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Mesomorphic *N*-alkylpyridinium dodecylsulphates

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Reaction of pyridine with 1-bromoalkanes leads to *N*-alkylpyridinium bromides which can be further reacted with silver dodecylsulphate to give *N*-alkylpyridinium dodecylsulphates in good yield. These salts are mesomorphic and their mesophases have been characterized by optical microscopy, DSC and X-ray scattering techniques.

1. Introduction

Certain anhydrous amphiphilic materials are known to show thermotropic mesophases. For example, the now classical studies of alkali metal carboxylates have shown that these compounds, which also exhibit lyotropic mesophases, possess a thermotropic lamellar phase, in addition to a number of disordered crystal phases [1]. Thermotropic phases of quaternized pyridines with simple halide anions have also been studied and in each case, an orthogonal S_A phase, S_B phase, or crystal E phase, is observed [2].

While many anhydrous, ionic liquid crystals are known, most contain either simple counterions (such as halide if the mesogenic part is cationic) or complex metal anions of the type $[MCl_4]^{n-}$ where n depends on the identity of M. In our work on metal-containing liquid crystal systems, we have studied the properties and mesomorphism of silver(I) complexes of alkoxystilbazoles (see figure 1) and had found that the mesomorphism was dependent to some degree on the nature of the anion, X^-. In particular, we had found that the use of alkylsulphate anions led to species with lower melting and clearing points and with interesting mesomorphism, such as the observation of cubic mesophases [3].

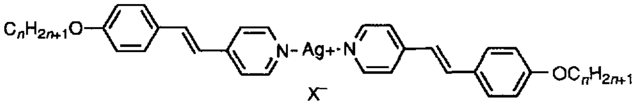

Figure 1. Structure of the mesomorphic silver(I) complexes.

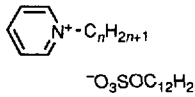

Figure 2. Structure of the *N*-alkylpyridinium dodecylsulphates.

We were therefore interested to see what effect such an amphiphilic anion might have on other mesogenic systems and therefore undertook the synthesis of some *N*-alkylpyridinium dodecylsulphates (see figure 2).

2. Synthesis

N-Alkylpyridinium dodecylsulphates (PyR_n DOS) were prepared in two steps. In the first, the relevant 1-bromoalkane was heated under reflux in DMF with pyridine for 3 to 5 d to give the *N*-alkylpyridinium bromide. This was subsequently reacted with AgDOS in ethanol to give the desired product. An homologous series was produced by varying the alkyl chain length from C_8 to C_{15}.

3. Mesomorphism

The compounds were investigated by optical microscopy, DSC and X-ray scattering.

By optical microscopy, each homologue from $n = 8$ to $n = 15$ showed a single smectic A phase, whose clearing point and range were reasonably independent of the chain length (see table 1). The texture of the phase was either homeotropic or focal-conic. In addition, the compounds showed a crystalline polymorphism which depended on the parity of the number of carbons in the alkyl chain. Thus, for salts with $n = 12$, 14 and 16, three crystal polymorphs were seen, while for $n = 11$, 13 and 15, only

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Table 1. Mesomorphism of the pyridinium salts.

Chain length	Transition	Temperature	ΔH/kJ mol^{-1}	ΔS/J K^{-1}mol^{-1}
8	Cr–S_A	71	49·1	142·7
	S_A–I	133	1·9	4·7
10	Cr–Cr′	81	27·3	77·1
	Cr′–S_A	82	24·8	69·9
	S_A–I	141	2·0	4·8
11	Cr–Cr′	83	33·9	95·2
	Cr′–S_A	85	19·0	53·1
	S_A–I	142	2·1	5·1
12	Cr–Cr′	66	7·2	21·2
	Cr′–Cr″	86	18·5	51·6
	Cr″–S_A	90	31·7	87·3
	S_A–I	153	1·8	4·2
13	Cr–Cr′	88	29·7	82·3
	Cr′–S_A	95	33·5	91·0
	S_A–I	157	2·0	4·7
14	Cr–Cr′	82	19·9	56·1
	Cr′–Cr″	89	14·7	40·6
	Cr″–S_A	100	42·3	113·4
	S_A–I	158	1·9	4·4
15	Cr–Cr′	89	18·3	50·6
	Cr′–S_A	110	38·8	101·3
	S_A–I	160	1·8	4·2

Table 2. Calculated and experimental *d*-spacings in the smectic A phase of the alkylpyridinium dodecylsulphates.

