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Ionic Liquid Crystals Derived from Amino Acids

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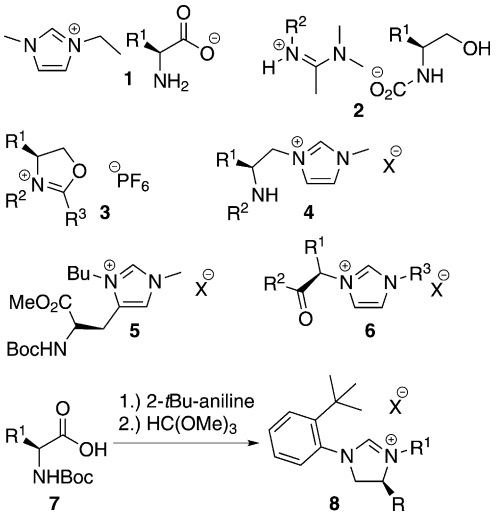
Abstract: Novel chiral amino acid derived ionic liquid crystals with amine and amide moieties as spacers between the imidazolium head group and the alkyl chain were synthesised. The key step in the synthesis utilised the relatively uncommon SO_3 leaving group in a microwave-assisted reaction. The mesomorphic properties of the mesogens were determined by differential scanning calorimetry (DSC), polarising optical microscopy (POM) and X-ray diffraction. All liquid crystalline salts exhibit a smectic A mesophase geometry with strongly interdigitated bilayer structures. An increase of the steric bulk of the stereogenic centre hindered the formation of mesophases. In case of phenylalanine-derived derivatives a mesomorphic behaviour was observed for shorter alkyl chains as compared to other amino acid derivatives indicating an additional stabilising effect by the phenyl moiety.

Keywords: amino acids · amino alcohols · chiral pool · ionic liquids · liquid crystals

Introduction

The combination of ionic liquids (ILs) and liquid crystals (LCs) results in ionic liquid crystals (ILCs), which possess chemical and physical properties found in both families of compounds, that is, fluidity, low vapour pressure and ionic conductivity from the ILs and anisotropic physical properties such as birefringence and orientational order from the LCs. Consequently, they can be used in a manifold of applications.[1] The insertion of a stereogenic centre leads to chiral ILCs, which are interesting compounds due to their promising applications for asymmetric synthesis, stereoselective polymerisation, chiral chromatography, transport membranes for CO_2 and NMR chiral discrimination.[2] Recently, we synthesised chiral imidazolium and pyridinium ILCs starting from (*R*)-citronellol as a natural precursor.[3] Due to the price of the starting material and difficulties with the upscaling, we wanted to use cheaper chiral building blocks, which could be efficiently converted into chiral ILCs. Amino acids from the chiral pool seemed to be ideal precursors for this purpose due to their good availability and their low price. Most examples, which use amino acids as precursors or reagents, are from task-specific ILs,[2e,g,h,4] where the amino acid can be either the cation[2g,j] or the anion.[2d,f,5] In the case of ILs with amino acid anions 1-ethyl-3-methylimidazolium hydroxide was neutralised with the neat amino acid[2d,5] to yield compounds **1** (Scheme 1). Alternatively, the amino acids were reduced to the corresponding amino alcohols and mixed with an amidine[2f,6] to get the desired products **2**. To introduce an amino acid into the cation there are often more synthetic steps required. Reduction to the amino alcohols and further reactions to the oxazolinium derivatives[2j] **3** or conversion with methylimidazole to the imidazolium-based ILs **4**, comprising an amine,[2g] are necessary. Other approaches have been published recently, such as the use of the pre-existing imidazole ring in histidine **5**,[2h,7] the assembly of the imidazole ring through a condensation of the amino acid with glyoxal, formaldehyde and aqueous ammonia[8] or ammonium acetate[9] to yield compounds **6** or the reaction of the protected amino acids **7** with 2-*tert*-butylaniline and further conversion with trimethylorthoformate to give compounds **8**.[10]



Scheme 1. Ionic liquids derived from amino acid. Boc = butyloxycarbonyl, *t*Bu = *tert*-butyl.

LCs are broadly classified into two categories, according to the dependency as to how their liquid crystalline phases

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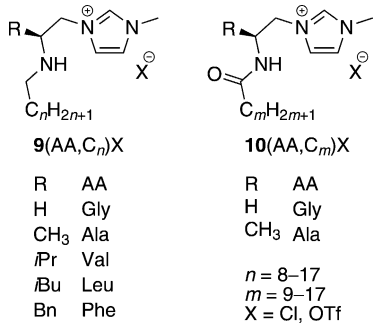
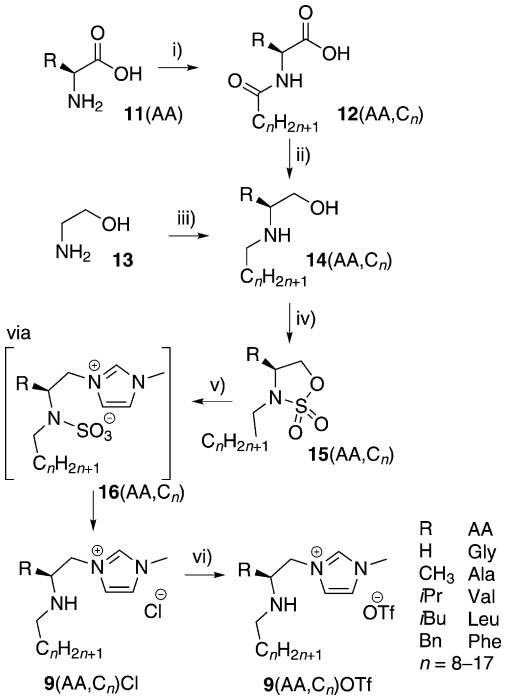
are formed. The two most common of these groups are lyotropic (solvent dependent) and thermotropic (temperature dependent). There are some examples in the literature where LCs derived from amino acids form the lyotropic mesophases. One type consists of hexa(phenylethinyl)benzene with terminal amino acid esters.[11] Another example describes third generation amino acid-based dendrons, in which the lyotropic and thermotropic mesophases are partly stabilised by ammonium and carboxylate units.[12] Furthermore, charged LCs have been reported, where the neat amino acid is used as cation.[13] There are fewer examples for amino acid-derived dendritic thermotropic LCs.[12] There are also other approaches in the synthesis of thermotropic LCs derived from amino acids like the formation of bisamino acid esters[14] or the introduction of aromatic,[15] amide[16] or ester[17] groups, but these examples are all uncharged LCs. To the best of our knowledge, we here describe the first example of an amino acid derived thermotropic imidazolium ILC bearing amine **9**(AA,C_n)X or amide moieties **10**(AA,C_m)X (Scheme 2). The results regarding the synthesis and the mesomorphic properties are discussed below.



