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A series of 1,4-piperazinium di-*n*-alkyl sulphates was synthesized and compared with an analogous series of 1,5-homopiperazinium di-*n*-alkyl sulphates. Their thermotropic liquid crystalline behaviour was studied by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction. For the piperazinium salts, two ordered smectic phases were established, in which the lateral packing of the molecules within the layers is rectangular or tetragonal. Both phases are characterized by an alternate periodic packing of the positive and negative ionic groups in the polar sublayer, while the lipophilic sublayers of the alkyl chains are in a disordered conformation. Substitution of the piperazinium by the less symmetrical homopiperazinium group disfavours organization within the smectic layer and as a result smectic A phases were obtained.

1. Introduction

Amphiphilic molecules were rather unduly ignored compared with rigid-rod molecules in the early investigations of the exhibition of thermotropic liquid crystalline behaviour [1]. In recent years however it has been well established that ionic amphiphilic salts, including protonated amines [2], aliphatic quaternary ammonium salts [3], carboxylates [4], sulphonates [5] and pyridinium salts [6] exhibit thermotropic liquid crystalline behaviour, and the subject has been extensively studied and reviewed [7]. It should be noted that these amphiphiles, in addition to forming thermotropic liquid crystals, are primarily known for their ability to organize in water forming micelles, vesicles or a diversity of lyotropic liquid crystals; for this reason these salts were characterized as amphotropic [8, 9]. The type of liquid crystalline character obtained from these compounds results from an interplay of the length and the number of lipophilic chains and of the type of polar heads and their functionalization, and also from the nature of counter ions. Functionalization through quaternization of tertiary aliphatic amines by employing appropriate organic halides proved especially fruitful for producing various liquid crystalline phases [3]. Protonated ammonium salts [2], as expected, lack this possibility and liquid crystalline diversification was not as rich compared with quaternaries [7].

Dipolar amphiphilic compounds also exhibit a diversity of liquid crystalline phases dependent on the polar head groups and on the type and length of the spacer between the polar heads. Thus, early examples of dipolar amphiphiles with two pyridinium head groups attached to a biphenylene core, with appropriate chain length spacers, exhibited smectic liquid crystalline phases [10]. All aliphatic bis(quaternary) amphiphilic ammonium salts [11] exhibited smectic phases one of which, at least, resembled the smectic T phase [11(*b*)] first reported by Alami *et al.* [12]. On the other hand a hydrophilic oligo(oxyethylene) spacer has been introduced in geminal dialkylammonium surfactants which, depending on the length of the spacer and temperature, exhibited L_β and L_α phases [13]. 1,4-Dialkyl-1,4-diazoniabicyclo[2.2.2]-octane dibromides [14], with an aliphatic bicyclic moiety inserted between two long aliphatic chains, also gave rise to a smectic T phase.

In the present study, and within the framework of preparing multi-polar amphiphiles, the synthesis and characterization of materials based on piperazinium and homopiperazinium *n*-alkyl sulphates (see the scheme) were investigated. In the first place we investigated the extent to which a minor structural modification, for instance, the replacement of piperazinium with the homopiperazinium di-cation, affects the liquid crystalline character of these compounds. Secondly, the effect of the alkyl chain length of the alkyl sulphate counterion on the liquid crystallinity was investigated. The liquid

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Cn ⟶ OSO₃⁻ ⁺H₂N⟶NH₂⁺ ⁻O₃SO ⟶ Cn

Cn ⟶ OSO₃⁻ ⁺H₂N⟶NH₂⁺ ⁻O₃SO ⟶ Cn

n=10,12,14,16
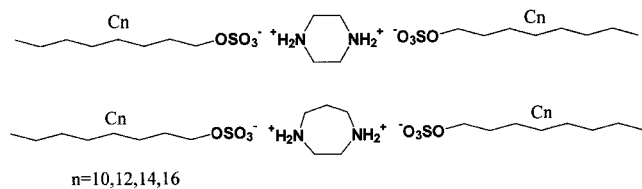
Scheme.

crystalline behaviour was studied by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC), and established by X-ray diffraction (XRD) studies. The assembly of the ionic species within the polar sub-layers due to the formation of hydrogen bonds between the piperazinium or homopiperazinium cations and the sulphate anions was investigated by FTIR spectroscopy.

2. Experimental
2.1. *Materials and synthesis*

Piperazine and homopiperazine were purchased from Aldrich and used without further purification. Sodium decyl sulphate and sodium dodecyl sulphate were purchased from Janssen, while sodium tetradecyl sulphate and sodium hexadecyl sulphate were obtained from Merck. All alkyl sulphates were recrystallized from benzene/methanol (4:1 v/v) before use.

2.1.1. *Synthesis of piperazinium and homopiperazinium bromides*

Piperazine and homopiperazine were dissolved in chloroform and protonated by adding excess of aqueous hydrobromic acid under intense agitation. The protonated products spontaneously precipitated and were filtered off and washed repeatedly with chloroform. The materials were exhaustively dried in vacuum over phosphorous pentoxide.

