Synthesis and mesophase behaviour of ionic liquid crystals[†]

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Received 11th April 2007, Accepted 24th May 2007

First published as an Advance Article on the web 8th June 2007 DOI: 10.1039/b705519f

N-Alkyl-pyridinium derivatives 1–3 and *N*-alkyl-stilbazolium halides 4–6 with hydroxy, methoxy and hydrogen 4'-substituents and long non-branched alkyl chains (n = 14, 16, 18, 20, 22) were synthesized and characterized by polarizing microscopy, differential scanning calorimetry and X-ray measurements. The compounds exhibit liquid crystalline SmA phases when heated above their melting point. Phenyl substitution in the 3- and 4-position of the pyridinium ring causes a large tendency to decrease the clearing temperature in comparison to the 4-methyl substituted *N*-alkyl-pyridinium salts. By elongation of the pyridinium ring to the 4'-substituted stilbazolium unit the clearing points of the new compounds 4-6 increase drastically up to temperatures \geq 200 °C in which partial decomposition of the compounds sets in. The length of the alkyl chains and the type of counter ions have large influences on the stability of the mesophase. Elongation of the alkyl chain length n increases the temperature range of the liquid crystalline phase. The counter ions increase the stability of the SmA phase in order $Cl^- > Br^- > I^- > BPh_4^-$. When $CH_3-C_6H_5SO_3^{-1}$ is introduced as an anion no liquid crystalline phase can be observed. UV/Vis measurements indicate the presence of a charge-transfer complex between the pyridinium cation and the iodide anion. Differences in the liquid crystalline behaviour of N-alkyl-4'-substituted stilbazolium halides 4-6 compared with N-alkyl-3- and -4-substituted-pyridinium derivatives 1-3may be explained by additional intramolecular charge-transfer and resulting strong dipole-dipole interactions between stilbazolium compounds.

1. Introduction

Ionic liquid crystals (LCs) can be considered as materials combining the properties of liquid crystals and ionic liquids. The ionic character means that some of the properties of ionic LCs may differ significantly from those of conventional liquid crystals.¹ The driving forces for the formation of ionic LCs are hydrophobic interactions of the alkyl groups and ionic, dipoledipole, cation $-\pi$ interactions as well as $\pi - \pi$ stacking of the core groups. Therefore, the properties and stabilities of LC phases should depend on the relative contributions of these interaction forces, depending on the structures of the individual molecules from each series. From the literature is known that *N*-alkyl-4-methyl-pyridinium,² 1-*n*-alkyl-4-cyano-pyridinium bromides,³ hexafluorophosphate salts of alkyl-substituted imidazolium, pyridinium and 3- and 4-methyl-pyridinium cations⁴ as well as 1-alkyl-pyridinium bromides⁵ exhibit SmA mesophases. Tabrizian et al.⁶ compared the thermotropic behaviour of 1-n-alkyl-(4-methyl or 4-tolyl)-pyridinium bromides with alkyl chain lengths from 12 to 22. The clearing temperatures are similar in both cases, when n = 22, indicating that the ionic forces are primarily responsible for maintaining the layer structure of the compounds up to high temperature. Smectic phases were found also for N-alkyl-pyridinium and 1-alkyl-3-methyl-imidazolium salts having chloride, tetrachlorocobaltate(II) and tetrachloronickelate(II) counter ions.⁷ Most of the investigations were carried out on pyridinium derivatives with a single aromatic core. Therefore, we studied the effect of the elongation of the aromatic core in order to get a deeper insight into the relationship between molecular π -electron structure and supramolecular behaviour.

Here we report four series of LC molecules including *N*-alkyl-4-methyl-pyridinium halides **1a–g**, *N*-alkyl-4-phenyl-pyridinium salts **2a–j**, *N*-alkyl-3-phenyl-pyridinium salts **3a–f** and the vinylene-conjugated *N*-alkyl-4'-substituted-stilbazo-lium halides **4a–g**, **5a–f** and **6a–f** (Scheme 1). The compounds were synthesized in order to study the influence of the



Scheme 1 Structures of the *N*-alkyl-3- and -4-substituted-pyridinium salts 1-3 and *N*-alkyl-4'-substituted-stilbazolium salts 4-6; n = number of C atoms in the non-branched alkyl chain.

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Fig. 1 a) Fan-shaped texture in the smectic A phase of 2e at 152 °C on cooling. b) Grainy texture in mesophase M of compound 2c at 100 °C on cooling. c) Transition temperatures T (°C) as a function of the alkyl chain length *n* for *N*-alkyl-4-phenyl-pyridinium bromides 2a, 2c, 2e, 2g.

alkyl-chain length, the counter ions and the different substituents at the pyridinium ring on the LC behaviour. Compared with the pyridinium derivatives 1-3, stilbazolium compounds 4-6 should exhibit much stronger dipole–dipole interactions, in addition to the ionic forces.

2. Results

Measurements by polarizing microscopy on the *N*-alkyl-3- and -4-substituted-pyridinium salts of type **1–3** and *N*-alkyl-4'-substituted-stilbazolium salts **4–6** show focal-conic fan textures with homeotropic regions characteristic for a smectic A phase, SmA (Fig. 1a). In the case of **1–3**, the low clearing enthalpies ΔH_c between 0.05 and 1.2 kJ mol⁻¹ are also in line with the presence of a SmA phase. The salts **4–6** have stronger dipolar interactions inducing an increase of ΔH_c between 0.3 and 15.7 kJ mol⁻¹.