Scheme 2. Amino acid imidazolium derivatives with amine **9**(AA,C_n)X and amide moieties **10**(AA,C_m)X. *i*Pr = isopropyl, *i*Bu = isobutyl, Bn = benzyl.

Results and Discussion

Synthesis: The synthesis of the amino-substituted ILCs **9**-(AA,C_n)X is shown in Scheme 3. The synthesis was accomplished either through the amidation of the amino acid **11** (*S*-alanine, *S*-leucine, *S*-phenylalanine, *S*-valine) with an acyl chloride[18] and subsequent reduction[2g] or in the case of aminoethanol **13** conversion with a bromoalkane[19] to the corresponding amino alcohols **14**(AA,C_n) in moderate to good yields. A racemisation of the enantiopure starting material during the reduction process could be excluded due to single-crystal investigations (see the Supporting Information) and optical rotation experiments. The use of halide leaving groups for the quaternisation was not possible due to the poor reactivity and consequently a relatively uncommon SO_3 leaving group was used instead.[20] This leaving group was inserted through the reaction of the secondary amino alcohol **14**(AA,C_n) with thionyl chloride and subsequent oxidation to the sulfamidate species **15**(AA,C_n) (56–

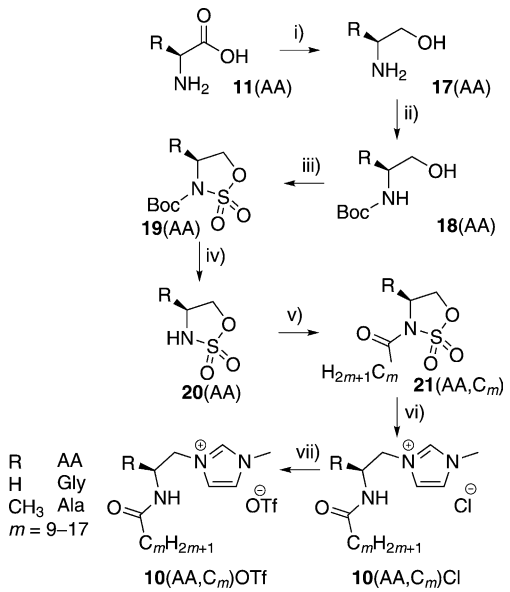


Scheme 3. Synthesis of amine imidazolium derivatives **9**(AA,C_n)X. Reagents and conditions: i) Acyl chloride, $NaOH_{aq}$, 0 °C, 18 h. ii) 1) $NaBH_4$, I_2, THF, reflux, 18 h; 2) $NaOH_{aq}$, reflux, 18 h. iii) Bromoalkane, NEt_3, EtOH, reflux, 18 h. iv) 1) $SOCl_2$, imidazole (Im), CH_2Cl_2, −78 °C→RT, 18 h; 2) $RuCl_3$, $NaIO_4$, CH_2Cl_2, H_2O, 0 °C, 2 h. v) 1) MeIm, microwave, 140 °C, 2 h; 2) Et_2O·HCl, MeOH, reflux, 18 h; 3) $NaHCO_3$, CH_2Cl_2. vi) NaOTf (Tf = trifluoromethanesulfonyl), MeCN, reflux, 1 h.

84 %).[21] The sulfamidate **15**(AA,C_n) was reacted with methylimidazole in a microwave-assisted reaction leading to the zwitterionic species **16**(AA,C_n), which was further converted to the corresponding imidazolium salt **9**(AA,C_n)Cl with an etheric HCl solution (29–99 %). A detailed tabular survey of the yields is given in the Supporting Information.

The synthesis of the amide compounds **10**(AA,C_m)X commenced with the reduction of the amino acids **11** to the amino alcohols **17**(AA) (67–85 %) (Scheme 4),[22] which were protected with the Boc group to give compounds **18**(AA)[23] in good yields (89–99 %) and subsequently converted to the corresponding sulfamidate species **19**(AA) with thionylchloride and $NaIO_4$ (71–88 %).[24] After deprotection with trifluoroacetic acid (TFA) to **20**(AA)[25] (74–98 %) and amidation under Steglich conditions[26] (16–56 %) the sulfamidates **21**(AA,C_m) were reacted in a microwave-assisted reaction with methylimidazole to the amide species **10**(AA,C_m)Cl in moderate to good yields (46–99 %).