2.1.2. *Synthesis of 1,4-piperazinium di-n-alkyl sulphates and 1,5-homopiperazinium di-n-alkyl sulphates (n = 10, 12, 14, 16)*

To 0.1 mol of piperazinium or homopiperazinium bromide, dissolved in water, 0.25 mol of *n*-alkyl sodium sulphate, also dissolved in water, was added. For the higher members of the series slight heating was required to dissolve the salts. The precipitated salts were filtered off, washed with hot water and recrystallized from ethanol. The resulting salts were exhaustively dried in vacuum over phosphorous pentoxide and their structures established by ^{1}H NMR and elemental analysis. ^{1}H NMR (500 MHz, DMSO-d₆) for 1,4-piperazinium di-*n*-alkyl sulphates: $\delta = 8.85$ (s, NH_2^+), 3.70 (t, $^-OSO_3CH_2CH_2$) 3.25 (t, $^+NH_2CH_2CH_2NH_2^+$), 1.45 (m, $^-OSO_3CH_2CH_2$), 1.25 (m, $^-OSO_3CH_2CH_2(CH_2)_nCH_3$), 0.85 (t, CH_3) and for 1,5-homopiperazinium di-*n*-alkyl sulphates: $\delta = 8.35$

(s, NH_2^+), 3.70 (t, $^-OSO_3CH_2CH_2$), 3.45 (t, $^+NH_2CH_2CH_2NH_2^+$), 3.25 (t, $^+NH_2CH_2CH_2CH_2NH_2^+$), 2.15 (m, $^+NH_2CH_2CH_2CH_2NH_2^+$), 1.45 (m, $^-OSO_3CH_2CH_2$), 1.25 (m, $^-OSO_3CH_2CH_2(CH_2)_nCH_3$), 0.85 (t, CH_3). Elemental analyses for 1,4-piperazinium di-*n*-alkyl sulphates: $C_{24}H_{54}N_2S_2O_8$: calc. C 51.22, H 9.67, N 4.98, S 11.39; found C 50.93, H 9.41, N 4.78, S 11.23%. $C_{28}H_{62}N_2S_2O_8$: calc. C 54.34, H 10.10, N 4.53, S 10.36; found C 54.23, H 10.33, N 4.81, S 10.51%. $C_{32}H_{70}N_2S_2O_8$: calc. C 56.94, H 10.45, N 4.15, S 9.50; found C 57.14, H 10.54, N 4.16, S 9.76%. $C_{36}H_{78}N_2S_2O_8$: C 59.14, H 10.75, N 3.83, S 8.77; found C 58.68, H 10.78, N 3.89, S 8.97%. Elemental analyses for 1,5-homopiperazinium di-*n*-alkyl sulphates: $C_{25}H_{56}N_2S_2O_8$: calc. C 52.05, H 9.79, N 4.86, S 11.12; found C 52.21, H 10.01, N 4.89, S 11.07%. $C_{29}H_{64}N_2S_2O_8$: calc. C 55.03, H 10.19, N 4.43, S 10.13; found C 54.90, H 10.22, N 4.44, S 10.29%. $C_{33}H_{72}N_2S_2O_8$: C 57.52, H 10.53, N 4.07, S 9.31; found C 57.88, H 10.65, N 4.11, S 9.61%. $C_{37}H_{80}S_2N_2O_8$: calc. C 59.64, H 10.82, N 3.76, S 8.60; found C 59.67, H 10.99, N 3.82, S 8.61%.

2.2. *Characterization*

Liquid crystal textures were observed using a Leitz–Wetzlar polarizing microscope equipped with a Linkam hot-stage. Thermotropic polymorphism was investigated by differential scanning calorimetry employing a DSC-10 calorimeter (TA instruments) at heating/cooling rates of $10^\circ C\ min^{-1}$. Thermal stability was assessed by thermogravimetry employing a TGA 2050 analyzer (TA instruments) at a heating rate of $10^\circ C\ min^{-1}$. Liquid crystalline phases were investigated by XRD using CuK$_{\alpha 1}$ radiation from a Rigaku rotating anode X-ray generator (operating at 50 kV, 100 mA) and an R-AXIS IV image plate. Powder samples were sealed in Lindemann capillaries and heated using an INSTEC hot-stage. FTIR studies were made using a Nicolet Magna 550 spectrometer coupled with a VLT-2 variable temperature cell (Research & Industrial Instruments Company).