N-Alkyl-4-phenyl-pyridinium salts 2a-j

The salts **2a** and **2b** with n = 16 do not form any LC phases. The stability of the liquid-crystalline phase of compounds **2d–i** increases markedly with increasing alkyl chain length n (see Table 1). The phase diagram of the salts with a bromide anion is presented in Fig. 1c. Elongating the chain has no large influence on the melting temperature of the compounds, while the clearing temperature increases drastically. The SmA temperature range ΔT increases from 22 °C up to 70 °C for the bromides **2e** (n = 20) and **2g** (n = 22).

Salts 2c, 2e and 2g do show an unknown mesophase which is named M in this paper. Differential scanning calorimetry (DSC) of compounds 2e and 2g shows on heating first a large-enthalpy transition (melting point) followed by two transitions with a smaller enthalpy change indicating the presence of two mesophases (Table 1). On cooling from the isotropic liquid, first the formation of a fan-texture with homeotropic regions is observed under the polarising microscope, an indication of a smectic A phase. During the second phase transition the viscosity of the sample increases and a grainy texture is formed, the so-called M phase (see Fig. 1b). Only a small transition enthalpy for the formation of the M phase was detected by DSC on cooling. This mesophase M, appearing also for compound 2c, could not be identified by X-ray methods up to now, therefore the exact phase type cannot be assigned yet.

Table 1 also contains thermal data for *N*-alkyl-4-phenylpyridinium iodides **2b**, **d**, **h**. Compared with the bromides, iodides have similar melting temperatures and generally lower clearing points with increasing alkyl chain length n.

The anion effect was investigated in more detail for salts **2f-j** having 22 carbon atoms in the lateral chain. A large influence on the temperature range of the SmA phase was observed when replacing the bromide by iodide, chloride and tetraphenylborate. Compound **2j** with *p*-toluenesulfonate as anion exhibits no liquid crystalline phase. The melting temperatures of the salts with bromide and iodide anions are similar but the clearing temperature decreases in the order $CI^- > Br^- > I^- > BPh_4^-$, with increasing ion radius r_{X^-} (Table 2). Replacing the bromide with chloride leads to a decrease of the melting point and a strong increase in the clearing point of the salt **2f**. For this compound at temperatures higher than 200 °C partial decomposition is observed.

Compound 2g shows the additional mesophase M from 98 °C to 109 °C, which is observed only for the two Br^- compounds 2c and 2e bearing different chain lengths (see Fig. 1c).

The formation of a smectic A phase was confirmed by X-ray investigations on aligned samples of compounds **2e** and **2i**. The diffraction patterns show first and second order layer

Table 1 Transition temperatures $T(^{\circ}C)$ and enthalpies ΔH (kJ mol⁻¹) from differential scanning calorimetry for *N*-alkyl-4-phenyl-pyridinium salts **2a–j**; ΔT ($^{\circ}C$) = temperature range of the smectic A phase

			Phase transitions $T/^{\circ}C$								
Comp.	п	X^{-}	ΔH	$\Delta H/kJ mol^{-1}$							
2a	16	Br ⁻	Cr	86 49	Iso					_	
2b	16	I ⁻	Cr	83 41	Iso						
2c	18	Br^-	Cr	89 50.5	М	114 0.2	Iso			_	
2d	18	I-	Cr	90 51.9	SmA	98 0.05	Iso			8	
2e	20	Br ⁻	Cr	95 46.8	М	134 1.1	SmA	156 0.12	Iso	22	
2f	22	Cl ⁻	Cr	72 53.6	SmA	213 1.9	Iso			141	
2g	22	Br^{-}	Cr	98 56.9	М	109 0.3	SmA	179 0.7	Iso	70	
2h	22	Ι-	Cr	95 66.3	SmA	161 0.7	Iso			66	
2i	22	$B(C_6H_5)_4^{-1}$	Cr	78 67.2	SmA	151 1.2	Iso			73	
2j	22	C ₇ H ₈ SO ₃ ⁻	Cr	94 52.6	Iso						

Table 2 Influence of the size of the counter ion on the mesophase stability. r_{X^-} (nm) = ionic radius of Cl⁻, Br⁻, I⁻, BPh₄^{-,8} T (°C) = transition temperature; ΔH (kJ mol⁻¹) = transition enthalpy; Cr = crystalline state; SmA = smectic A phase; Iso = isotropic liquid state, d (nm) = layer distance at different temperatures (T (°C), given in parentheses)

	2f					2g							2h					2i				
$X^{-}_{r_{X}}$	C1 ⁻ 0.18	1				Br ⁻ 0.19	6						I ⁻ 0.22	22				BPh 0.42	14 ⁻ 11			
$T \\ \Delta H \\ d$	Cr	72 53.6	SmA	213 1.9	Iso ^a	Cr 3.76 3.71	98 56.9 (130) (150)	М	109 0.3	SmA	179 0.7	Iso	Cr 3.95 3.86	95 66.3 5 (130) 5 (150)	SmA	161 0.7	Iso	Cr 	78 67.2 (150)	SmA	151 1.2	Iso
^a Pai	tial d	ecompo	osition o	observ	ed.																	

reflections on the meridian in the small angle region along with a diffuse outer scattering with a maximum of the intensity on the equator (Fig. 2a and b, and S1 and S2 in the ESI†). This indicates a layer structure with liquid-like distributed lateral distances of the molecules, the long axes of the molecules being parallel to the layer normal. The maximum of the outer diffuse scattering of **2e** at D = 0.45 nm, corresponds to the average lateral distance of the molecules of about 0.5 nm and is typically found for alkyl chains.⁹ In case of **2i** this value is slightly enhanced to 0.48 nm corresponding to an average lateral distance of the chains of about 0.54 nm, which may be explained by packing requirements described below.