The use of the Boc protecting group and the additional reaction steps were necessary due to the formation of the dihydrooxazols **22** (see the Supporting Information). The poor yield of the amidation might be explained as follows. With a decreasing chain length of the carboxylic acid and therefore an increasing reactivity, the yield of the desired sulfamidates **21**(AA,C_m) decreased and an increase of the amidation/esterification side product **23a**–**23c** was observed (see the Supporting Information). Furthermore, with an increas-



Scheme 4. Synthesis of imidazolium derivatives bearing an amide group **10**(AA,C_m)X. Reagents and conditions: i) 1) $NaBH_4$, I_2, THF, reflux, 18 h; 2) $NaOH_{aq}$, reflux, 18 h or 1) $LiAlH_4$, THF, reflux, 18 h; 2) K_2CO_{3aq}, 0 °C, 2 h. ii) Boc_2O, NEt_3, CH_2Cl_2, RT, 18 h. iii) 1) $SOCl_2$, pyridine, MeCN, −20→0 °C, 2 h; 2) $RuCl_3$, $NaIO_4$, MeCN, H_2O, 0 °C, 1 h. iv) TFA, CH_2Cl_2, RT. v) dicyclohexlycarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), carboxylic acid, CH_2Cl_2, 0 °C→RT, 20 h. vi) 1) MeIm, MeCN, microwave, 80 °C, 4 h; 2) Et_2O·HCl, MeOH, reflux, 18 h; 3) $NaHCO_3$, CH_2Cl_2. vii) NaOTf, MeCN, reflux, 1 h.

ing steric hindrance of the R group a decreased reactivity and hence, lower yields (for R = H, CH_3) or indeed no conversion in the case of R = Bn was observed. Other esterification methods, for example, the Yamaguchi reaction[27] or the use of *N*′-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide (EDCI) failed to show any conversion of the compound possessing the Bn moiety.

Due to thermal decomposition of the chloride salts at high temperatures (see the Supporting Information) an anion exchange from Cl to OTf was performed (66–99%) for both the amine **9**(AA,C_m)Cl and amide species **10**(AA,C_m)Cl. For an overview with a detailed summary of the yields see the Supporting Information.

Mesomorphic properties: The imidazolium salts **9**(AA,C_n)X and **10**(AA,C_m)OTf were investigated by polarised optical microscopy (POM) and differential scanning calorimetry (DSC). Only the glycine, alanine and phenylalanine derivatives showed mesomorphic properties, whereas the compounds derived from valine and leucine showed only crystalline behaviour. All liquid crystalline compounds displayed focal conical domains and maltese cross textures under POM investigation, which indicated a SmA mesophase geometry. A typical example is shown in Figure 1.

Phase transitions and mesophase ranges were obtained from calorimetric investigations. DSC traces of **9**(Gly,C_{15})OTf are shown in Figure 2 as an example and additional DSC traces of **10**(Gly,C_{13})OTf, **9**(Ala,C_{15})OTf and **9**(Phe,C_{11})Cl can be found in Figure S4 in the Supporting Information. The melting and clearing points for the second/third heating and first/second cooling cycles are identical. The deviation of the first heating from the second and third heating cycle could be due to inhomogeneity of the sub-

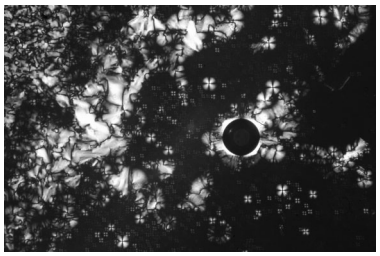


Figure 1. Typical texture of the imidazolium salt **9**(Phe,C_{11})Cl at 60 °C upon cooling from the isotropic phase. Focal conical textures and maltese crosses indicative for a SmA mesophase. (maginification: 200×, cooling rate: 10 K min^{-1}). Due to homeotropic alignment silanised slides were used.

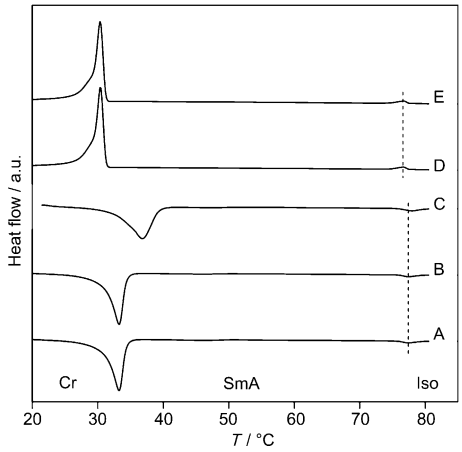


Figure 2. DSC traces of compound **9**(Gly,C_{15})OTf (heating/cooling rate: 10 K min^{-1}). A) Third heating, B) second heating, C) first heating, D) first cooling, E) second cooling cycle.

stance (i.e., isolating air bubbles, different crystal modifications). Compounds **9**(Gly,C_n)OTf, **10**(Gly,C_m)OTf and **9**(Ala,C_n)OTf showed small differences (≈2–4 K) of the melting and crystallisation temperatures due to supercooling, whereas the values for **9**(Phe,C_n)OTf were higher (≈20 K). This could be due to π–π interactions of the Ph units and hence hindered crystallisation leading to broader mesophase widths of the cooling cycles. The results are summarised in Table 1 and visualised for liquid crystalline compounds in Figure 3.

In most cases, the mesophase ranges increased with an increasing alkyl chain length (except for **9**(Gly,C_{17})OTf). The compounds exhibited melting points between 31 and 56 °C and clearing points up to 116 °C. For the glycine-derived amino triflates **9**(Gly,C_n)OTf a minimum chain length of fourteen (i.e., n+1) is required to obtain SmA phases,

Table 1. DSC data and melting points of the imidazolium compounds **9**(AA,C_n)X and **10**(AA,C_m)OTf (second heating, heating/cooling rate: 10 K min^{-1}).