3. Results and discussion
3.1. *Thermal and optical studies*

The thermal stability of the salts was studied by thermogravimetry. Piperazinium derivatives start decomposing at temperatures above $150^\circ C$. At $140^\circ C$ the weight loss was less than 0.1% for all samples. However at $200^\circ C$, i.e. below their clearing temperatures (see below), the weight loss was between 1% for the hexadecyl and 4% for the decyl sulphate piperazinium derivatives. Homopiperazium derivatives exhibit essentially the same behaviour. They are thermally stable up to about $150^\circ C$, with weight loss less than 0.1%, but they degrade severely at higher temperatures. Weight losses at $200^\circ C$ range from 1% for

the highest member to about 9% for the lowest. These results were duly taken into account especially during the DSC and X-ray experiments.

The mesomorphic properties of the compounds were studied by POM and DSC. On heating on a microscope slide, piperazinium derivatives melted at temperatures between 109 and 117°C depending on the chain length. The crystals were transformed to soft birefringent materials, suggesting the presence of an ordered mesophase, while at temperatures above c. 130°C they turned into high viscosity fluids with ill developed textures. On further heating, decomposition occurred before isotropization and therefore it was not possible to obtain well developed textures on cooling from the isotropic phase.

Thermal transitions observed by optical microscopy were in line with DSC results (table 1). The first high enthalpy transition depended on the alkyl chain length and was basically related to the melting of the aliphatic chains. The second low enthalpy transition was essentially unaffected by chain length, suggesting therefore a reorganization within the polar sublayers (see also results from the X-ray experiments). On cooling, the reverse phase transition was observed with a hysteresis of about 3°C, while the transition from the ordered smectic phase to the crystalline phase was observed with a hysteresis of about 20°C, showing the significance of nucleation. The second DSC runs were identical to the first, showing the thermodynamic stability of the observed phases.

Homopiperazinium derivatives exhibit a low enthalpy crystal–crystal transition before melting to a fluid mesomorphic phase (table 2). Oily streak textures could be observed using the polarizing microscope, indicating the presence of SmA phases. The compounds again degrade thermally below isotropization and therefore it was not possible to obtain well developed textures. Upon cooling from the smectic A phase the reverse phase transitions were observed with a hysteresis of about 20°C. DSC runs were intentionally restricted to relatively low temperatures in order to avoid thermal decomposition; it was therefore possible to obtain second DSC runs identical to the first.

3.2. *X-ray investigation of the piperazinium derivatives*

The X-ray diffraction patterns of the crystal phases of the piperazinium derivatives contain a large number of sharp reflections showing the existence of well developed three-dimensional lattices. More than four equidistant small angle reflections indicate a lamellar arrangement of the molecules, as also observed with long chain piperazinium bis(n-alkanoates) [15, 16]. The lamellar periods estimated from the small angle reflections grow linearly with the number n of carbon atoms in the alkyl chains (figure 1) according to the equation: $d/\text{Å} = 7.4_{\pm 0.1} + 1.21_{\pm 0.01}\,n$, deduced from a least-squares fit of the experimental data. The Y-intercept of the straight line provides an estimate of the thickness of the polar sublayers and is consistent with the length of the piperazinium group ($\sim 5.6\,\text{Å}$) in the chair conformation, as reported for the crystalline structures of analogous salts [17, 18], and the radius of the sulphate group ($\sim 5\,\text{Å}$) [19] if some overlapping of the ions is assumed. The slope of the line represents the increase in thickness of the lamellae due to the increase of the alkyl chain by one methylene group. This value is close to half the length of one zigzag in a fully extended paraffin chain ($2.54/2 = 1.27\,\text{Å}$) [20] suggesting that the alkyl chains are interdigitated and tilted. The tilt angle estimated from the experimental data, $\cos^{-1}(\text{slope}/1.27)$ [21], is about 17 degrees. In

Table 1. Phase transition temperatures (onset) and enthalpies for the piperazinium derivatives.

n	$T_1/°C$	$\Delta H_1/\text{kJ mol}^{-1}$	$T_2/°C$	$\Delta H_2/\text{kJ mol}^{-1}$
10	109.2	39.0	127.4	3.9
12	112.1	52.4	127.3	3.8
14	115.4	73.3	127.0	3.3
16	117.5	80.5	127.2	3.5

Table 2. Phase transition temperatures (onset) and enthalpies for the homopiperazinium derivatives. T_k coresponds to a crystal–crystal transition, T_s to a crystal–smectic A transition.

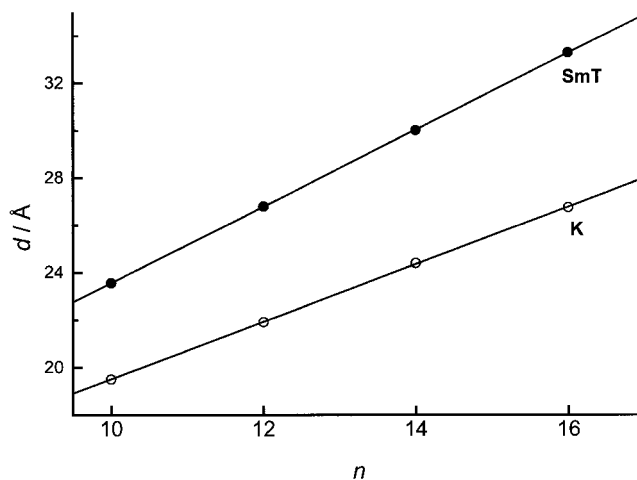| n	$T_k/°C$	$\Delta H_k/\text{kJ mol}^{-1}$	$T_s/°C$	$\Delta H_s/\text{kJ mol}^{-1}$
10	78.5	3.3	101.7	44.1
12	92.1	8.1	109.8	59.1
14	92.8	5.8	110.1	63.0
16	100.9	9.8	111.4	68.1