Chain length	8	9	10	11	12	13	14	15
d(experimental)/Å	26·2	—	27·5	28·1	28·8	29·7	30·3	31·0
d(calculated)/Å	32·0	33·3	34·5	35·8	37·0	38·3	39·5	40·8

two polymorphs were observed. The exception to this pattern was the compound with $n = 10$ which had only two polymorphs.

4. X-ray measurements

X-ray scattering measurements were made to investigate further the observed mesophase in these compounds.

Experiments carried out on the mesophase confirmed the lamellar structure and the liquid-like nature of the two-dimensional arrangement within each layer. Combined with the optical microscopy, this confirms the phase assignment as S_A.

The calculated *d*-spacing for the molecules (see table 2), which refers to the combined molecular lengths of both the cation and the anion, increase linearly with increasing chain length as expected and with a gradient (see figure 3) of 1·26 Å/methylene group. However, the *d*-spacings observed in the X-ray experiment are significantly shorter than these values; furthermore, they increase at a rate of only 0·69 Å/methylene group.

Since we know from the optical microscopy that the phase is orthogonal, we cannot invoke any significant tilting of the polarizable molecular cores to explain this discrepancy.

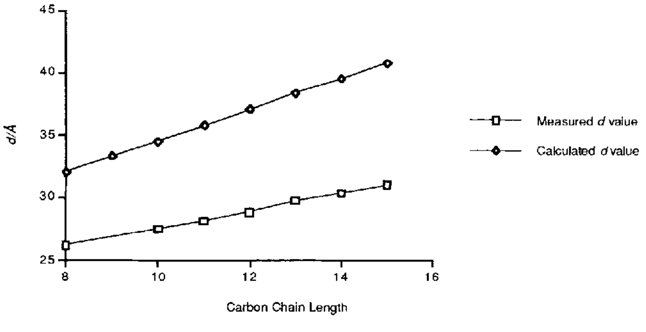

Figure 3. Variation of the observed and calculated *d*-spacing as a function of aliphatic chain length.

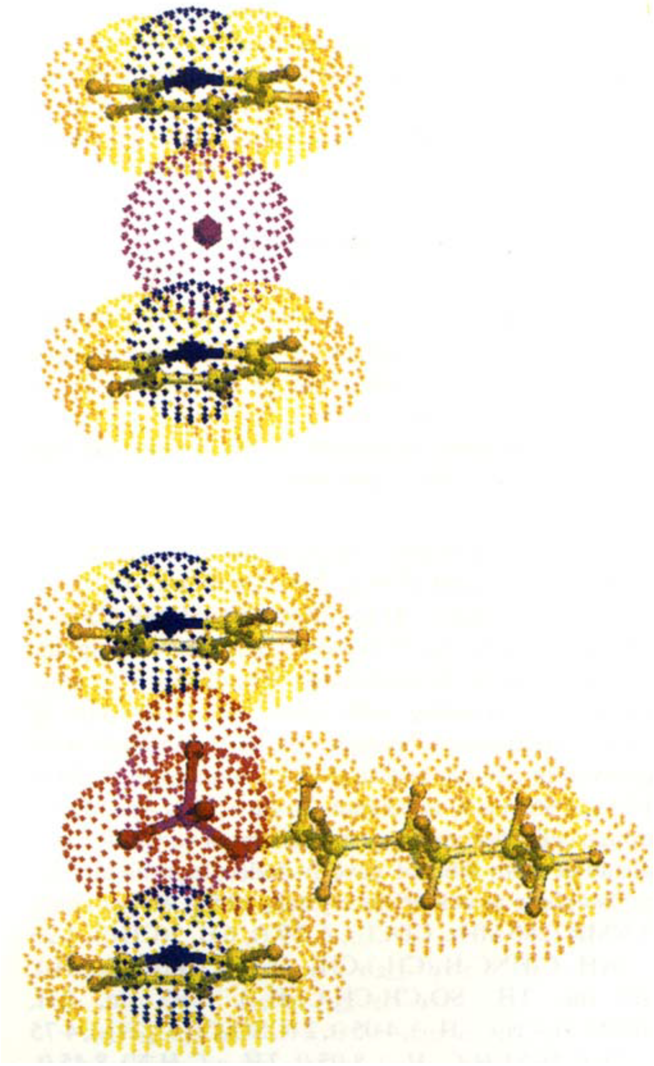

Figure 4. Molecular modelling image to show the greater separation of pyridinium rings by an alkylsulphate compared to a bromide anion.