Compound	Phase	Transition T [°C] (enthalpy [kJ mol^{-1}])	Phase	Transition T [°C] (enthalpy [kJ mol^{-1}])	
9(Gly,C_{17})Cl	Cr	62[a]			I
9(Gly,C_{13})OTf	Cr	31 (18.8)	SmA	76 (0.5)	I
9(Gly,C_{15})OTf	Cr	44 (12.5)	SmA	115 (0.6)	I
9(Gly,C_{17})OTf	Cr	51 (27.7)	SmA	116 (0.9)	I
10(Gly,C_{13})Cl	Cr	37[a]			I
10(Gly,C_{15})Cl	Cr	39[a]			I
10(Gly,C_{17})Cl	Cr	67[a]			I
10(Gly,C_{15})OTf	Cr	37 (17.0)	SmA	84 (0.3)	I
10(Gly,C_{17})OTf	Cr	43 (17.0)	SmA	106 (0.2)	I
9(Ala,C_{15})Cl	Cr	52[a]			I
9(Ala,C_{15})OTf	Cr	35 (22.4)	SmA	58 (0.6)	I
10(Ala,C_{15})Cl	Cr	40[a]			I
10(Ala,C_{17})Cl	Cr	54[a]			I
10(Ala,C_{15})OTf	Cr	55 (15.3)			I
9(Val,C_{15})Cl	Cr	38[a]			I
9(Leu,C_{15})Cl	Cr	27[a]			I
9(Phe,C_8)Cl	Cr	34 (17.9)[b]	SmA	55 (0.6)	I
9(Phe,C_{19})Cl	Cr	56 (19.2)	SmA	87 (1.0)	I
9(Phe,C_{11})Cl	Cr	53 (11.1)	SmA	113 (0.9)	I
9(Phe,C_{13})Cl	Cr	57[a]			I

[a] DSC data could not be obtained due to exothermal decomposition. Therefore, melting points were determined. [b] Due to a monotropic behaviour the first cooling cycle is indicated.

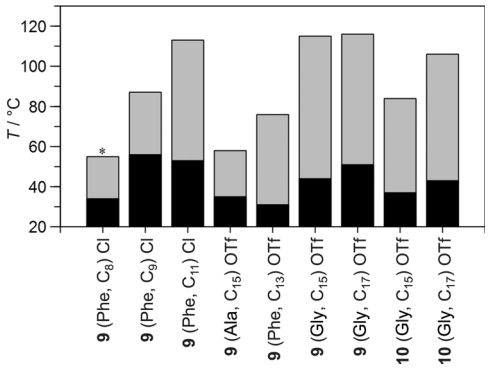


Figure 3. Mesophase stabilities of the imidazolium derivatives. * = A monotropic phase behaviour was observed. Black = Cr, grey = SmA.

whereas the corresponding amido triflates **10**(Gly,C_m)OTf required a chain length of fifteen. In comparison with their amido counterparts **10**(Gly,C_{15})Cl and **10**(Gly,C_{17})Cl the two amino triflates **9**(Gly,C_{15})OTf and **9**(Gly,C_{17})OTf showed increased melting and clearing transitions and thus broader mesophase ranges than their linear 1-alkyl-3-methylimidazolium triflate analogous of similar chain length,[28] despite the higher polarity and the higher tendency of the amide tether to form intermolecular hydrogen bonds as compared to the amine tether. For the alanine-derived amino triflates **9**(Ala,C_n)OTf again a total chain length of sixteen was necessary to induce mesomorphism. Neither the alanine-derived amides **10**(Ala,C_m)X nor the valine- or leucine-derived amines **9**(Val,C_n)X or **9**(Leu,C_n)X, respectively, revealed any liquid crystalline properties. This may be taken as evidence that the layered packing of the ILCs is very sensitive to steric hindrance, which can not be overcome by additional stabilisation due to hydrogen bonding.[29] In contrast, the phenylalanine-derived amino chlorides **9**(Phe,C_n)Cl showed already SmA phases with a total chain length of nine carbon atoms. This could be due to π–π interactions of the Ph units. After an anion exchange from Cl to OTf the liquid crystalline properties of the phenylalanine compounds **9**(Phe,C_n)OTf were completely lost.

X-ray investigation: The proposed SmA phase geometry was confirmed by small- and wide-angle X-ray diffraction measurements (SAXS and WAXS, respectively). In Figure 4 a representative WAXS pattern of **9**(Gly,C_{17})OTf is shown with a strong fundamental diffraction peak (001) in the small-angle region and a diffuse halo in the wide-angle region from the molten alkyl chains.

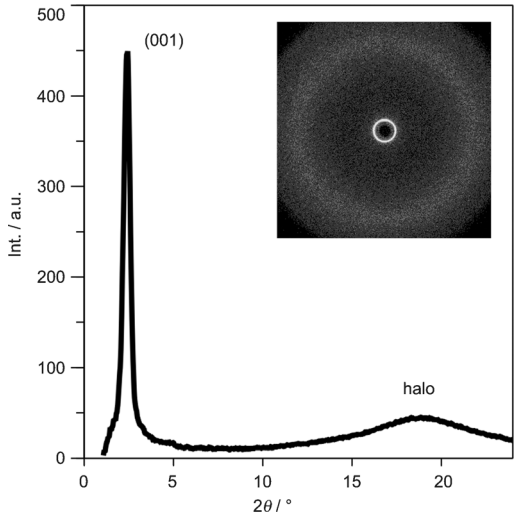


Figure 4. Diffraction pattern of **9**(Gly,C_{17})OTf at 89 °C with the corresponding WAXS image (small picture).

Layer spacings d_{001} were obtained at different temperatures by using a Gaussian distribution on the corresponding diffraction signal (001). All compounds showed a linear temperature dependency of the layer spacing (Figure 5). With increasing temperature the layer spacing decreased. These values indicate a bilayer structure of the molecules with strongly interdigitated alkyl chains and values of $L_{calcd} < d_{001} < 2L_{calcd}$, where L_{calcd} is the length of the fully extended molecule with an all-*trans* configuration of the alkyl moiety. For better comparison, layer spacings d_{red} at a reduced temperature (d_{001} at 0.95 T_{iso})[30] were determined (Tables 2 and 3). For example, the calculated molecular length of **9**(Gly,C_{17})OTf is 2900 pm,[31] whereas d_{red} is 3582 pm. This means that the mesogens are organised in a bilayer structure. The calculated layer spacing d_{calcd} is 3510 pm[31] (fully interdigitated alkyl chains of the cations 2530 pm plus two times the methylimidazolium core with 490 pm each), which is close to the d_{red} value of 3582 pm (Tables 2 and 3). Over-

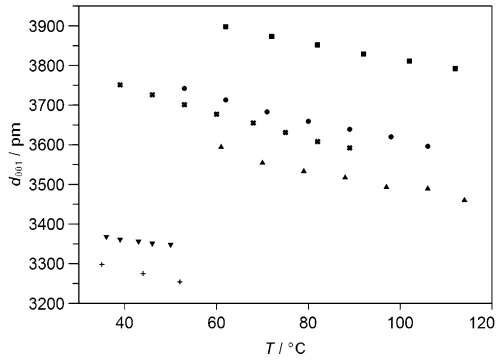


Figure 5. Temperature dependency of the d_{001} layer spacings obtained from SAXS investigations. + = **9**(Gly,C_{13})OTf, ▲ = **9**(Gly,C_{15})OTf, ● = **9**-(Gly,C_{17})OTf, × = **10**(Gly,C_{15})OTf, ■ = **10**(Gly,C_{17})OTf, ▼ = **9**-(Ala,C_{15})OTf.