Figure 1. Lamellar periods of piperazinium salts in the crystal (K) and smectic T phases as a function of the number n of carbon atoms of the alkyl chains.

every respect therefore the crystal structure is similar to those determined for piperazinium salts of long chain aliphatic acids [15, 16].

At temperatures above the first thermal transition, the diffraction patterns contained more than three equidistant sharp reflections in the small angle region attributed to the presence of a lamellar phase. In the wide angle region the patterns contained a diffuse band indicative of the liquid-like order of the alkyl chains and several sharp reflections (figure 2). These reflections appear in the same positions for all the piperazinium derivatives and can be indexed (table 3) according to a two-dimensional rectangular lattice with cell parameters $a = 13.03$, $b = 5.83$ Å. The reflection condition, $h0$: $h = 2n$, is consistent with the rectangular $p2mg$ plane group [22]. The observed lattice describes the periodic arrangement of the polar piperazinium sulphate groups since the alkyl chains are in a disordered conformation. However for the shorter C_{10} derivative, additional peaks were observed (table 4) and therefore the phase is characterized by an interlayer coupling which leads, from a formal point of view, to a true three-dimensional long range order. The observed reflections can be indexed according to a simple
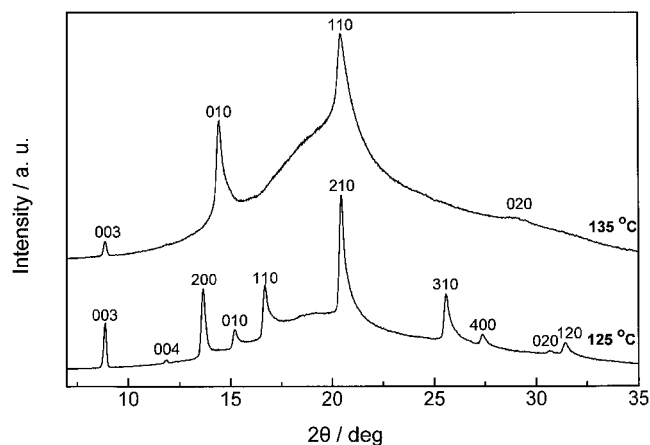

Figure 2. X-ray diffraction patterns of 1,4-piperazinium di-*n*-tetradecyl sulphate in the rectangular smectic phase at 125°C and in the smectic T phase at 135°C.

Table 3. X-ray diffraction data for the C_{12}–C_{16} piperazinium salts at 125°C; d^{obs} and d^{calc} are the observed and calculated spacings of the ($h\,k\,0$) reflections of a rectangular cell.

$h\,k\,l$	d^{obs}/Å	d^{calc}/Å
2 0 0	6.49	6.50
0 1 0	5.83	5.83
1 1 0	5.31	5.32
2 1 0	4.34	4.34
3 1 0	3.48	3.48
4 0 0	3.25	3.25
0 2 0	2.91	2.92
1 2 0	2.85	2.85

Table 4. X-ray diffraction data for the C_{10} piperazinium salt at 125°C; d^{obs} and d^{calc} are the observed and calculated spacings of the ($h\,k\,l$) reflections of a monoclinic cell.

$h\,k\,l$	d^{obs}/Å	d^{calc}
0 0 1	23.14	23.26
0 0 2	11.62	11.63
0 0 3	7.74	7.75
2 0 0	6.47	6.47
2 0 1	6.03	6.00
0 1 0	5.84	5.84
0 1 1	5.68	5.66
1 1 0	5.32	5.32
1 1 1 (shoulder)	~5.2	5.12
0 0 5	4.65	4.65
2 1 0	4.34	4.34
2 1 1	4.20	4.19
0 0 6	3.88	3.88
3 1 0	3.49	3.47
4 0 0	3.24	3.24
4 0 1	3.12	3.14
0 2 0	2.91	2.92
1 2 0	2.85	2.85

monoclinic cell with the same a and b parameters as above, while the c-axis is tilted slightly with respect to the layer normal ($a = 13.09$, $b = 5.85$, $c = 23.54$ Å, $\beta = 98.9°$). The reflection conditions, $h00$: $h = 2n$, $h0l$: $h = 2n$, were consistent with these observed for the two-dimensional lattice. The possible space groups that satisfy the reflection conditions are either Pc, cell choice 3 ($P1\alpha1$) or $P2/c$, cell choice 3 ($P12/\alpha1$) [22].