To describe the detailed molecular arrangement within the smectic A layers, it is necessary first to take into account that two cationic pyridinium rings presumably sandwich one dodecylsulphate anion, in a similar way to that described previously for substituted *N*-alkylpyridinium bromides [4]. Then, it is important to point out that in the case of the dodecylsulphate anion, the distance between the two rings is at least 7·5 Å, which is greater than that in the case of bromide anions (*c*. 6·1 Å), as shown by molecular modelling in figure 4. Finally, it is interesting also to note that the extrapolation of *d*(calculated) to $n = 0$ gives a value of 22 Å, corresponding roughly to the molecular length of one dodecylsulphate anion, similar to the extrapolation of *d*(experimental) to $n = 0$, where a value of 20·6 Å is found.

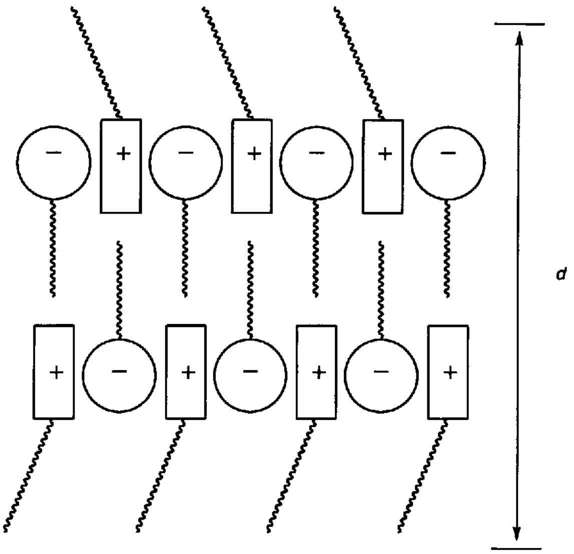

Figure 5. Proposed molecular arrangement in the smectic A phase of the *N*-alkylpyridinium dodecylsulphates.

All these experimental data suggest the model proposed in figure 5. Thus, the layer is formed by two, single, ionic sub-layers where the pyridinium rings sandwich the ionic part of the dodecylsulphate anion; these two sub-layers are separated by the aliphatic chains of the anion, which are, on average, standing upright. Finally, the two ionic sub-layers are covered by the aliphatic chains of pyridinium rings; these are, on average, strongly tilted and disorganized to ensure a compatible molecular area between the ionic and aliphatic parts. As a result, the layer spacing observed can be smaller than the total molecular length of the two species; moreover, the increase of the layer spacing as a function of the length of the alkylpyridinium unit can also be smaller than 1·27 Å/methylene group.

It should be pointed out that we reject the other types of distribution as shown in figure 6, since we have obtained a single layer arrangement, with a spacing much smaller than the molecular length. For example, in the case of the dodecyl member of the series, there is a difference of more than 8 Å between the layer spacing measured and the calculated molecular length; this difference cannot be attributed to a tilt of the aliphatic chains, as they are already quite constrained due to the lateral distance of about 8 Å between two pyridine rings. Finally, it is also interesting to note that, in the model proposed in figure 5, the smectic layers can slide over one another very easily.

Thus, these compounds are further examples of mesogens where the arrangement in the mesophase is largely determined by interionic interactions. Interestingly, these contrast with the related ionic species containing metal ions where a range of thermotropic mesophases, including nematics [3, 5] is observed. In the case of the silver salts which we have studied [3], this is probably due to the fact