Table 2. Comparison of the layer spacings d_{red} of the imidazolium compounds **9**(AA,C_n)OTf and **10**(Gly,C_m)OTf.

Compound	T_{red} [°C]	d_{red} [pm]	Compound	T_{red} [°C]	d_{red} [pm]
9(Gly,C_{13})OTf	72	3205	**9**(Ala,C_{15})OTf	55	3339
9(Gly,C_{15})OTf	109	3468	**10**(Gly,C_{15})OTf	83	3616
9(Gly,C_{17})OTf	110	3582	**10**(Gly,C_{17})OTf	107	3783

Table 3. Comparison of the calculated[31] and experimental layer spacings d_{red} of the imidazolium compounds **9**(AA,C_n) and **10**(Gly,C_m)OTf.

Compound	Alkyl chain length [pm]	2 × core [pm]	d_{calcd} [pm]	d_{red} [pm]
9(Gly,C_{13})OTf	2020	980	3000	3205
9(Gly,C_{15})OTf)	2270	980	3250	3468
9(Gly,C_{17})OTf)	2530	980	3510	3582
10(Gly,C_{15})OTf	1780	1820	3600	3616
10(Gly,C_{17})OTf	2040	1820	3860	3783
9(Ala,C_{15})OTf	2030	1380	3410	3339
9(Phe,C_9)Cl	1270	1380	2650	2617
9(Phe,C_{11})Cl	1520	1380	2900	2847

all, the layer spacings d_{001} increase with an increasing alkyl chain length. The temperature-dependent layer spacings of the phenylalanine compounds **9**(Phe,C_n)Cl can be found in Figure S1 in the Supporting Information.

The glycine amide derivatives showed increased d_{red} values compared to the amine compounds with the same chain lengths. Compounds **9**(Gly,C_{17})OTf and **10**-(Gly,C_{15})OTf displayed comparable d_{red} values, additionally the value of **9**(Ala,C_{15})OTf is between **9**(Gly,C_{15})OTf and **9**-(Gly,C_{13})OTf. This means that the stereogenic centre as well as the amide group hinders the interdigitation of the alkyl moieties, which is in good agreement with previous observations with citronellyl-derived side chains.[3] For all compounds the d_{red} values are close to the calculated d_{calcd} values, where a maximal degree of interdigitation up to the atom adjacent to the stereocentre or the amide group is assumed (Table 3, Figure 6).

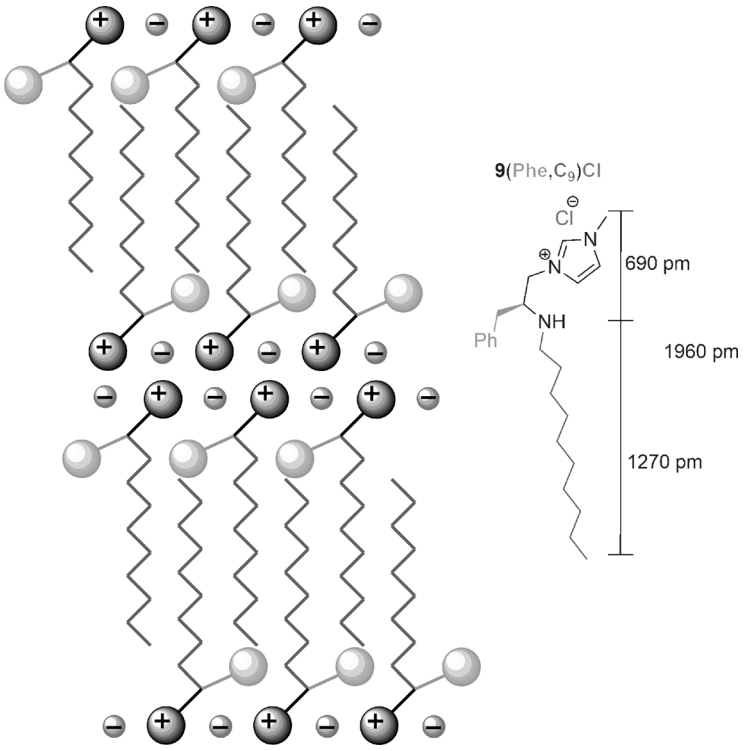


Figure 6. Proposed packing model of the smectic phase (left) and example of the calculated layer spacing d_{calcd} of **9**(Phe,C_9)Cl (right).

Conclusion

We have presented the first example of thermotropic chiral ILCs utilising amino acids as starting materials. The key step in the synthesis was the use of the relatively uncommon SO_3 leaving group. Imidazolium derivatives bearing amine and amide groups with different chain lengths and anions were synthesised. It turned out that the presence of mesophases was very sensitive to the steric hindrance in the amino acid derived tether. Only the glycine-derived amines **9**-(Gly,C_n)OTf (n = 13, 15, 17) and amides **9**(Gly,C_m)OTf (m = 15, 17) as well as the alanine-derived compound **9**-(Ala,C_{15})OTf revealed SmA phases. Valine and leucine derivatives were not mesomorphic. In contrast, despite the increased steric bulkiness of phenylalanine as compared to glycine, the phenylalanine-derived amine **9**(Phe,C_n)Cl (n = 8, 9, 11) showed stable mesophases for much shorter chain lengths suggesting beneficial π–π-stacking of the phenyl groups. It should be noted that no evidence for cholesteric mesomorphism was found.