The layer spacing for 2e is calculated as 3.55 nm at 130 °C. Since the long axes of the molecules are, on average, parallel to the layer normal, this distance is the length of the building unit of the layers. A CPK model for the molecular packing in the smectic A phase of compound 2e shows a head-to-tail arrangement of the molecules within the layer, and the bromide anion is localized between the aromatic rings (Fig. 2c). The thickness of the layer d calculated from this model is 3.55 nm, in agreement with the value obtained by X-ray measurements. Upon increasing the number of carbon atoms n in the alkyl chain from 20 to 22, the layer distance determined by the X-ray measurements increases to 3.76 nm for compound 2g at 130 °C, an expected enhancement for an elongation of the chains by two methylene groups. When the bromide ion is replaced by iodide, compound 2h, the thickness of the layer is 3.95 nm at the same temperature (for temperature dependence of the d values see ESI^{\dagger} Table S1). Obviously, the packing of the chains, most likely the degree of intercalation, is modified to accommodate the slightly bigger iodide ions. In the case of compound 2i the layer distance d is 3.7 nm at 150 °C, with its much larger tetraphenylborate¹⁰ counter ion which has a tetrahedral arrangement of the phenyl units. The comparatively small layer distance may be explained assuming a shortening of the effective chain length by a stronger disorder of the alkyl chains to fit the large space occupied by the anions. One hint of such stronger disorder may be the above-mentioned slightly enhanced D = 0.54 nm of the outer diffuse X-ray scattering for **2i**.

N-Alkyl-3-phenyl-pyridinium salts 3a-f

Changing the phenyl group from the *para* to the *meta* position, as shown for compounds **3a–f**, may influence the stability of the mesophase. The transition temperatures for compounds of type **3** are summarized in Table 3. Comparable to the *para*-substituted compounds **2**, the salts containing alkyl chains with $n \ge 18$ do form smectic A phases. No M phases were detected. By increasing the alkyl chain length to carbon number n = 22 the melting temperatures become lower than in the case of the *para*-substituted compounds **2a–j**, but the SmA temperature range become larger. The influence of the alkyl chain length on the transition temperatures of the bromides **3a, c, e** and **f** is summarized in Fig. 3a.

The X-ray diffraction pattern of an aligned sample of **3e** in the SmA phase at 129 °C (Fig. 3b) closely resembles the corresponding one of **2e** (Fig. 2a). The layer distance *d* amounts to 3.9 nm and the outer diffuse scattering shows its maximum at D = 0.46 nm. Upon increasing the length of the alkyl chains to 22 carbon atoms, the thickness of the layer decreases to 3.8 nm.

In order to compare the influence of the substituents at the pyridinium ring on the stability of the SmA phase, we synthesized the *N*-alkyl-4-methyl-pyridinium halides 1a-g with alkyl chains with $n \ge 14$. The transition temperatures and



Fig. 2 2D X-ray diffraction patterns of the smectic A phase for surface-aligned samples of a) 2e at 149 °C and b) 2i at 150 °C on cooling (the scattering of the isotropic liquid has been subtracted to enhance the visibility of the anisotropic distribution of the outer diffuse scattering); c) CPK model of compound 2e, assuming the all-*trans* conformation of the alkyl chains.

Table 3 Transition temperatures $T(^{\circ}C)$ and enthalpies $\Delta H (kJ mol^{-1})$ from differential scanning calorimetry for *N*-alkyl-3-phenyl-pyridinium halides **3a–f**. $\Delta T (^{\circ}C)$ = temperature range of the smectic A phase

			Phas							
Comp.	п	X^{-}	$\Delta H/$	$\Delta H/kJ \text{ mol}^{-1}$						
3a	16	Br ⁻	Cr	99 28.7	Iso					_
3b	16	I^-	Cr	77 30.6	Iso					—
3c	18	Br ⁻	Cr	45 31.4	SmA	82 0.34	Iso			37
3d	18	I-	Cr	44 27.1	SmA	65 1.0	Iso			21
3e	20	Br ⁻	Cr	54 33.4	SmA	131 0.8	Iso			77
3f	22	Br ⁻	Cr ₁	67 40.9	Cr ₂	106 41.8	SmA	149 1.1	Iso	43

enthalpies are presented in Table 4 showing that compounds 1 exhibit more stable mesophases ($n \ge 16$, larger ΔT values than 2 and the related compounds 3). Compounds of type 1 show focal conic textures characteristic of a SmA phase under polarizing optical microscopy. The packing of the molecules is considered to be interdigitated, with the anions sandwiched between the pyridinium rings.^{2,3,6} The values in Table 4 agree to a great extent with those from known compounds 1b, d and g.⁶

External charge-transfer of N-alkyl-3- and -4-substituted-pyridinium salts 1-3

Compounds 1–3 were investigated by UV/Vis spectroscopy and show deviations from the Lambert–Beer law indicating the presence of new species in solution in the case of iodides.

