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# The thermotropic mesophase structure of two long-chain alkyl pyridinium halides†

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The thermotropic phase transitions and the mesophase structure of two long-chain alkyl pyridinium halides are described. From small angle X-ray diffraction, optical microscopy, differential scanning calorimetry and dilatometry, the single liquid-crystalline phase found in each material is identified as smectic A. It is argued that the molecules within a layer are oriented alternately and packed in an interdigitated fashion, with the anions sandwiched between the pyridinium rings.

## 1. Introduction

It is well known that organic molecules composed of a rigid and polarizable elongated aromatic core, attached to one or two aliphatic chains, often give smectic liquid crystal phases when heated [1]. The same kinds of thermotropic smectic phases were observed many years ago in alkyl chain soaps of, for example, sodium, potassium and rubidium [2]. In both cases, the smectic layering is attributed to the location of the non-aliphatic portion of the molecules with respect to the attached aliphatic chains. The rigid aromatic cores in the former and the ionic carboxylic salts in the latter associate with one another in such a way that the non-aliphatic groups form sublayers which alternate with sublayers composed of the aliphatic chains.

Alkyl pyridinium halides can be considered to be a material that is intermediate to these two types of liquid crystal. Their non-aliphatic portion is ionized as in the case of the soaps, but there is also a hint of the rigid aromatic core albeit short. To date, these types of materials, and the nature of their liquid-crystalline phases, have not received considerable attention. Blumstein and Patel [3] investigated alkoxybenzoic acids, but these are characterized by hydrogen-bonding forces rather than by ionic forces. Recently, Sudhölter *et al.* [4] reported on the liquid-crystalline behaviour of a number of alkyl pyridinium amphiphiles. In all cases, the long hydrocarbon chain is not attached to the N (1 position) of the pyridinium ring, but is located at the 4 position for the single chain amphiphiles and in the 3 and 5 positions for the directly attached double-chain amphiphiles. The nitrogen is quaternized by either protonation or methylation.

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In contrast, the two materials whose thermotropic phases are reported on in this paper have the pyridinium nitrogen quaternized by the long-chain alkyl group, with a methyl group at the 4 position of the ring. A 22-carbon chain material is neutralized by the iodide ion, an 18-carbon chain material by the bromide ion. The thermotropic phase behaviour of the two compounds has been investigated using X-ray diffraction, differential scanning calorimetry, optical polarization microscopy, and dilatometry.

## 2. Experimental

The two compounds studied were 1-*n*-octadecyl-4-methylpyridinium bromide (**1**) and 1-*n*-docosyl-4-methylpyridinium iodide (**2**). Their chemical structures are shown in table 1. The materials were synthesized in the standard way [5]; that is, by the N-alkylation of 4-methylpyridine using stoichiometric quantities of the reagents in solution. The solvent used was dry 2-propanol. The reaction was performed at the boiling point of the solvent. The product crystallized on cooling, it was washed with dry ether and recrystallized in ethanol. The brominated product was a very light yellow powder, the iodinated one a pale pink powder. The results of their elemental analysis are listed in table 2. The starting products, 4-methylpyridine and *n*-octadecylbromide, were obtained from Aldrich. The *n*-docosyliodide was prepared using standard procedures [6]. The classical method involves the action of molecular iodine on *n*-docosanol (Aldrich) in the presence of red phosphorus.

Table 1. Chemical structures of the compounds.

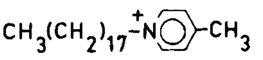
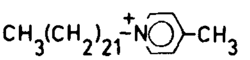
| Chemical structure | Compound No. |
|---|---|
|  Br$^-$ | (**1**) |
|  I$^-$ | (**2**) |

Table 2. Elemental analysis of the amphiphiles ($X$ = Br or I).

| | C | | H | | N | | $X$ | |
|---|---|---|---|---|---|---|---|---|
| Compound No. | Theor. | Exp. | Theor. | Exp. | Theor. | Exp. | Theor. | Exp. |
| (**1**) | 67·58 | 66·99 | 10·40 | 10·55 | 3·28 | 3·02 | 18·74 | 18·56 |
| (**2**) | 63·50 | 63·37 | 9·90 | 10·15 | 2·64 | 2·40 | 23·96 | 24·11 |