XRD experiments showed a nearly linear dependency of the layer spacing values d_{001} with a decreasing temperature and a bilayer alignment of the mesogens. The existence of an amide group or a stereogenic centre hinders the interdigitation of the alkyl chains leading to increased layer spacing values. Despite the absence of cholesteric phases the phenylalanine-derived ILCs provide the opportunity to use them as chiral dopands for known nematic ILCs,[32] which gives access to novel chiral ordered reaction media. The re-

sults also revealed that the counterion has a considerable influence on the mesomorphic properties and further SAR studies are needed to fully explore the effect of the anion.

Experimental Section

General methods: Commercially obtained chemicals were used as received. For a better clarity and simplicity a non-IUPAC nomenclature was used. Column chromatography was carried out on silica 60Dm (40–70 mm). For thin layer chromatography silica gel sheets TLC silica gel 60 F 254 from Merck were used. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance 300 and Avance 500 spectrometers at 296 K. FTIR spectra were recorded with a Bruker Vektor22 spectrometer with an MKII Golden Gate Single Reflection Diamant ATR system. Mass spectrometry was performed on a Varian MAT 711 mass spectrometer with EI ionisation (70 eV) and a Bruker micrOTOF Q with electrospray ionisation. Elemental analyses were performed on a Carlo Erba Strumentazione Elemental Analyzer Model 1106. Differential scanning calorimetry was performed by using a Mettler Toledo DSC822 with a heating/cooling rate of 10 K min^{-1} (±1 K), melting points (uncorrected) and mesophase textures were obtained by optical polarising microscopy by using an Olympus BX 50 polarising microscope combined with a Linkam LTS 350 hot stage. X-ray powder experiments were performed by using a Bruker Nanostar with a monochromatic $Cu_{K\alpha1}$ beam ($\lambda = 1.5405$ Å), which was obtained by using a ceramic tube generator (1500 W) with cross-coupled Göbel mirrors as the monochromator. Optical rotation values were measured with a Polarimeter 241 (Perkin–Elmer). Calibration of the patterns was carried out with the powder pattern of Ag-Behenate. Samples were prepared by using glass tubes (0.7 mm outside diameter) from Fa. Hilgenberg GmbH and tempered on a temperature-controlled hot stage (± 1 K).

General procedure for the amidation of the amino acids: The respective amino acid **11**(AA) (25.4 mmol) and NaOH (1.02 g, 25.4 mmol) were dissolved in H_2O (16 mL). At 0 °C the corresponding neat acyl chloride (28.0 mmol) and NaOH (1.02 g, 25.4 mmol) dissolved in H_2O (16 mL) were added simultaneously. The reaction mixture was allowed to reach room temperature and stirred for 18 h. The aqueous phase was acidified to pH 3 with HCl (37 %), extracted with CH_2Cl_2 (3×20 mL) and the combined organic phases were dried over anhydrous $MgSO_4$. After evaporation of the solvent the crude product **12**(AA,C_n) was used in the next step without further purification. For long-chained acyl chlorides ($\geq C_{12}$) a H_2O/EtOH mixture was used instead and additional EtOH was added to solve the precipitate if necessary.

General procedure for the synthesis of the amino alcohols 14(AA,C_n): The corresponding amido alcohol **12**(AA,C_n) (25.3 mmol) was dissolved in dry THF (100 mL) and $NaBH_4$ (4.79 g, 126.5 mmol) was added in small portions. A solution of I_2 (23.5 g, 88.5 mmol) in THF (50 mL) was added dropwise to the reaction mixture at room temperature and after complete addition the solution was stirred under reflux for 18 h. After cooling to room temperature MeOH (21 mL, 500 mmol) was added carefully and the solvents were removed under reduced pressure. The residue was dissolved in 2 N NaOH (6.07 g, 152 mmol) in H_2O (38 mL) and stirred under reflux for 18 h. After cooling to room temperature the aqueous phase was extracted with CH_2Cl_2/EtOAc (1:1; 3×20 mL) and the combined organic phases were dried over anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure the crude product was purified by flash chromatography (1) EtOAc, 2) MeOH/EtOAc 1:1) to yield **14**(AA,C_n).

(*S*)-2-(Dodecylamino)-3-phenylpropan-1-ol (14(Phe,C_{11})): White solid (3.63 g, 11.3 mmol, 48 %); m.p. 54 °C; $[\alpha]_D^{20} = -4.7$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, trimethylsilane (TMS)): $\delta = 0.88$ (t, J = 6.8 Hz, 3H; CH_3), 1.20–1.35 (m, 18H; CH_2), 1.37–1.50 (m, 2H; NCH_2CH_2), 2.42 (br s, 2H; NH, OH), 2.53–2.69 (m, 2H; $NHCH_2$), 2.70–2.86 (m, 1H; $PhCH_2$), 2.87–2.97 (m, 1H; NCH), 3.34 (dd, J = 5.5, J = 10.7 Hz, 1H; CH_2OH), 3.63 (dd, J = 3.8, J = 10.7 Hz, 1H; CH_2OH), 7.14–7.35 ppm (m, 5H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 14.1$ (CH_3), 22.7, 27.1, 29.36, 29.44, 29.58, 29.60, 29.64, 29.66, 29.93, 31.9 (CH_2), 37.8 ($PhCH_2$), 46.9 (NCH_2), 60.2 (NCH), 62.1 (CH_2O), 126.5 (*p*-Ar), 128.6 (*o*-Ar), 129.2 (*m*-Ar), 138.2 ppm (*i*-Ar); FTIR (ATR): $\tilde{\nu} = 3268$ (w), 3029 (w), 2917 (vs), 2849 (s), 2733 (w), 2015 (w), 1967 (w), 1605 (w), 1492 (w), 1469 (m), 1453 (m), 1377 (w), 1343 (w), 1246 (w), 1110 (m), 1046 (w), 1029 (m), 977 (w), 955 (w), 934 (m), 897 (w), 849 (m), 815 (m), 767 (w), 744 (m), 727 (m), 718 (s), 697 (vs), 658 (w), 649 (w), 641 (w), 619 (w), 599 cm^{-1} (m); MS (ESI): m/z: 320 [M+H$^+$], 302 [M+H$^+$ −H_2O], 228, 186, 117, 105, 91; HRMS (ESI): m/z calcd for $C_{21}H_{38}NO^+$: 320.2948 [M+H$^+$]; found: 320.2933; elemental analysis calcd (%) for $C_{21}H_{37}NO$: C 78.94, H 11.67, N 4.38; found: C 78.94, H 11.60, N 4.26.