To gain a better understanding of this effect the spectral properties of *N*-octadecyl-4-phenyl-pyridinium iodide **2d** in 1,2-dichloroethane were investigated (see Fig. 4). The UV/Vis spectrum shows two absorption bands at 219 nm and 305 nm and with increasing concentration a new one at 370 nm. A plot of the maximum absorbances at 305 and 370 nm *versus* concentration shows deviations from the Lambert–Beer law which indicates that additional ion pairs are formed in solution. The long wavelength absorption corresponds to a charge-transfer band which arises from an ion pair between the iodide anion as electron donor and the pyridinium ring as

Table 4 Transition temperatures $T(^{\circ}C)$ and enthalpies ΔH (kJ mol⁻¹) from differential scanning calorimetry for *N*-alkyl-4-methyl-pyridinium halides **1a–g**. ΔT ($^{\circ}C$) = temperature range of the smectic A phase. The values in parentheses correspond to those reported in reference 6

	Phase transitions $T/^{\circ}C$										
Comp.	п	X^{-}	ΔH_{ℓ}	/kJ mol ⁻¹				$\Delta T/^{\circ}C$			
1a	14	Br^{-}	Cr	77 25 4	Iso			_			
1b	16	Br^-	Cr	85 (84) 39.1 (44)	SmA	119 (109) 0.3 (0.3)	Iso	34			
1c	16	I^-	Cr	67 11.1	SmA	104 0.3	Iso	37			
1d	18	Br ⁻	Cr	82 (92) 38.8 (59)	SmA	168 (158) 0.8 (0.7)	Iso	86			
1e	18	I^-	Cr	84 44.6	SmA	142 0.6	Iso	58			
1f	20	Br ⁻	Cr	84 51.6	SmA	197 0.9	Iso	113			
1g	22	Br ⁻	Cr	91 (94) 75.4 (69)	SmA	207 (206) 1.1 (2)	Iso	116			

acceptor.¹¹ This ion pairing in solution will support the suggested structure in the CPK models in Fig. 2c and 3c with the localization of X^- near the pyridinium ring. The concentration dependence experiment of N-octadecyl-4phenyl-pyridinium iodide 2d presented in Fig. 4 shows a shift of the maximum of the absorbance from 305 nm at concentration of 1 \times 10⁻⁵ mol 1⁻¹ to 297 nm at 7 \times 10^{-5} mol 1^{-1} . This may confirm the existence of a second charge-transfer band which may be assigned to a electronic transition from the highest occupied molecular orbital (HOMO) of the iodide ion to two closely located vacant molecular orbitals in the pyridinium ion.¹² When the iodide ion was replaced by the more electrophilic bromide, the charge-transfer band was no longer present, and a linear correlation of Lambert-Beer plot indicated that no other light absorbing species are formed in solution (see ESI[†] Fig. S3).

N-Alkyl-4'-substituted-stilbazolium halides 4-6

In comparison to the simple ionic compounds 1, 2 and 3 the stilbazolium compounds 4, 5 and 6 exhibit both ionic and appreciable dipolar interaction forces. This can be easily explained by the chemical structure allowing strong mesomeric interactions between the methoxy and hydroxy groups as



Fig. 3 a) Transition temperatures of compounds **3a**, **c**, **e**, **f** as a function of the chain length *n*. b) 2D X-ray diffraction pattern of the smectic A phase for the surface-aligned sample **3e** at 129 $^{\circ}$ C on cooling (the scattering of the isotropic liquid has been subtracted to enhance the visibility of the anisotropic distribution of the outer diffuse scattering). c) CPK model of compound **3e**.



Fig. 4 a) Concentration dependence of the absorbance of N-octadecyl-4-phenyl-pyridinium iodide 2d in 1,2-dichloroethane, l (path length of the quartz cell) = 1 cm. b) Lambert–Beer plot.

electron donors and the quaternary ammonium group as an acceptor (intramolecular charge-transfer). Therefore, it was of interest to investigate the LC properties of the stilbazolium halides with hydroxy, methoxy and, for comparison, hydrogen substituents at the donor position 4' and long alkyl chains at the quaternary ammonium group, compounds **4–6**. The influence of these structural changes, including the counter ions, on the mesophase behaviour of the compounds **4–6** was investigated by polarizing microscopy, differential scanning calorimetry and X-ray diffraction.

Investigations by polarizing microscopy on compounds 4 with $n \ge 14$ show the formation of focal-conic fan and homeotropic textures characteristic for smectic A phases. The influence of the length of the hydrocarbon chains attached to the quaternary ammonium group on the transition temperatures of the mesophases for **4a–g** is shown in Table 5. An increase in the clearing point was observed with increasing length of the alkyl chain. At temperatures higher than 200 °C the compounds may partially decompose as can be derived from decreasing clearing points after heating the substances several times into the isotropic liquid.