The temperatures of the phase transitions and their enthalpies were measured with a Perkin–Elmer DSC 2 apparatus, using sealed aluminium pans. The heating and cooling rates were 2·5°C/min. The transition temperatures were verified, and the microscopic textures observed, with a Leitz polarizing microscope equipped with a Mettler FP52 hot-stage. X-ray diffraction patterns of powdered samples, in Lindemann capillaries, were recorded photographically using monochromatic copper K$\alpha_1$ radiation ($\lambda$ = 1·54 Å) and a vacuum Guinier focusing camera equipped with a bent-quartz monochromator. Dilatometric measurements were obtained with a dilatometer of the classic Bekkedahl type which has been described elsewhere [7]. Briefly, the technique consists of reading mercury levels as a function of temperature, where a known weight of degassed sample and a known weight of mercury in a dilatometer are immersed in a temperature-controlled bath, in this case a bath of zinc granules.

## 3. Results

### 3.1. *Differential scanning calorimetry*

The endothermic peaks related to the crystal-to-mesophase transition are located at 91·6°C and 99·0°C for the brominated product (**1**) and the iodinated product (**2**), respectively. The corresponding enthalpies are 58·6 and 66·5 kJ/mol. The endothermic peaks related to the mesophase-to-isotropic transition are located at 158·0°C and 198·3°C for products (**1**) and (**2**), respectively. The corresponding enthalpies are 0·67 and 3·68 kJ. With decreasing temperature, there is a slight lowering of the isotropic phase by a few degrees for product (**2**). This is probably related to some degradation that likely occurs at the elevated temperatures required to obtain the isotropic phase [5]. It is noteworthy that the temperature range of the mesophase is considerably broader for product (**2**) than for product (**1**).

Crystal–crystal transitions were observed at 63°C and 78°C for product (**2**) with increasing temperature; none were observed for product (**1**).

### 3.2. *Optical polarizing microscopy*

The transition temperatures observed through the microscope confirm completely those detected by D.S.C. On cooling from the isotropic to the mesomorphic phase, a few characteristic blue focal conic-like textures are obtained; most of the sample remains homeotropic until the mesophase-to-crystal transition occurs (figures 1 and 2).

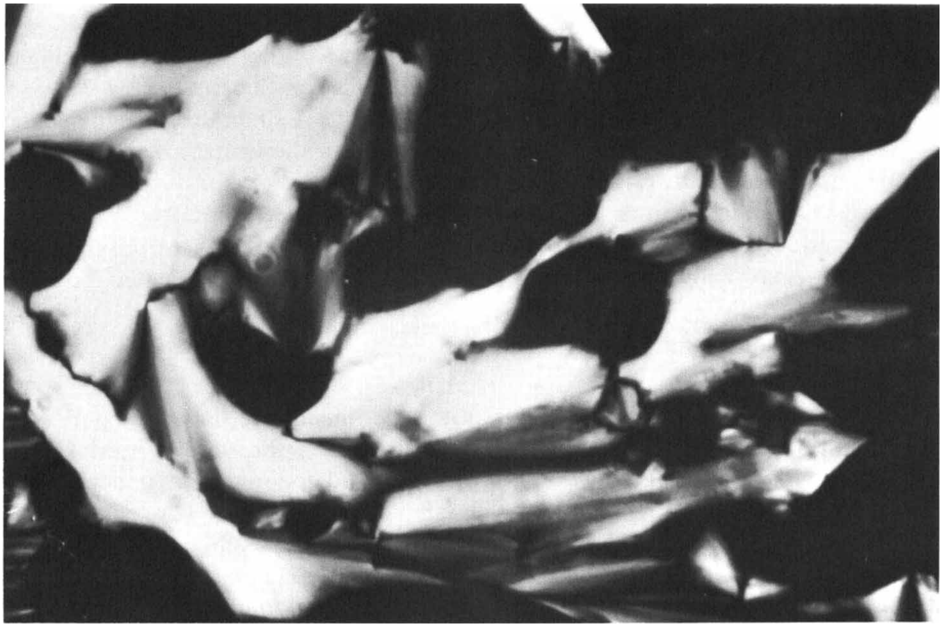


Figure 1. Focal conic and homeotropic textures of product (**1**) at 146°C (crossed polars, initial magnification 300 ×).