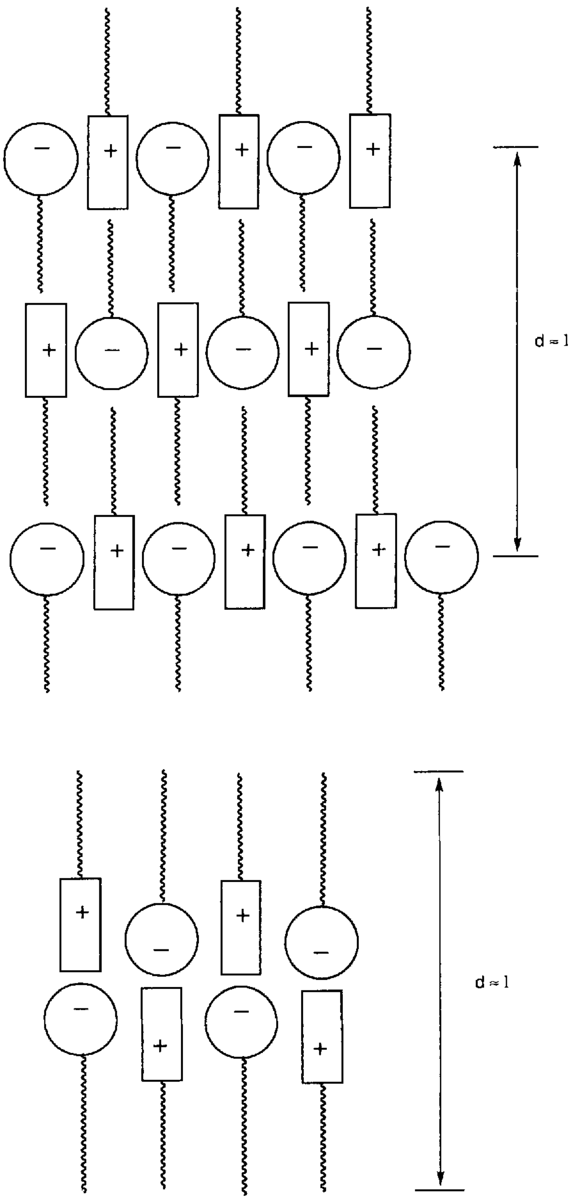

Figure 6. Alternative molecular arrangement in the smectic A phase of the *N*-alkylpyridinium dodecylsulphates.

that the cation and anion are very closely associated, and hence the anion cannot really be described as 'free'; an analogy with a lateral alkyl chain is perhaps better in these systems. However, such a distinction is not so clear in the ionic palladium complexes of Ghedini where significant interionic Pd–BF_4 interactions are less likely [5].

5. Experimental

5.1. *Analysis*

^1H NMR spectra were recorded on a 60 MHz Perkin–Elmer R12B spectrometer using $CDCl_3$ as the solvent. Microanalyses were carried out by the University of Sheffield microanalysis service.

The mesomorphic behaviour of the compounds was determined as described previously [3].

5.2. *Synthesis of* N-*dodecylpyridinium dodecylsulphate*

1-Bromododecane (5·01 g, 2·04 mmol) was added together with pyridine (1·47 g, 1·86 mmol) to DMF (25 cm^3) and heated at reflux for 72 h. Ether was added to precipitate the product and the mixture left to crystallize at 0°C. After filtering and washing with ether, cream crystals of *N*-dodecylpyridinium bromide (0·64 g, 1·95 mmol) were dissolved in ethanol and added to a solution of AgDOS (0·73 g, 1·95 mmol) in ethanol (70 cm^3). This was filtered through celite before removing solvent *in vacuo*. Recrystallization from ethanol gave *N*-dodecylpyridinium dodecylsulphate as colourless crystals, (0·8 g, 80 per cent), ^1H NMR (250 MHz, $CDCl_3$), δ 0·9 (t, 6 H, $2(CH_3)$), 1·25 (s, 36 H, $C_5HNC_2H_4(C\underline{H}_2)_9CH_3$, $O_3SOC_2H_4(C\underline{H}_2)_9CH_3$), 1·65 (m, 2 H, $SO_4CH_2C\underline{H}_2C_{10}H_{21}$), 1·95 (m, 2 H, $C_5H_5NCH_2C\underline{H}_2C_{10}H_{21}$), 4·05 (t, 2 H, $SO_4C\underline{H}_2C_{11}H_{23}$), 4·75 (t, 2 H, $C_5H_5NC\underline{H}_2C_{11}H_{23}$), 8·05 (t, 2 H, *o*-$C_5H_5N$), 8·45 (t, 2 H, *p*-$C_5H_5N$), 9·20 (dd, 1 H, *m*-$C_5H_5N$). Microanalysis, expected: C (67·8), H (10·8), N (2·7), S (6·2). Found: C (67·8), H (11·1), N (2·6), S (6·6) per cent.

The following *N*-alkylpyridinium bromides and *N*-alkylpyridinium dodecylsulphates were prepared by identical methods as described above. Experimental data are to be found in table 3.

Table 3. Microanalysis data for the *N*-alkylpyridinium dodecylsulphates.

	Calculated (found)				Yield/per cent	
Chain	C	H	N	S	Br	DOS
10	66·8 (67·5)	10·6 (10·8)	2·9 (2·9)	6·6 (6·5)	19	23
11	67·3 (67·3)	10·7 (11·0)	2·8 (2·9)	6·4 (6·6)	20	66
12	67·8 (67·8)	10·8 (11·2)	2·7 (2·6)	6·2 (6·6)	64	80
13	68·3 (68·2)	10·8 (11·1)	2·7 (2·4)	6·1 (6·3)	30	77
14	68·7 (69·4)	11·0 (11·3)	2·6 (2·6)	5·9 (6·3)	29	84
15	69·1 (69·0)	11·1 (11·2)	2·5 (2·3)	5·8 (5·8)	53	90

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