When the counter ion is changed from bromide to iodide both the melting point and the clearing point decrease drastically meaning that the stability of the smectic A phase is influenced by the size of the anion. The stability range of the

Table 5 Transition temperatures $T(^{\circ}C)$ and enthalpies ΔH (kJ mol⁻¹) from differential scanning calorimetry of *N*-alkyl-4'-hydroxy-stilbazolium halides **4a–g**. $\Delta T(^{\circ}C)$ = temperature range of the smectic A phase

			Phas	$\Delta T/^{\circ}C$				
Comp.	п	X^{-}	$\Delta H/2$					
4a	14	Br^-	Cr	173 7 5	Sm	186 03	Iso	13
4b	16	Br^-	Cr	177 12.0	SmA	221 2.0	Iso ^a	≥44
4c	16	I^-	Cr	143 2.3	SmA	181 9.5	Iso	38
4d	18	Br^-	Cr	172 22.6	SmA	230 0.9	Iso ^a	≥58
4 e	18	I_	Cr	130 17.6	SmA	184 6.81	Iso	54
4f	20	Br^{-}	Cr	172 14.7	SmA 2.6	260	Iso ^a	≥88
4g	22	Br ⁻	Cr	176 17.3	SmA	245 3.5	Iso ^a	≥68
^a Partial	decor	mpositi	on obs	erved.				

mesophase is shifted to lower temperatures, at which less decomposition effects can be expected and X-ray investigations are possible. Powder patterns of *N*-octadecyl-4'-hydroxy-stilbazolium iodide **4e** have been recorded, from which a layer distance *d* of 3.85 nm is obtained for the SmA phase at 160 °C. A similar supramolecular arrangement can be expected from the molecular packing model presented in Fig. 5b showing a head-to-tail orientation of the stilbazolium unit with the anion sandwiched between the aromatic rings. Thus this model is assumed as representative for compounds of type **4**.

A growing of bâtonnets (see Fig. 5a) followed by the formation of a fan-shaped texture is observed on cooling by polarizing microscopy. Partial decomposition is not only evident from the microscopic observations of gas bubbles in the melt, but also by the lowering of the clearing point in the second and third cooling. Due to decomposition of the samples, the transition temperatures are given for the first heating, but the SmA texture was observed by polarizing microscopy even at higher temperatures. In all cases the stilbazolium compounds exhibit a tendency to supercool before crystallization or to form glasses.

Methoxy substituted stilbazolium halides 5 show large temperature ranges of the LC phases (see Table 6). The compounds with $n \ge 16$ have relatively low melting points with small increase by increasing alkyl chain length. Upon cooling from the isotropic liquid the formation of a fan-shaped texture is observed by polarizing microscopy.

Compounds **6a–f** with $n \ge 18$ show, under polarizing microscopy, focal conic textures characteristic for SmA. Substitution of methoxy group by hydrogen increases the



Fig. 5 a) Texture of *N*-octadecyl-4'-hydroxy-stilbazolium iodide **4e** at 164.3 °C. b) CPK model of *N*-eicosyl-4'-hydroxy-stilbazolium bromide **4f**.

Table 6 Transition temperatures T (°C) and enthalpies ΔH (kJ mol⁻¹) from differential scanning calorimetry of *N*-alkyl-4'-methoxy-stilbazolium halides **5a–f**. ΔT (°C) = temperature range of the smectic A phase

			Phase	Phase transitions $T/^{\circ}C$						
Comp.	п	\mathbf{X}^{-}	$\Delta H/k$	$\Delta T/^{\circ} C$						
5a	14	Br^-	Cr	231 4 2	SmA	247 6 97	Iso ^a	≥16		
5b	16	Br^{-}	Cr	54 9.4	SmA	227 2.83	Iso ^a	≥173		
5c	18	Br ⁻	Cr	63 15.7	SmA	255 5.9	Iso ^a	≥192		
5d	18	I_	Cr ₁	67 10.4	Cr ₂	245 15.7	Iso ^a			
5e	20	Br ⁻	Cr	68 16.8	SmA	227 2	Iso ^a	≥159		
5f	22	Br ⁻	Cr	75 18.5	SmA	214 2.1	Iso ^a	≥139		
^a Partial	decor	npositi	on obse	erved.						

melting points resulting in a decreasing of the mesophase temperature range (see Table 7).

Compound **6d** with iodide anion does not form LC phases. Compared with series **2**, compounds **6** have only the additional C=C double bond between the aromatic rings, which may indicate that series **2** and **6** should have similar liquid crystalline behaviour. Both of the series display SmA phases on heating. Compounds **2** with bromide anion show an additional phase M, which is not present in the case of salts **6**. Compared with bromides **2**, the SmA temperature range is larger in the case of salts **6**. Also, a relatively large increase of the melting and clearing points was observed for salts **6**, leading to a partial decomposition at temperatures higher than 200 °C. The increase of the transition temperatures may be attributed to the elongation of the aromatic core by a C=C double bond which will induce additional π - π interactions in the case of **6**.

3. Discussion

N-Alkyl-3- and -4-substituted-pyridinium salts 1–3 and N-alkyl-4'-substituted-stilbazolium compounds 4–6 display

Table 7 Transition temperatures T (°C) and enthalpies ΔH (kJ mol⁻¹) from differential scanning calorimetry of *N*-alkyl-stilbazolium halides **6a–f**

			Phase transitions $T/^{\circ}C$						
Comp.	n	\mathbf{X}^{-}	$\Delta H/2$	$\Delta T/^{\circ}C$					
6a	14	Br ⁻	Cr	209 2.9	Iso ^a			_	
6b	16	Br^{-}	Cr	200 2.2	Iso				
6c	18	Br^-	Cr	153 4.8	SmA	217 2.5	Iso ^a	≥64	
6d	18	I_	Cr	189 10.6	Iso				
6e	20	Br^-	Cr	141	SmA 2.6	216 0.3	Iso ^a	≥75	
6f	22	Br ⁻	Cr	149 4.4	SmA	247 1.3	Iso ^a	≥98	
^a Partial	decor	npositi	on obs	erved.					