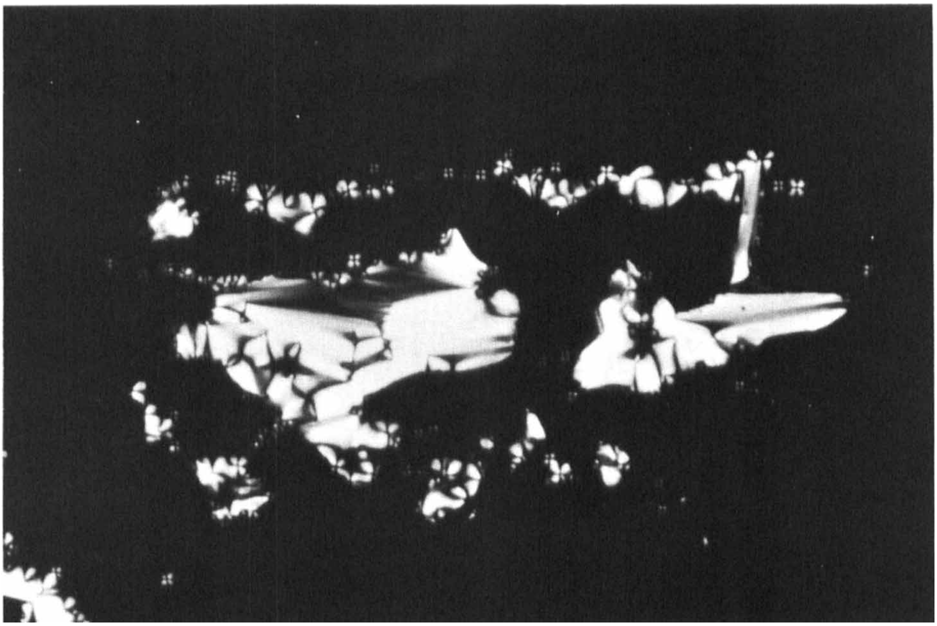


Figure 2. Focal conic and homeotropic textures of product (**2**) at 170°C (crossed polars, initial magnification 300 ×).

### 3.3. *X-ray diffraction*

Sharp Bragg reflections at both low and wide angles attest to the crystalline state of the product at temperatures below what was designated previously as the crystal-mesophase transition temperature. At higher temperatures, until the isotropic state is reached, the X-ray diffraction pattern is very simple. There is a sharp reflection at small angles, along with a second order reflection, and a diffuse band at larger angles. The low angle reflection corresponds to a distance or layer thickness of 34–35 Å and 39–40 Å for products (**1**) and (**2**), respectively (figure 3). A slight decrease in distance (about 1 Å) is observed with increasing temperature, in the temperature range from the crystal-mesophase transition to about 120°C.

The maximum in the intensity of the diffuse reflection corresponds to a spacing of 4·4 Å for product (**1**) and 4·5 Å for product (**2**). This spacing, and the diffuse nature of the band, is normally associated with the lateral distribution of oriented molecules in a liquid-like state.

### 3.4. *Dilatometry*

Results for product (**1**), from two separate experiments, are shown in figure 4. To measure the volume of a specimen, using dilatometry, the sample must first be properly degassed. Normally, two or three heating and cooling cycles under vacuum are sufficient for obtaining well-degassed samples. For product (**1**) some bubbles continued to be expelled even after four or five cycles, possibly indicating slight chemical degradation rather than incomplete degassing. Hence, it was decided that the measurements (figure 4) taken in the mesophase for a sample freshly degassed by four to five cycles are sufficiently reliable for calculating the molar volume to an accuracy of 1 per cent. Measurements were not attempted for product (**2**) since the