On further heating, above the second transition observed by DSC, the diffraction patterns contain 3 equidistant sharp small angle reflections, a diffuse band centred at about 4.5 Å, two rather sharp peaks in the wide angle region located at 6.15 and 4.35 Å (figure 2) for all the investigated piperazinium derivatives and a very low intensity peak at 3.0 Å. These peaks can be indexed as the (0 1 0), (1 1 0) and (2 0 0) reflections of a square lattice consistent with the existence of a smectic T phase in which the ionic groups are arranged periodically according to a two-dimensional tetragonal lattice [12, 14, 21]. The cell parameter, $a = 6.15$ Å, is the same for all the derivatives studied meaning that the packing of the piperazinium sulphate groups inside the polar sublayers is again totally independent of the length of the alkyl chains. For the short alkyl chain C_{10} derivative, the diffractogram contains additionally the (0 1 1) and (1 1 1) peaks, while the (0 2 0) peak is clearly observed. The existence of three-dimensional correlation arises from long range coulombic interactions of the ionic charges apparently due to the smaller distance between the polar sublayers. However, since the electrical interactions are stronger inside the polar sublayers than between them, the smectic layers are able to slip over

each other rather easily [21] and therefore the phase can be characterized as liquid crystalline. A similar behaviour has been observed in the smectic T phase of dialkyl-1,4-diazoniabicyclo[2.2.2]octane dibromide derivatives [14].

The lamellar periods in the orthogonal and tetragonal phases are approximately identical, differing only by about 0.5%. They grow linearly with the number of carbon atoms in the alkyl chains according to the equation $d/\text{Å} = 7.4_{\pm 0.1} + 1.61_{\pm 0.01}n$ for the orthogonal phase at 125°C, and $d/\text{Å} = 7.4_{\pm 0.1} + 1.62_{\pm 0.01}n$ for the tetragonal phase at 135°C (figure 1). The values of the Y-intercept indicate that the thickness of the polar sublayers in the smectic phases is equal to that of the crystal phase. Thus, the rearrangement of the head groups during the thermal transitions is taking place at constant thickness, as already observed in the case of quaternary alkyl-ammonium salts exhibiting smectic T phases [21]. The values of the slopes obtained in the smectic phases were larger than those in the crystal phase and also higher than that of a fully extended paraffin chain suggesting that in the smectic phases the melted alkyl chains were no longer interdigitated, figure 3 (*a*). The small difference in the lamellar thickness between the two smectic phases is simply a result of the thermal expansion of the volume of the aliphatic part of the molecules.

A better description of the arrangement of the ionic head groups inside the polar sublayers of the smectic phases requires the determination of the number of molecules per unit cell. The molecular area S, i.e. the surface covered by each molecule in the layers, can be estimated utilizing the observed linear dependence of the smectic period d on the number n of carbon atoms in the alkyl chains and the assumption of additivity of the partial volumes of the polar and apolar parts of the molecules [12, 21]. From the measured slope of the straight line ($2V_{CH2}/S$) and the known volume of one methylene group [23] ($V_{CH2} = 28.5\,\text{Å}^3$ at 125°C and $28.7\,\text{Å}^3$ at 135°C), the molecular area S covered by the alkyl chains can be calculated. In the smectic T phase the area determined using this approximation, $35.4\,\text{Å}^2$, was very close to the area of the square unit cell ($6.15^2 = 37.8\,\text{Å}^2$). Each tetragonal unit therefore contains one polar group, while the molten alkyl chains fill the space above and below the piperazinium moieties. Essentially the same area covered by the aliphatic chains was obtained in the orthogonal phase, clearly suggesting that each rectangular unit cell, having an area of $13.03 \times 5.83 = 76.0\,\text{Å}^2$, contains two polar groups. On the basis of the observed symmetry of the orthogonal cell, the number of groups inside it and the sizes of the piperazinium and sulphate ions quoted above, a herringbone-type arrangement is proposed, figure 3 (*b*). The sulphate groups are quite probably located between the ammonium groups in order to ensure perfect alternation of the positive and negative charges and minimize the electrostatic repulsions. Increasing the temperature, a reorganization of the polar groups is observed resulting in a slight increase of the molecular area, but without affecting the lamellar spacing. This observation most probably supports the assumption of a rotational motion of the piperazinium groups in the SmT phase. Therefore their positions in space become equivalent and the tetragonal packing is favoured. Evidently, the positions of the piperazinium and sulphate ions are at the corners and centres of the square lattice, figure 3 (*c*).

