these 9 mesogens are summarized in Figure 11. The imidazolium compounds exhibited more stable SmC phases than the amidinium and guanidinium mesogens. All 3 imidazolium mesogens showed an enantiotropic SmC phase over at least 25 K, while in the case of the guanidinium and amidinium head



FIGURE 9 Tilt angle versus temperature difference to the SmA-SmC phase transition for (A) **Gua(C₆)Br** and **Gua(C₈)Br** and (B) **Am(C₆)Br** and **Am(C₈)Br**

TABLE 2 Optical tilt angle θ , layer shrinkage, X-ray tilt angle θ_{Xray} , and for **Gua(C₆)Br**, **Gua(C₈)Br**, and **Am(C₆)Br** 10 K below the SmA to SmC phase transition

	θ/deg	Layer Shrinkage/%	$\theta_{\rm Xray}/^{\circ}$	R Value
Gua(C ₆)Br	27.3	12.0	28.3	1
Gua(C ₈)Br	37.3	12.7	29.1	0.78
Am(C ₆)Br	16.6	7.2	21.9	>1

groups, only the homologs with spacer lengths of 6 and 8 formed an SmC phase. Furthermore, these SmC phases were only monotropic in the case of $Gua(C_6)Br$, $Gua(C_8)Br$, and $Am(C_8)Br$. Only $Am(C_6)Br$ showed an enantiotropic SmC phase over a temperature range of approximately 10 K.

The smectic layer shrinkage in the SmC phase 10 K below the SmA-to-SmC phase transition of the imidazolium compounds measured by X-ray scattering was much smaller than those of amidinium and guanidinium bromides. In the case of imidazolium mesogens, it was in the range of 4% for $MIM(C_4)Br$ to



FIGURE 10 Orientational order parameter S_2 versus temperature T in the SmA phase of **Gua(C₆)Br** and **Am(C₈)Br** measured on cooling

2.3% for **MIM(C₈)Br** (Figure 12 and Kapernaum et al^[25]). The layer shrinkage of the 2 guanidinium mesogens was about 12%, while it was 7.2% for **Am(C₆)Br**.

The maximum tilt angles of the imidazolium compounds were in the range of $30^{\circ[25]}$ (Figure 12 inset for **MIM(C₈)Br**). This is quite similar to the values for **Gua(C₆)Br** and the 2 amidinium mesogens of about 25°. The maximum tilt angles of **Gua(C₈)Br** were with 38° slightly higher than those of imidazolium bromides. The azobenzene mesogens from the 3 series therefore exhibit usual tilt angles in their SmC phases.

Due to the small layer shrinkage of the imidazolium compounds, their figures of merit for the de Vries character, namely, their *R* values, were much smaller than the ones of the amidinium and guanidinium compounds. The *R* value for **Gua(C₆)Br** and **Am(C₆)Br** was approximately 1, and it was 0.78 for **Gua(C₈)Br**, which indicates conventional behavior. For the imidazolium compounds, *R* values of 0.61 for **MIM(C₄)Br**, 0.54 for **MIM(C₆)Br**, and 0.48 for **MIM(C₈)Br** were calculated.^[25] This means that the amidinium and guanidinium mesogens show conventional behavior, while the imidazolium series exhibits aspects of de Vries-like behavior with a layer



FIGURE 11 Phase transition temperatures *T* on heating (top) and cooling (bottom) for the mesogens with guanidinium ($Gua(C_n)Br$), amidinium ($Am(C_n)Br$), and imidazolium ($MIM(C_n)Br$) head groups measured by polarizing optical microscopy (POM)



FIGURE 12 Layer spacing *d* and tilt angle θ versus temperature difference to the SmA-SmC phase transition *T*-*T*_{AC} for the imidazolium mesogen **MIM**(**C**₈)**Br**^[25]

shrinkage that is smaller than what is expected from the optical tilt angles.

To summarize the results on the 3 azobenzene series, we found the most stable and therefore broadest smectic

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phase range for the mesogens with imidazolium head group, while the smectic phase ranges of the mesogens with amidinium and guanidinium head groups were similar to each other and significantly less broad than for the imidazolium head group (see Figure 11). Furthermore, we observed that the imidazolium head group was the strongest SmC promoting head group of all 3 and led to the most stable SmC phases. The amidinium as well as the guanidium head group led to less stable SmC phases. Of these 2 head groups, the amidinium head group seemed to be more SmC promoting, as $Am(C_6)Br$ was the only mesogen of these 2 series that formed an enantiotropic SmC phase. Although we observed de Vries-like behavior with a reduced layer shrinkage with respect to the optical tilt angles in the imidazolium series, the guanidinium as well as the amidinium compounds exhibited conventional behavior with the layer shrinkage in the SmC phase being in accordance with their optical tilt angles.

To rationalize these different behaviors of the head groups, their geometries and elongations were considered. All 3 head groups were modeled with only a methyl group as substituent, and their energies were minimized. Figure 13 shows the 3 head groups as well as their dimensions, which are in agreement with the obtained X-ray crystal structure data discussed above.