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SmA phases upon heating above their melting point. The formation of lavered structures is attributed to the attachment of the aliphatic chains to an ionic group. The length of the alkyl chains n plays an important role in the stability of the pyridinium salts. By increasing the length of the alkyl chain for compounds of type 1-3 the melting points remain nearly constant and the clearing temperatures increase. This may be explained by increasing hydrophobic stabilization of the aromatic unit by alkyl groups. Compounds of type 3 show a shorter temperature range of the SmA phase with increasing length of the alkyl chain from 20 to 22 carbon atoms. This result was confirmed by X-ray investigations where we found also that the layer distance d decreases from 3.9 nm to 3.8 nm upon increasing the alkyl chain by two carbons. Interestingly, compounds 6 do not show a decrease of the layer distance upon increasing the chain length from 20 to 22 carbons.

The methyl group in the *para*-position of the pyridinium ring, compounds 1, induces a large stability of the mesophase. When the aromatic core is extended by replacing the methyl group with a phenyl substituent, compounds 2, the clearing temperatures decrease indicating that an aromatic core destabilizes the mesophase. Additionally, it leads to the formation of an ordered intermediate mesophase M. The M phase was observed only in the case of *N*-alkyl-4-phenylpyridinium salts having bromide as counter ion. The more bulky 3-phenyl-pyridinium head group in 3 lowers the melting points drastically and reduces the temperature range of LC phases. The temperature range of the SmA phase increases upon attaching substituents to the pyridinium unit in the order 4-methyl (1) > 3-phenyl (3) > 4-phenyl (2).

By changing the anion from iodide to bromide and then to chloride, compounds 2f-h, the tendency to form LC phases increases. Reducing the size of the anion leads to a better stabilization of the layers, also supported by observations on CPK models, because an anion with a smaller size is readily accommodated near the pyridinium cation. When the halides are replaced with tetraphenylborate, which is composed of four phenyl units arranged tetrahedrally and has a larger size than the halides, the clearing temperature decreases. For instance, upon increasing the size of the counter ion from iodide ($r_{I^-} = 0.22$ nm, $r_{I^-} =$ ionic radius of iodide) to tetraphenylborate ($r_{\text{BPh4}^-} = 0.42 \text{ nm}, r_{\text{BPh4}^-} = \text{ionic radius of}$ tetraphenylborate) the clearing temperature decreases by 10 °C. Therefore, we can conclude that the increase in the clearing points is caused by the decrease in the size of the anion in the order chloride > bromide > iodide > tetraphenylborate (see Table 2). The presence of the flat anion *p*-toluenesulfonate, compound 2i, indicates that the tendency to form a SmA phase is suppressed.

Kosaka *et al.*¹³ investigated *N*-alkyl-stilbazolium compounds having the electron accepting NO₂ group at the 4'-position of the stilbazolium head group. These compounds containing alkyl chains up to ten carbons and bromide as counter ion show a relatively narrow temperature range of the mesophase. Replacing the bromides with chlorides the mesophase stability increases and the compounds will thermally decompose. Upon using an dialkylamino group at the 4'-position in the stilbazolium core and alkyl chains with 14 to

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18 carbon atoms attached to the pyridinium ring, the temperature range of the mesophase decreases drastically.¹⁴

These examples indicate the influence of the 4'-substitution at the stilbazolium group on the LC properties. N-Alkyl-4'-substituted-stilbazolium salts 4-6, which form also SmA phases, have the electron donor hydroxy and methoxy group at the 4'-position and the electron accepting unit with character at the pyridinium group inducing strong dipoledipole interactions in addition to the ionic forces. The DSC measurements of compounds 4-6 show peaks corresponding to crystal-crystal, crystal-mesophase and mesophase-isotropic liquid transitions (Tables 5-7), with significant changes in enthalpies ΔH . For instance, in the case of **6f**, ΔH decreases from 4.4 kJ mol⁻¹ for the crystal-melting transition to 1.3 kJ mol⁻¹ for the SmA phase-isotropic transition. Above 200 °C an increase of the baseline was observed due to partial decomposition. It is found that the substituents in the 4'-position increase the stability of the mesophase in the order $OCH_3 > OH > H.$

The stilbazolium compounds **4–6** show higher temperatures of the SmA–isotropic liquid transition in comparison to the pyridinium salts of type **1–3**. Thus, thermal decomposition of the salts upon heating above 200 °C has a major influence on the stability of their mesophases. Therefore, besides the ionic interactions, the liquid crystalline behaviour is influenced, in the case of salts **4** and **5**, also by dipolar interactions by introducing hydroxy and methoxy groups in the 4'-position of the stilbazolium unit. Generally, the salts with bromide anion show an increase of the mesophase temperature range ΔT with increasing alkyl chain length *n*.