General procedure for the alkylation of ethanolamine: A solution of ethanolamine **13** (0.72 g, 11.7 mmol), the corresponding bromoalkane (5.85 mmol) and NEt_3 (0.65 g, 6.44 mmol) in EtOH (60 mL) was stirred under reflux for 18 h. After cooling to room temperature the solvent was removed under reduced pressure. The residue was dissolved in water and extracted with CH_3Cl (3×20 mL) and the combined organic phases were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude product was recrystallised from EtOAc to obtain the pure secondary amino alcohol **14**(Gly,C_n).

2-(Octadecylamino)ethanol (14(Gly,C_{17})): White solid (1.15 g, 3.67 mmol, 63 %); m.p. 45 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 0.88$ (t, J = 6.7 Hz, 3H; CH_3), 1.20–1.36 (m, 32H; CH_2), 1.44–1.53 (m, 2H; OCH_2CH_2), 1.74 (br s, 2H; NH, OH), 2.57–2.65 (m, 2H; NCH_2), 2.75–2.80 (m, 2H; $NHCH_2CH_2OH$), 3.60–3.66 ppm (m, 2H; CH_2OH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 14.1$ (CH_3), 22.7, 27.3, 29.37, 29.57, 29.63, 29.67, 29.70, 31.9 (CH_2), 49.5 (CH_2NH), 50.9 ($NHCH_2CH_2OH$), 60.9 ppm (CH_2OH); FTIR (ATR): $\tilde{\nu} = 2922$ (vs), 2852 (s), 2361 (w), 1466 (m), 1059 (w), 908 (s), 733 (vs), 645 cm^{-1} (w); MS (ESI): m/z: 314 [M+H$^+$], 296 [M+H$^+$−H_2O]; HRMS (ESI): m/z calcd for $C_{20}H_{44}NO^+$: 314.3417 [M+H$^+$]; found: 314.3428.

General procedure for the synthesis of sulfamidates 15(AA,C_n): Imidazole (4.52 g, 66.4 mmol) was dissolved in CH_2Cl_2 (60 mL), the mixture was cooled to 0 °C and a solution of $SOCl_2$ (1.45 mL, 2.37 g, 19.9 mmol) in CH_2Cl_2 (30 mL) was added dropwise. The solution was slowly warmed to room temperature and stirred for an additional hour. After cooling to −78 °C a solution of the respective amino alcohol **14**(AA,C_n) (9.49 mmol) in CH_2Cl_2 (60 mL) was added dropwise and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was filtered over celite and washed with CH_2Cl_2 (50 mL). The organic phase was washed with water (2×50 mL), dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (60 mL) and $NaIO_4$ (4.73 g, 22.1 mmol) dissolved in H_2O (50 mL) was added. After cooling to 0 °C, $RuCl_3$ (0.30 g, 1.42 mmol) was added and the reaction mixture was stirred vigorously at 0 °C for 2 h and afterwards for 18 h at room temperature. The phases were separated, activated charcoal (2 g) was added to the organic phase and the solution was stirred overnight. Anhydrous $MgSO_4$ was added and after filtration over celite the solvent was removed under reduced pressure to yield the sulfamidates **15**(AA,C_n).

(*S*)-4-Benzyl-3-dodecyl-1,2,3-oxathiazolidine 2,2-dioxide (15(Phe,C_{11})): Yellow oil (2.72 g, 7.14 mmol, 82 %); $[\alpha]_D^{20} = -7.9$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 0.88$ (t, J = 6.8 Hz, 3H; CH_3), 1.17–1.39 (m, 18H; CH_2), 1.54–1.69 (m, 2H; CH_2), 2.75–2.87 (m, 1H; $PhCH_2$), 2.91–3.02 (m, 1H; NCH_2), 3.10–3.25 (m, 2H; NCH_2, $PhCH_2$), 3.73–3–87 (m, 1H; NCH), 4.19 (dd, J = 5.8, J = 8.7 Hz, 1H; CH_2OS), 4.33 (dd, J = 6.5, J = 8.7 Hz, 1H; CH_2OS), 7.13–7.38 ppn (m, 5H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 14.1$ (CH_3), 22.7, 26.8, 27.8, 29.13, 29.35, 29.47, 29.56, 29.63, 31.9 (CH_2), 38.5 ($PhCH_2$), 47.5 (NCH_2), 61.1 (NCH), 70.4 (CH_2OS), 127.4 (*p*-Ar), 129.00, 129.13 (*o*-/*m*-Ar), 135.2 ppm (*i*-Ar); FTIR (ATR): $\tilde{\nu} = 2922$ (s), 2853 (m), 1710 (w), 1604 (w), 1467 (w), 1456 (w), 1343 (s), 1180 (vs), 1030 (w), 978 (m), 831 (w), 796 (s), 748 (m), 700 (s), 628 (w), 587 cm^{-1} (w); MS (ESI): m/z: 404 [M+Na$^+$], 382 [M+H$^+$], 320, 302, 186; HRMS (ESI): m/z calcd for $C_{21}H_{35}NNaO_3S^+$: 404.2230 [M+Na$^+$]; found: 404.2231; elemental analysis calcd (%) for $C_{21}H_{35}NO_3S$: C 66.10, H 9.25, N 3.67; found: C 65.89, H 9.12, N 3.47.