3.3. *X-ray investigation of the homopiperazinium derivatives*

The X-ray patterns of the homopiperazinium derivatives contain more than four equidistant small angle reflections at room temperature, indicating the lamellar arrangement of the molecules; a large number of sharp reflections in the wide angle region reveal the existence of well developed crystal phases. The lamellar periods determined from the small angle reflections are only slightly larger than those of the piperazinium derivatives. They grow linearly with the number n of carbon atoms of
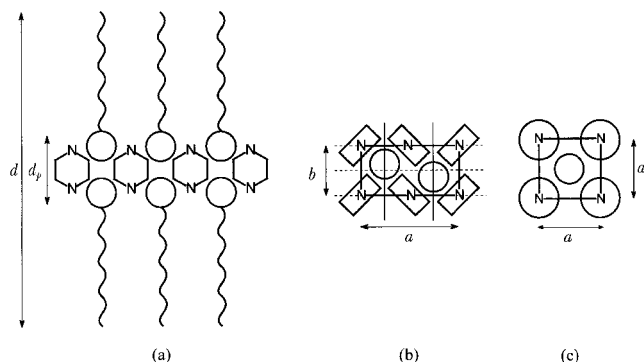

Figure 3. Schematic view of the proposed molecular arrangement in the ordered smectic phases. (*a*) The positive ammonium and negative sulphate ions alternate within the polar sublayers to minimize the coulombic repulsions. The lipophilic sublayers consist of alkyl chains in a disordered conformation. (*b*) Top view of the arrangement of the ionic species in the rectangular unit cell. The piperazinium groups (oblongs) are positioned on the axes of the unit cell while the sulphate groups (circles) are located within the cell to achieve strict alternation of positive and negative charges. The thin lines represent the mirror planes, and the dashed lines the glide planes of the rectangular *p2mg* space group. (*c*) Top view of the polar sublayer of the smectic T phase. Upon heating, the positions of the piperazinium groups, now represented as circles, become equivalent, possibly due to their rotational motion. As a result, the rectangular lattice is transformed into a square lattice having the same thickness, d_p, and a slightly larger molecular area per molecule.

the alkyl chains (figure 4) according to equation $d/\text{Å} = 8.4_{\pm 0.2} + 1.11_{\pm 0.02}n$. The thickness of the polar sublayers is greater by about 1 Å than that of the piperazinium derivatives. Since the size of the homopiperazinium group [24], ~ 6 Å, is only slightly larger than that of the piperazinium group, this difference is apparently due to the less symmetrical shape of the homopiperazinium moiety. The alkyl chains are again interdigitated forming single layers and tilted by about 29 degrees in order to compensate for the larger cross-sectional area of the polar groups.

At temperatures above the crystal–smectic A transition, the diffraction patterns contain three sharp equidistant small angle reflections related to the smectic ordering, and a diffuse wide angle reflection centred at 4.5 Å indicating that the alkyl chains are in a disordered conformation. The smectic periods measured increase linearly with the number of carbon atoms in the aliphatic chains (figure 4) according to the equation $d/\text{Å} = 9.6_{\pm 0.5} + 1.69_{\pm 0.04}n$ at 130°C. From the slope of the d vs. n straight line, the area S covered in the plane of the smectic layers by one molecule may be determined as above, using the known volume of one methylene group (28.6 Å^3 at 130°C). The value determined (33.8 Å^2) is smaller than that found for the smectic phases of the piperazinium salts. The smaller molecular area and the larger thickness of the polar sublayer indicate that not only the alkyl chains, but also the polar head groups are arranged in a disordered fashion within the smectic A phase [21].

3.4. *Infrared spectroscopy of the piperazinium and homopiperazinium derivatives*

The strong interactions of the positive and negative ions through coulombic forces allow them, in principle, to form hydrogen-bonded networks, as in the case of
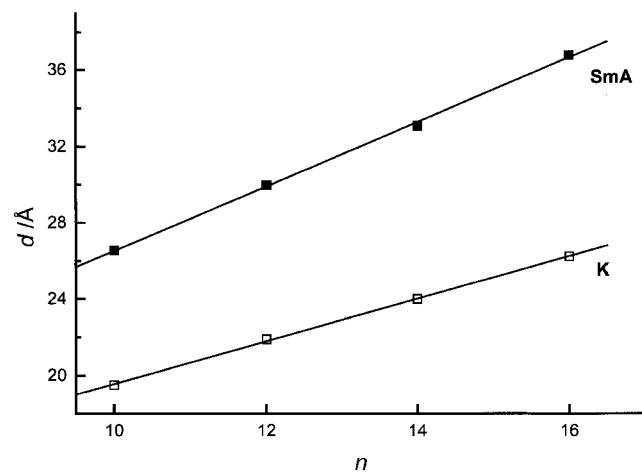

Figure 4.   Lamellar periods of the homopiperazinium salts in the crystal (K) and smectic A phases as a function of the number n of carbon atoms in the alkyl chains.