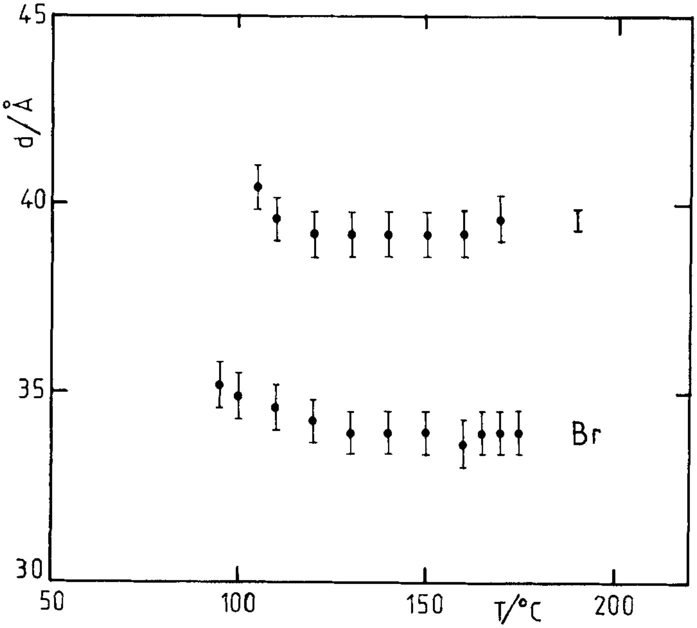


Figure 3. Layer spacings of products (1) and (2) as a function of temperature, determined from small angle X-ray diffraction.

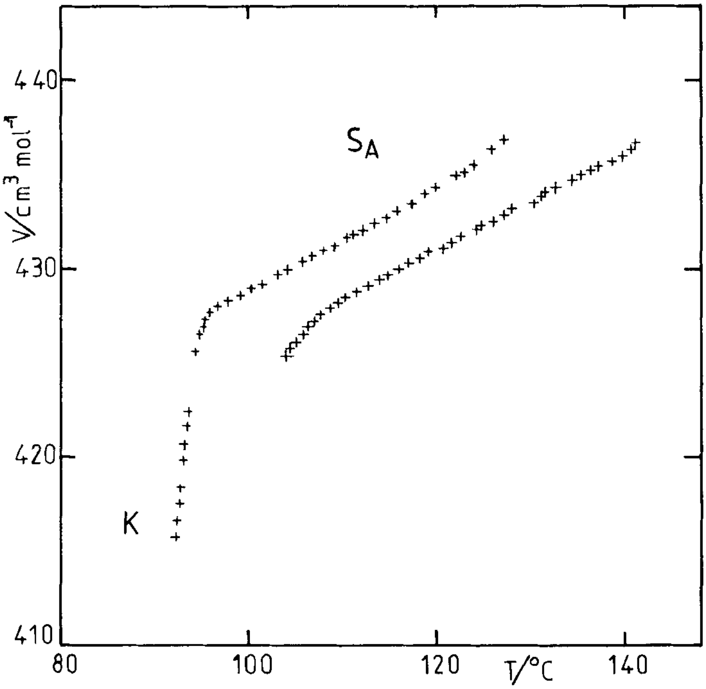


Figure 4. Volumes as a function of temperature for product (1), determined from dilatometry (two separate experiments).

considerably higher temperatures required to degas this sample are definitely accompanied by degradation (as indicated by X-ray measurements when samples have been heated to temperatures above 200°C).

## 4. Discussion

The simple diffraction patterns obtained for the mesophase of the two products are typical of those normally obtained from either smectic A or smectic C mesophases. The microscopy observations suggest specifically a smectic A mesophase, since homeotropic textures are not normally observed for smectic C mesophases. To determine a reasonable model for the structure of this phase, it is useful to consider the molecular areas involved and to compare the calculated molecular length with the layer spacing determined experimentally.