Whereas N,N-dimethylamino moieties in guanidinium and amidinium head groups possess rotational freedom with an energy barrier of 47 to 53 kJ mol^{-1} as determined previously by variable temperature NMR for related guanidinium salts,^[45] resulting in a 3D oval shape for guanidinium and a 3D spherical shape for amidinium units, the heterocyclic N-methylimidazolium head group consists of a flat shape (see Figure 13). These 3D shapes together with the elongations of the head groups lead to an increase of the volume of the head group from the small and flat imidazolium head group to the spherical amidinium head group to the biggest egg-shaped guanidinium head group. In non-ILCs, it was found that flexible and bulky groups at the end of the molecules cause an increase of the tilt of the aromatic cores due to the entropic pressure caused by the bulky end groups.^[46,47] In our case, the mesogens behave completely contradictory to these earlier observations. The bulkiest head group, the guanidinium head group, has the lowest tendency to form SmC phases, while the smallest head group, imidazolium, shows most SmC phases with the broadest temperature range of all 3 mesogens.

We therefore suggest aromaticity as another structural characteristic that leads to the huge differences in the behavior of the 3 groups of ionic mesogens. Nanosegregation between the rigid aromatic cores and the flexible aliphatic side chains is usually the driving force for the formation of smectic phases in nonionic



FIGURE 13 Molecular models of the 3 head groups *N*-methylimidazolium, dimethylamidinium, and tetramethylguanidinium with an additional methyl group. The structures were energy-minimized by molecular modeling

rod-shaped thermotropic mesogens.^[48] By adding an additional aromatic group at the end of the molecule, attractive noncovalent π - π interactions between these aromatic groups can improve the nanosegregation. Stronger nanosegregation enhances the stability of smectic phases, and it also stabilizes the SmC phase as stronger nanosegregation reduces the out-of-layer fluctuations, and this minimizes the entropic cost of molecular tilt in a smectic structure.^[21,46] The aromatic imidazolium head groups can form $\pi^+ - \pi^+$ interactions between the positively charged aromatic rings.^[49,50] These π^+ - π^+ interactions have been shown in simulations by Nagata and his coworkers to enhance the layering in ionic liquids.^[51] It should be noted that in the solid state structure of the imidazolium salt MIM(C₄)Br, no face-to-face orientation was observed, but a dimer, where the imidazolium moieties are shifted approximately 1 moiety to the next stack (Figure S1B). The tilt angle between the neighbor moieties is 17.8(4)°. Nevertheless, there is a weak electrostatic interaction characterized by the distances C2C-N1D of

3.508(7) Å, C2C-C3D of 3.594(8) Å, and N2C-C3D of 3.702(7) Å. The experimentally observed dimers in the solid state resemble the diagonal conformers calculated by Matthews,^[49] where reduction in Coulomb repulsion facilitates cation-cation close contact. As the nonaromatic head groups amidinium and guanidinium cannot form these $\pi^+ - \pi^+$ interactions, it can be concluded that the nanosegregation in the case of the aromatic imidazolium head group might be stronger than for the nonaromatic amidinium or guanidinium head groups. This stronger layering then leads to broader smectic phases, and it also stabilizes the SmC phase. The stronger layering and therefore higher translational order of the mesogens with imidazolium head group can also explain that we found de Vries-like behavior for the imidazolium ILCs, while we could not observe it for the ILCs with amidinium and guanidinium head groups. It was stated by Lagerwall et al^[52] and later experimentally confirmed by Nonnenmacher et al^[44] that de Vries behavior originates from the unusual combination of exceptionally low orientational order with strong 1D translational order. This means that the increase in nanoseggregation caused by the π^+ - π^+ interactions of the imidazolium head groups can also lead to stronger de Vries-like behavior.

3 | CONCLUSION

We have demonstrated that the linear aromatic core azobenzene is indeed an SmC-promoting group in ILCs in agreement with previous work by Ujie,^[17,18] Zhang,^[19] and Westphal.^[24] SmC phases in ILCs have also been observed with other linear cores like tolane^[24] or terphenylene,^[11] while in cases where the connecting group has a slight bent structure, like 1,3,4-oxadiazole,^[53] the SmC phase is absent. However, the head group seems to have a critical influence on the stability of the SmC phase and the layer shrinkage after the SmA-to-SmC phase transition. While in the case of these 3 groups of azobenzene mesogens, the influence on the phase behavior of the effective volume of the head group is negligible; the aromaticity of the head group seems to influence the phase behavior strongly. The aromatic π^+ - π^+ interactions of the N-methylimidazolium head groups increase the nanosegregation in these smectic phases, and therefore, the stability of the smectic phases as well as the stability of the SmC phase and the tendency toward de Vries-like behavior with minimum SmA \rightarrow SmC layer contraction is increased with respect to the 2 other groups of azobenzene ILCs with tetramethylguanidinium or dimethylamidinium head group. In addition, we have introduced for the first time amidinium units as suitable ILC head groups supporting SmC phases. Further work

in particular with respect to the counterion and the role of hydrogen bonding interaction is necessary to fully elucidate the formation of SmC phases in ILCs in general.

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