guanidinium sulphonate derivatives [25, 26]. Indeed, as reported in the literature, the piperazinium di-cation is hydrogen-bonded to four different carboxylate anions in the crystalline phase of piperazinium bis(*n*-alkanoates) [16, 18]. Additionally, in the case of a piperazine ethane sulphonic acid derivative [27], dimers are formed due to the formation of hydrogen bonds between the nitrogen of the piperazine and the oxygen of the sulphonate group. FTIR spectroscopy was used to investigate the hydrogen bonding both in the crystalline and in the ordered and disordered smectic phases of the piperazinium and homopiperazinium derivatives. In the crystalline phase, the spectra of both series of compounds contain in the 3300–3000 cm^{-1} N–H stretching region (which is the most suitable for the study of hydrogen bond formation of amines [21, 26]) two absorption bands which are not present in the spectra of the corresponding piperazinium and homopiperazinium hydrobromides. The bands located at 3120 and 3027 cm^{-1} for the P12 compound and at 3135 and 3025 cm^{-1} for the H12 compound clearly indicate that the NH groups are hydrogen-bonded to the sulphate groups (it should be noted that the change of the S=O stretching bands upon hydrogen bonding is much less pronounced [27]). Their positions also suggest that the binding is much stronger in the case of the piperazine derivative [28]. Upon heating the P12 derivative, the bands remain unchanged up to the smectic T phase where the bands become broader, although they are centred at the same position. The hydrogen bonding formation is therefore not essentially affected in the orthogonal smectic phase and is slightly distorted in the smectic T phase. These results are in line with those reported for another series of hydrogen-bonded compounds forming smectic T phases [21]. In the case of the H12 derivative, the bands become broader and decrease significantly in intensity upon heating in the smectic A phase. It is thus verified that the polar groups are assembled in a disordered manner within the smectic layers.

4.   Concluding remarks

Alkyl sulphate piperazinium salts melt forming two ordered smectic mesophases in which the ionic groups in the polar sublayer are arranged according to a rectangular lattice at low temperatures and to a tetragonal lattice at higher temperatures. The occurrence of such uncommonly observed phases is certainly related to the chemical structure of the mesomorphic compounds. The ionic groups interact predominantly through coulombic forces and through hydrogen bonding, resulting in systems of two-dimensional order. In this manner, strict alternation of positive and negative charges is achieved as required by thermodynamics [12]. The shape of the ions however plays a critical role in the overall

packing. Thus, a small modification of the positive ion can destroy the order within the smectic layer as was the case with the alkyl sulphate homopiperazinium derivatives where simple smectic A phases were observed.

References

[1] KELKER, H., and HATZ, R., 1980, *Handbook of Liquid Crystals* (Weinhem-Basel: Verlag Chemie).

[2] (*a*) BUSICO, V., CORRADINI, P., and VACATELLO, M., 1982, *J. phys. Chem.*, **86,** 1033; (*b*) BUSICO, V., CERNICCHLARO, P., CORRADINI, P., and VACATELLO, M., 1983, *J. phys. Chem.*, **87,** 1631; (*c*) GAULT, J. D., GALLARDO, H. A., and MÜLLER, H. J., 1985, *Mol. Cryst. liq. Cryst.*, **130,** 163.

[3] (*a*) IWAMOTO, K., OHNUKI, K., SAWADA, K., and SENO, M., 1981, *Mol. Cryst. liq. Cryst.*, **73,** 95; (*b*) MALLIARIS, A., CHRISTIAS, C., MARGOMENOU-LEONIDOPOULOU, G., and PALEOS, C. M., 1982, *Mol. Cryst. liq. Cryst.*, **82,** 161; (*c*) PALEOS, C. M., MARGOMENOU-LEONIDOPOULOU, G., and MALLIARIS, A., 1988, *Mol. Cryst. liq. Cryst.*, **161,** 385; (*d*) MICHAS, J., PALEOS, C. M., and DAIS, P., 1989, *Liq. Cryst.*, **5,** 1737; (*e*) SÜDHOLTER, E. J. R., ENGBERTS, J. B. F. N., and DE JEU, W. H., 1982, *J. phys. Chem.*, **86,** 1908; (*f*) BAZUIN, C. G., GUILLON, D., SKOULIOS A., and ZANA, R., 1986, *J. Phys. Fr.*, **47,** 927; (*g*) PALEOS, C. M., ARKAS, M., SEGHROUSHNI, R., and SKOULIOS, A., 1995, *Mol. Cryst. liq. Cryst.*, **268,** 179; (*h*) ARKAS, M., YANNAKOPOULOU, K., PALEOS, C. M., WEBER, P., and SKOULIOS, A., 1995, *Liq. Cryst.*, **18,** 563; (*i*) ARKAS, M., PALEOS, C. M., and SKOULIOS, A., 1997, *Liq. Cryst.*, **22,** 735; (*j*) MATHIS, A., GALIN, M., GALIN, J. C., HEINRICH, B., and BAZUIN, C. G., 1999, *Liq. Cryst.*, **26,** 973.