4. Experimental

The reagents were purchased from Aldrich, Acros and Fluka. All the solvents were dried using general standard procedures. The investigated compounds were dried for at least two days under vacuum (2 Torr) at temperatures below the melting points or maximum 100 °C for high melting salts and using P₂O₅ as drying agent. ¹H and ¹³C NMR spectra were recorded using Varian Unity 200 or 400 spectrometers. The calorimetric measurements were made using a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating-cooling rate of 10 °C min⁻¹. In the case of pyridinium salts 1–3, the transition temperatures, which are summarized in Tables 1-4, correspond to the second heating. Due to a partial decomposition of the stilbazolium salts, the transition temperatures presented in Tables 5-7 correspond to the first heating. The samples were heated to ca. 120 °C before DSC measurements to remove traces of water. Thermogravimetric measurements were made using a STA 409 instrument (Netzsch) and show that the compounds start to decompose at temperatures above 200 °C. Salts 2e and 5e show by thermogravimetric analysis a loss of weight at 100 °C which corresponds to 0.8 mol water (2.78%) for salt 2e and 0.16 mol water (0.52%) for salt 5e. ESI-MS spectra were obtained using a Finnigan LQC spectrometer (Thermo Electron Corp.). The microscopic investigations were performed by a Nikon Optiphot 2 polarizing microscope which was connected with a Mettler FP 82 HT heating stage. X-Ray investigations on powder-like samples were carried out

with Guinier equipment (film camera and goniometer, both by Huber) with samples in a temperature-controlled heating stage using quartz-monochromatized CuKa radiation (calibration of the film patterns with the powder pattern of $Pb(NO_3)_2$). Two-dimensional patterns for aligned samples on a temperature controlled heating stage were recorded with a 2D detector (HI-STAR, Siemens). The substances had to be heated, for orientation, into the isotropic liquid during the sample preparation for the X-ray investigations. Furthermore, the samples for the Guinier measurements were sealed in glass capillaries (1 mm), those for the 2D measurements were drops on a glass plate aligned at the sample/glass or at the sample/air interface. Taking into account the influences of water and partial decomposition (see above), the transition temperatures and even the phases observed under the conditions of the different X-ray measurements may differ from each other and from those found by the other methods. The UV/Vis measurements were made on a UV 3101 PC spectrometer (Shimadzu Co.).

General procedure for preparation of compounds 1-3

The following procedure was used generally for the preparation of N-alkyl-3- and -4-substituted-pyridinium salts 1–3.

Preparation of **2e**: 4-Phenyl-pyridine (3.22 mmol, 0.5 g) and 1-bromoeicosane (3.22 mmol, 1.17 g) were heated in 10 ml of dried toluene for 10 h at 100–110 °C. After cooling to room temperature, the crude product was purified by washing with diethyl ether and recrystallization from ethanol to give a white powder of *N*-eicosyl-4-phenyl-pyridinium bromide. Yield: 61.80% (1.99 mmol).

N-Eicosyl-4-phenyl-pyridinium bromide **2e**: ¹H NMR (CDCl₃, *J*/Hz, 400 MHz) δ = 9.44 (d, *J* = 6.64, 2 H, Ar-*H*), 8.23 (d, *J* = 6.64, 2 H, Ar-*H*), 7.77 (m, 2 H, Ar-*H*), 7.56–7.51 (m, 3 H, Ar-*H*), 4.90 (t, *J* = 7.3, 2 H, CH₂), 2.02–1.99 (m, 2 H, CH₂), 1.37–1.18 (m, 34 H, CH₂), 0.84 (t, *J* = 7.8, 3 H, CH₃). ¹³C NMR (CDCl₃, 100 MHz) δ = 156.24, 145.02, 133.53, 132.34, 129.89, 127.79, 124.95, 61.25, 31.9, 31.86, 29.68, 29.63, 29.59, 29.50, 29.36, 29.33, 29.09, 26.14, 22.66, 14.07. Anal. calc. for C₃₁H₅₀BrN·H₂O (Calc.) C: 69.64%, H: 9.80%, Br: 14.94%, N: 2.62%, (Found) C: 69.57%, H: 9.79%, Br: 15.01%, N: 2.62%.

N-Eicosyl-3-phenyl-pyridinium bromide **3e**: ¹H NMR (CDCl₃, *J*/Hz, 400 MHz) δ = 9.54 (s, 1 H, Ar-*H*), 9.34 (d, *J* = 6.02, 1 H, Ar-*H*), 8.55 (d, *J* = 8.09, 1 H, Ar-*H*), 8.14–8.11 (m, 1 H, Ar-*H*) 7.84 (d, *J* = 6.84, 2 H, Ar-*H*), 7.53–7.44 (m, 3 H, Ar-*H*), 5.09 (t, *J* = 7.3, 2 H, CH₂), 2.03–1.97 (m, 2 H, CH₂), 1.36–1.17 (m, 34 H, CH₂), 0.84 (t, *J* = 6.7, 3 H, CH₃).¹³C NMR (CDCl₃, 100 MHz) δ = 143.1, 142.6, 142.3, 141.2, 132.6, 130.6, 129.8, 128.4, 127.7, 62.3, 32.9, 32.2, 31.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 29.2, 28.8, 28.2, 26.1, 22.7, 14.1. Anal. calc. for C₃₁H₅₀BrN·0.5H₂O (Calc.) C: 70.77%, H: 9.70%, N: 2.66%, (Found) C: 70.78%, H: 10.12%, N: 2.02%.

Preparation of **2f**–**j**: Compound **2h** was prepared by a modified ion-exchange procedure¹⁵ using Dowex 1 × 8-400, ion exchange resin (Acros), *N*-docosyl-4-phenyl-pyridinium bromide **2g**, NaI and methanol: 10 g of Dowex resin was suspended in 100 ml water for 2 h. After removing the water, the resin was washed with NaI (or NaCl, NaB(C_6H_5)₄,

 $CH_3-C_6H_5-SO_3H$) solution three times. The resin was kept in contact for 2 days with the third part of NaI solution and then filtered. The ratio of **2g**/NaI was 1/10. 100 mg of salt **2g** (0.18 mmol) was dissolved in 10 ml of methanol and mixed with resin. After keeping the resin in contact with the salt **2g** for two days, the product was extracted with methanol and washed with water to remove the excess of NaI. The solvent was evaporated by distillation and pure **2h** was obtained. Compounds **2f–j** were investigated by ESI-MS and no bromide ion was identified in their spectra, which indicates that the exchange procedure was complete.

