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A new smectic mesophase with two dimensional tetragonal symmetry from dialkyldimethylammonium bromides: S_T

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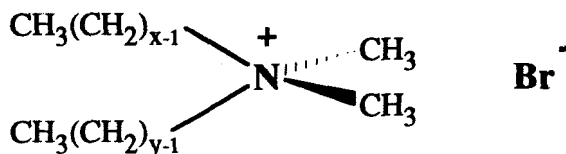
A series of *N,N*-di-*n*-alkyl-*N,N*-dimethylammonium bromides was synthesized and characterized. Its thermotropic liquid-crystalline behaviour was studied by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction. A novel smectic mesophase was thus identified, in which the lateral packing of the molecules within the layers is ordered and tetragonal in symmetry.

1. Introduction

In this article, we present evidence for the existence of a new type of smectic mesophase, which involves a tetragonal ordered arrangement of the molecules within the layers. To the best of our knowledge, such a mesophase has never before been described in the literature, although it clearly corresponds to one of the five possible two dimensional crystallographic lattices [1]. We propose to designate it by the symbol S_T .

For the sake of clarity, it is useful to stress immediately that this new type of thermotropic mesophase should not be confused with the S_Q mesophase, also of tetragonal symmetry, reported to occur with the pure (+, +) or (-, -) enantiomers of 2-octyl terephthalylidene-bis-aminocinnamate [2]. On account of its structural similarity to the so-called smectic D liquid crystals [3], this S_Q phase was indeed presented as a smectic phase; but it is not layered at all and its structure is actually three dimensional with 340 molecules per unit cell.

The S_T thermotropic mesophase to be described below was observed with a series of two-chain surfactants, namely the dialkyldimethylammonium bromides (referred to as C_xC_yDMABr)

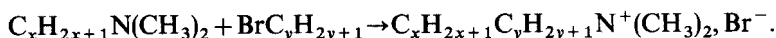


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Studies of micellar solutions of short chain homologues and lyotropic mesophases of some long chain homologues of these surfactants have already been reported [4–6].

2. Materials

The C_xC_yDMABr compounds considered in the present work were prepared as already described [4–6], according to



Alkyldimethylamines and bromoalkanes (from Aldrich and Fluka) were distilled before use whenever required. In 100 ml of dry ethanol used as a solvent, 0.11 mol of alkylbromide was added to 0.1 mol of amine, and the quaternization reaction was conducted under reflux (at 80°C) for 48 to 72 h in the absence of light. The pale yellow, crude product obtained after complete evaporation of the solvent was recrystallized thrice from filtered ethyl acetate solution (containing small amounts of ethanol to enhance the solubility); crystallization was induced by slowly cooling the saturated solutions to room temperature. The purity of the resulting compounds, checked by elemental analysis (see the table), was found to be satisfactory.

The thermal stability of the compounds was assessed by thermogravimetry using a Mettler TC10A instrument coupled with a TA processor and a Mettler M3 balance. A typical thermogram, registered for $C_{18}C_{18}DMABr$, is shown in figure 1. Additional thermograms registered at constant temperature as a function of time showed the samples to withstand heating at 100°C for 12 hours with no measurable loss in weight. This result ensured that the compounds investigated would be unaffected during the thermal studies planned in this work, especially during the rather lengthy X-ray experiments at high temperature.

Elemental analysis of C_xC_yDMABr (calculated values in parentheses).