[4] (*a*) BUSICO, V., FERRARO, A., and VACATELLO, M., 1985, *Mol. Cryst. liq. Cryst.*, **128,** 243; (*b*) GIROUD-GODQUIN, A. M., MARCHON, J. C., GUILLON, D., and SKOULIOS, A., 1986, *J. phys. Chem.*, **90,** 5502; (*c*) MALLIARIS, A., PALEOS, C. M., and DAIS, P., 1987, *J. phys. Chem.*, **91,** 1149.

[5] (*a*) MATSUNAGA, Y., and NISHIDA, K., 1988, *Bull. chem. Soc. Jpn.*, **61,** 3435; (*b*) MATSUNAGA, Y., and TSUJIMURA, T., 1991, *Mol. Cryst. liq. Cryst.*, **200,** 103.

[6] (*a*) KNIGHT, G. A., and SHAW, B. D., 1938, *J. chem. Soc.*, 682; (*b*) TABRIZIAN, M., SOLDERA, A., COUTURIER, M., and BAZUIN, C. G., 1995, *Liq. Cryst.*, **18,** 475; (*c*) CRUZ, C., HEINRICH, B., RIBEIRO, A. C., BRUCE, D., and GUILLON, D., 2000, *Liq. Cryst.*, **27,** 1625.

[7] (*a*) SKOULIOS, A., and GUILLON, D., 1988, *Mol. Cryst. liq. Cryst.*, **165,** 317; (*b*) PALEOS, C. M., 1994, *Mol. Cryst. liq. Cryst.*, **243,** 159.

[8] BLUNK, D., PRAEFCKE, K., and VILL, V., 1998, in *Handbook of Liquid Crystals*, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill (Weiheim: Wiley-VCH), pp. 305–340.

[9] (*a*) TSCHIERSKE, C., 1996, *Prog. polym. Sci.*, **21,** 775; (*b*) DECHER, G., and RINGSDORF, H., 1993, *Liq. Cryst.*, **13,** 57.

[10] HESSEL, V., RINGSDORF, H., FESTAG, R., and WENDORFF, H., 1993, *Macromol. Chem.*, **14,** 707.

[11] (*a*) KOKKINIA, A., PALEOS, C. M., and DAIS, P., 1990, *Mol. Cryst. liq. Cryst.*, **186,** 239; (*b*) FULLER, S., SHINDE, N. N., TIDDY, G. J. T., ATTARD, G. S., and HOWELL, O., 1996, *Langmuir*, **12,** 1117.

[12] ALAMI, E., LEVY, H., ZANA, R., WEBER, P., and SKOULIOS, A., 1993, *Liq. Cryst.*, **13,** 201.

[13] DREJA, M., GRAMBERG, S., and TIEKE, B., 1998, *Chem. Commun.*, 1371.

[14] OHTA, K., SUGIYAMA, T., and NOGAMI, T., 2000, *J. mater. Chem.*, **10,** 613.

[15] BRISSE, F., DENAULT, J., and SANGIN, J.-P., 1982, *J. appl. Crystallogr.*, **15,** 279.

[16] VENKATRAMANI, L., and CRAVEN, B. M., 1991, *Acta Cryst. B*, **47,** 968.

[17] AAKERÖY, C. B., BAHRA, G. S., and NIEUWENHUYZEN, M., 1996, *Acta Cryst. C*, **52,** 1471.

[18] BRISSE, F., and VANIER, M., 1982, *Acta Cryst. B*, **38,** 3060.

[19] JENKINS, H. D. B., and THAKUR, K. P., 1979, *J. chem. Educ.*, **56,** 576.

[20] KITAIGORODSKII, A. I., 1961, *Organic Chemical Crystallography* (New York: Consultants Bureau).

[21] ARKAS, M., TSIOURVAS, D., PALEOS, C. M., and SKOULIOS, A., 1999, *Chem. Eur. J.*, **5,** 3202.

[22] *International Tables for Crystallography*, 1987, vol. A, edited by T. Hahn, 2nd Edn (Dordrecht: D. Reidel Publishing Company).

[23] GUILLON, D., SKOULIOS, A., and BENATTAR, J. J., 1986, *J. Phys. Fr.*, **47,** 133.

[24] ESTIENNE, J., DAVIDOVICS, G., PIERROT, M., BALDY, A., ROSENBERG, J., and ROBERT, G., 1986, *Acta Cryst. C*, **42,** 496.

[25] RUSSELL, V. A., ETTER, M. C., and WARD, M. D., 1994, *J. Am. chem. Soc.*, **116,** 1941.

[26] MATHEVET, F., MASSON, P., NICOUD, J.-F., and SKOULIOS, A., 2002, *Chem. Eur. J.*, **8,** 2248.

[27] WOUTERS, J., HÄMING, L., and SHELDRICK, G., 1996, *Acta Cryst. C*, **52,** 1687.

[28] BELLAMY, L. J., 1975, *The Infrared Spectra of Complex Molecules*, 3rd Edn (London: Chapman and Hall).