General procedure for the preparations of the imidazolium chlorides 9-(AA,C_n)Cl: The corresponding sulfamidate **15**(AA,C_n) (1.52 mmol) and

methylimidazole (0.12 mL, 0.13 g, 1.52 mmol) were given in an microwave vial and irradiated in a microwave at 140 °C for 1 h. The residue was dissolved in MeOH, a solution of Et_2O·HCl (2 mL) was added and the reaction mixture was heated to reflux overnight. The solvent was removed and the crude product was either recrystallised from EtOAc or washed several times with Et_2O and EtOAc to obtain the imidazolium chloride **9**(AA,C_n)Cl.

(*S*)-3-(2-(Dodecylamino)-3-phenylpropyl)-1-methyl-1*H*-imidazol-3-ium chloride (9(Phe,C_{11})Cl): White solid (0.35 g, 0.84 mmol, 61 %); recrystallised from EtOAc; $[\alpha]_D^{20} = -17.7$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 0.88$ (t, 6.8 Hz, 3H; CH_3), 1.06–1.42 (m, 22H; CH_2), 2.44–2.52 (m, 1H; NCH_2), 2.55–2.65 (m, 1H; NCH_2), 2.65–2.74 (m, 1H; $PhCH_2$), 2.85–2.94 (m, 1H; $PhCH_2$), 3.12–3.23 (m, 1H; NCH), 4.06 (s, 3H; $ImCH_3$), 4.29 (dd, $J = 6.9$, $J = 13.7$ Hz, 1H; CH_2Im), 4.33 (dd, $J = 2.9$, $J = 13.7$ Hz, 1H; CH_2Im), 7.13–7.44 (m, 7H; ArH), 10.39 ppm (s, 1H; NCHN); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): $\delta = 14.1$ (CH_3), 22.7, 27.1, 29.35, 29.42, 29.62, 29.64, 29.67, 29.81, 31.9 (CH_2), 36.6 ($ImCH_3$), 37.8 ($PhCH_2$), 47.1 (NCH_2), 52.4 (CH_2Im), 58.6 (NCH), 122.1, 123.0 (Im), 127.0 (*i*-Ar), 128.9, 129.2 (*o*-/*m*-Ar), 137.0 (*i*-Ar), 139.0 ppm (NCHN); FTIR (ATR): $\tilde{\nu} = 3399$ (w), 2923 (m), 2853 (w), 1573 (w), 1455 (w), 1169 (w), 903 (vs), 723 (vs), 650 cm^{-1} (s); MS (ESI): *m*/*z*: 384 [M^+], 302 [$M^+ - C_4H_6N_2$], 198; HRMS (ESI): *m*/*z* calcd for $C_{25}H_{42}N_3^+$: 384.3373 [M^+]; found: 384.3375; DSC: Cr 53 °C (11.1 kJ mol^{-1}); SmA 113 °C (0.9 kJ mol^{-1}) I.

General procedure for the anion exchange: The respective imidazolium chloride **9**(AA,C_n)Cl (0.13 mmol) was dissolved in MeCN (10 mL), the corresponding sodium or potassium salt (0.14 mmol) was added and stirred under reflux for 1 h. After cooling to room temperature the solvent was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 (10 mL) and filtered. The solvent was removed under reduced pressure to obtain the imidazolium derivative **9**(AA,C_n)OTf.

(*S*)-3-(2-(Tetradecylamino)-3-phenylpropyl)-1-methyl-1*H*-imidazol-3-ium triflate (9(Phe,C_{13})OTf): Yellow oil (62 mg, 0.11 mmol, 99 %); $[\alpha]_D^{20} = -13.5$ ($c = 1.0$, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 0.88$ (t, 6.9 Hz, 3H; CH_3), 1.06–1.36 (m, 26H; CH_2), 2.41–2.48 (m, 1H; NCH_2), 2.50–2.58 (m, 1H; NCH_2), 2.58–2.66 (m, 1H; $PhCH_2$), 2.74–2.83 (m, 1H; $PhCH_2$), 3.06–3.14 (m, 1H; NCH), 3.93 (s, 3H; $ImCH_3$), 4.03 (dd, $J = 7.0$, $J = 14.0$ Hz, 1H; CH_2Im), 4.25 (dd, $J = 3.4$, $J = 14.0$ Hz, 1H; CH_2Im), 7.11–7.40 (m, 7H; ArH), 9.02 ppm (s, 1H; NCHN); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): $\delta = 14.1$ (CH_3), 22.7, 27.1, 29.37, 29.42, 29.61, 29.63, 29.67, 29.68, 29.70, 29.85, 31.9 (CH_2), 36.4 ($ImCH_3$), 38.0 ($PhCH_2$), 47.1 (NCH_2), 52.5 (CH_2Im), 58.5 (NCH), 120.7 (q, $J = 320.4$ Hz, CF3), 122.5, 123.3 (Im), 127.0 (*i*-Ar), 128.9, 129.1 (*o*-/*m*-Ar), 137.0 (*i*-Ar), 137.6 ppm (NCHN); FTIR (ATR): $\tilde{\nu} = 3115$ (w), 2923 (s), 2853 (m), 1573 (w), 1456 (w), 1377 (w), 1255 (vs), 1224(s), 1158 (vs), 1030 (vs), 908 (w), 732 (m), 702 (m), 666 (w), 637 (vs), 573 cm^{-1} (m); MS (ESI): *m*/*z*: 412 [M^+], 330 [$M^+ - C_4H_6N_2$], 226, 149 [M^-]; HRMS (ESI): *m*/*z* calcd for $C_{27}H_{46}N_3^+$: 412.3686 [M^+]; found.: 412.3683; calcd for $CF_3O_3S^-$: 148.9515 [M^-]; found: 148.9526; elemental analysis calcd (%) for $C_{28}H_{46}F_3N_3O_3S$: C 59.87, H 8.25, N 7.48; found: C 59.80, H 8.18, N 7.12.

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