General procedure for the preparation of compounds 4-6

The following procedure was used generally for the preparation of *N*-alkyl-4'-substituted-stilbazolium salts **4–6**.

Preparation of **4d**: 1-Octadecyl-4-methyl-pyridinium bromide (0.94 mmol, 0.4 g), 4-hydroxy-benzaldehyde (0.94 mmol, 0.11 g), piperidine (0.12 ml) and dry ethanol (5 ml) were heated under reflux for 8 h. Upon cooling the reaction to room temperature the product precipitated. The resulting red precipitate was filtered, washed with diethyl ether and recrystallized from ethanol to give 60% (0.56 mmol), red powder.

N-Octadecyl-4'-hydroxy-stilbazolium bromide **4d**: ¹H NMR (DMSO, *J*/Hz, 400 MHz) $\delta = 8.77$ (d, J = 6.64, 2 H, Ar-*H*), 8.06 (d, J = 6.84, 2 H, Ar-*H*), 7.89 (d, J = 16.18, 1 H, C*H*), 7.56 (d, J = 8.71, 2 H, Ar-*H*), 7.18 (d, J = 16.18, 1 H, C*H*), 6.78 (d, J = 8.71, 2 H, Ar-*H*), 4.40 (t, J = 7.3, 2 H, C*H*₂), 1.87–1.83 (m, 2 H, C*H*₂), 1.24–1.20 (m, 30 H, C*H*₂), 0.83 (t, J = 6.8, 3 H, C*H*₃). ¹³C NMR (DMSO, 100 MHz) $\delta = 160.5$, 153.3, 143.6, 141.4, 130.2, 125.8, 122.9, 119.1, 116.1, 59.3, 31.2, 30.3, 28.9, 28.7, 28.6, 28.5, 28.2, 25.3, 21.9, 13.8. Anal. calc. for C₃₁H₄₈BrNO (Calc.) C: 70.17%, H: 9.12%, N: 2.64%, (Found) C: 70.73%, H: 9.45%, N: 2.64%.

N-*Eicosyl-4'-methoxy-stilbazolium bromide* **5e**: ¹H NMR (CDCl₃, *J*/Hz, 400 MHz) δ = 9.04 (d, *J* = 6.02, 2 H, Ar-*H*), 8.00 (d, *J* = 6.02, 2 H, Ar-*H*), 7.67 (d, *J* = 15.97, 1 H, C*H*), 7.57 (d, *J* = 8.71, 2 H, Ar-*H*), 7.00 (d, *J* = 15.82, 1 H, C*H*), 6.90 (d, *J* = 8.71, 2 H, Ar-*H*), 4.71 (t, *J* = 7.01, 2 H, C*H*₂), 3.82 (s, 3 H, OC*H*₃), 1.95–1.91 (m, 2 H, C*H*₂), 1.28–1.18 (m, 34 H, C*H*₂), 0.84 (t, *J* = 6.8, 3 H, C*H*₃). ¹³C NMR (CDCl₃, 125 MHz) δ = 162.1, 153.8, 144.1, 142.0, 130.4, 127.3, 123.7, 119.7, 114.6, 60.8, 55.4, 31.9, 31.8, 31.7, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.0, 26.1, 22.6, 14.1. Anal. calc. for C₃₄H₅₄BrNO·0.2H₂O (Calc.) C: 70.79%, H: 9.44%, Br: 13.88%, N: 2.43%, (Found) C: 70.51%, H: 9.63%, Br: 13.95%, N: 2.39%.

N-Octadecyl-stilbazolium bromide **6c**: ¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 9.15 (d, J = 6.64, 2 H, Ar-H), 8.07 (d, J = 6.84, 2 H, Ar-H), 7.71 (d, J = 16.39, 1 H, CH), 7.68–7.60 (m, 2 H, Ar-H), 7.42–7.38 (m, 3 H, Ar-H), 7.16 (d, J = 16.86, 1 H, CH), 4.77 (t, J = 7.3, 2 H, CH₂), 1.98–1.88 (m, 2 H, CH₂), 1.28–1.19 (m, 30 H, CH₂), 0.84 (t, J = 6.8, 3 H, CH₃). ¹³C NMR (CDCl₃, 100 MHz) δ = 153.41, 144.35, 142.16, 134.48, 130.98, 129.18, 128.43, 124.25, 122.21, 61.08, 31.96, 31.78, 29.74, 29.70, 29.64, 29.55, 29.41, 29.39, 29.13, 26.18, 22.72, 14.14. Anal. calc. for C₃₁H₄₈BrN·0.5H₂O (Calc.) C: 71.12%, H: 9.36%, N: 2.67%, (Found) C: 71.02%, H: 9.62%, N: 2.52%.

Acknowledgements

Financial support of this work by Deutsche Forschungsgemeinschaft (GRK 894) is gratefully acknowledged. We would like to thank Dr T. Müller for the thermogravimetric analysis and Dr R. Kluge for the ESI-MS measurements.

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