The calculated lengths of the molecules in their most extended configurations (using CPK Atomic Models) are 30 and 35 Å for products (**1**) and (**2**), respectively, when the counterion is not taken into account. The layer thickness determined from the X-ray results is larger by 4–5 Å for both products. This immediately indicates either that the counterion, whose size is of the correct order of magnitude, must be added to the calculated length, giving rise to a single-layered structure, or that the molecules must be packed in some kind of bilayer structure.

An estimate of the average molecular area occupied by the molecules in the plane of the layers would be useful in judging the validity of any proposed structure. An experimental value of this parameter can be determined for product (**1**) from the lamellar thickness, $d$, and from the molar volume, $V$. The average area $S$ occupied by two molecules is

$$S = 2V/(Nd),$$

where $N$ is the Avogadro constant. From figure 4, it is evident that $V$ can be taken as $430\,\mathrm{cm^3/mol}$. The value for $S$ is therefore $42\,\text{Å}^2$.

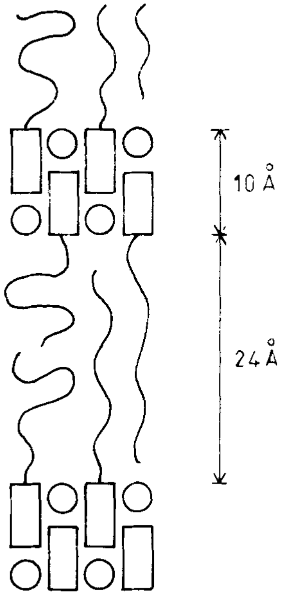


Figure 5. Schematic representation of the mesophase structure of products (**1**) and (**2**), the numbers referring to (**1**). Rectangle: methyl pyridinium; circle: anion; wavy line: aliphatic chain.

The representation sketched in figure 5 would seem to provide the most reasonable model, the spacing indicated referring specifically to product (**1**). The packing is of an interdigitated type with the anions sandwiched between the pyridinium rings. It can be viewed as a single layer of molecules that are oriented in alternating fashion, with the anion lying along the elongational axis of the molecules. Several considerations support the proposed model. First, the layer spacings determined experimentally are equal to the calculated molecular lengths when the axial anion is taken into account (the diameters of the bromide and iodide ions are 3·9 and 4·4 Å, respectively [8]). Second, the lateral location of the anion relative to the pyridinium group, probably displaced somewhat from the centre of the ring towards the nitrogen atom where the positive charge is most likely concentrated [9], seems appropriate from the standpoint of electrostatic interactions. It should be clear that, since the interlayer distance depends only on the molar volume and the molecular area, the amount of displacement of one polar group relative to the neighbouring polar group has no effect on the interlayer distance. Third, the total molecular area determined for two molecules, and its comparison with what can be determined for the polar and aliphatic moieties, respectively, is consistent with the model. According to the model, the minimum molecular area required by the polar moiety for two neighbouring molecules in a layer is that of the 4-methylpyridinium head group plus that of the anion. The maximum molecular area required is twice that of two head groups. For the head group, this value must be similar to the area of 24 $Å^2$ estimated by Sudhölter *et al.* [4] for the 1-methylpyridinium group. The bromide ion occupies an area of 12·3 $Å^2$, based on a value of 1·96 Å for its crystal ionic radius [8]. Thus, the total molecular area required by the polar moiety of two molecules is between 36·3 and 48 $Å^2$. It is satisfying that the value determined experimentally is between the two extremes. It is also in agreement with the literature values of 21–30 $Å^2$ per rigid aromatic stem of mesogens [10]. Literature values for the molecular area of disordered alkyl chains in lyotropic [11] and thermotropic [10] liquid crystals are 23–50 $Å^2$. In the present study, since the alkyl chains most likely interpenetrate, but to an unknown extent (figure 5), their molecular area per molecule must lie between the extremes of 42 $Å^2$ for no interpenetration and 21 $Å^2$ for complete interpenetration, based on the value of $S$ determined experimentally.

As a final comment, it is to be understood that within the smectic layers the organization of the molecules is liquid-like, as is characteristic of a smectic A structure. Therefore, the model presented should be considered to give merely an average picture of the ordering of the molecules, an ordering which is in fact a dynamic one.

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