<i>x</i>	<i>y</i>	C/%	H/%	N/%	Br/%
12	12	67.0 (67.5)	12.4 (12.2)	2.6 (3.0)	16.9 (17.3)
12	14	68.0 (68.5)	12.6 (12.3)	2.4 (2.9)	15.3 (16.3)
12	16	68.5 (69.5)	12.6 (12.4)	2.3 (2.7)	14.2 (15.4)
12	18	70.2 (70.3)	12.7 (12.5)	2.4 (2.6)	14.6 (14.6)
14	14	70.7 (71.0)	13.1 (12.6)	2.2 (2.4)	13.7 (13.9)
14	16	68.2 (70.2)	12.8 (12.5)	2.3 (2.6)	13.7 (14.6)
14	18	69.1 (69.5)	12.6 (12.4)	2.5 (2.7)	14.9 (15.4)
16	16	70.6 (71.0)	12.9 (12.6)	2.1 (2.4)	13.7 (13.9)
16	18	70.4 (71.7)	12.9 (12.7)	2.0 (2.3)	13.2 (13.3)
18	18	71.3 (72.3)	12.9 (12.8)	1.9 (2.2)	12.0 (12.7)

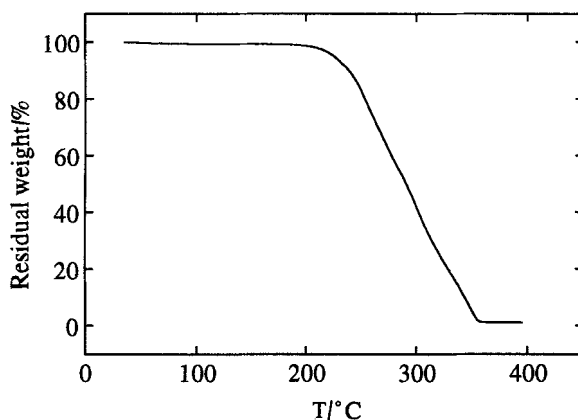


Figure 1. Thermogravimetric graph for $C_{18}C_{18}DMABr$, registered in nitrogen upon heating at $10^{\circ}C\ min^{-1}$.

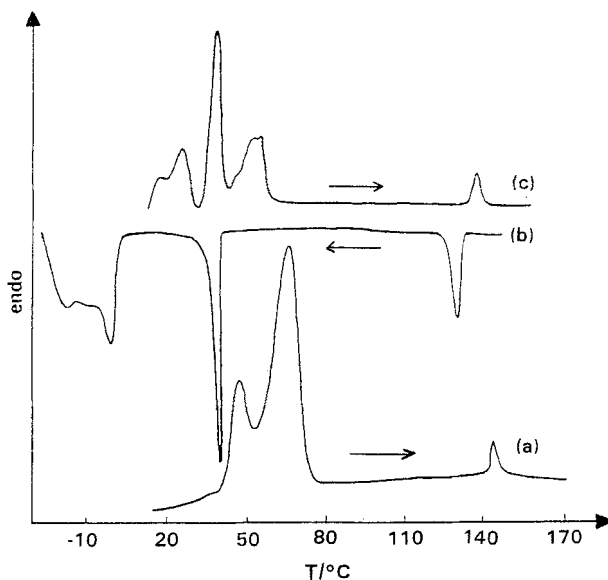


Figure 2. Differential scanning calorimetry graphs for $C_{12}C_{16}DMABr$ registered at a constant heating or cooling rate of $10^{\circ}C\ min^{-1}$: (a) heating of a fresh sample, (b) cooling from the melt, (c) second heating of a sample recrystallized from the melt.

3. Thermotropic polymorphism

The polymorphic phase behaviour of the compounds listed in the table was studied by differential scanning calorimetry (Perkin–Elmer DSC 4, heating and cooling rates of $10^{\circ}C\ min^{-1}$ and polarizing optical microscopy (Leitz Orthoplan, Mettler FP82 hot stage). Typical DSC thermograms are shown in figure 2. The transition from the liquid-crystalline to the crystalline state always shows a marked hysteresis upon cooling, simply related as usual to the induction period of crystallization. In addition, the crystalline state at low temperature, especially when reached by cooling from the melt, shows a complex polymorphism, with a variety of coexisting metastable crystal forms. As a result, the melting transition into the liquid crystal is difficult to detect



(a)

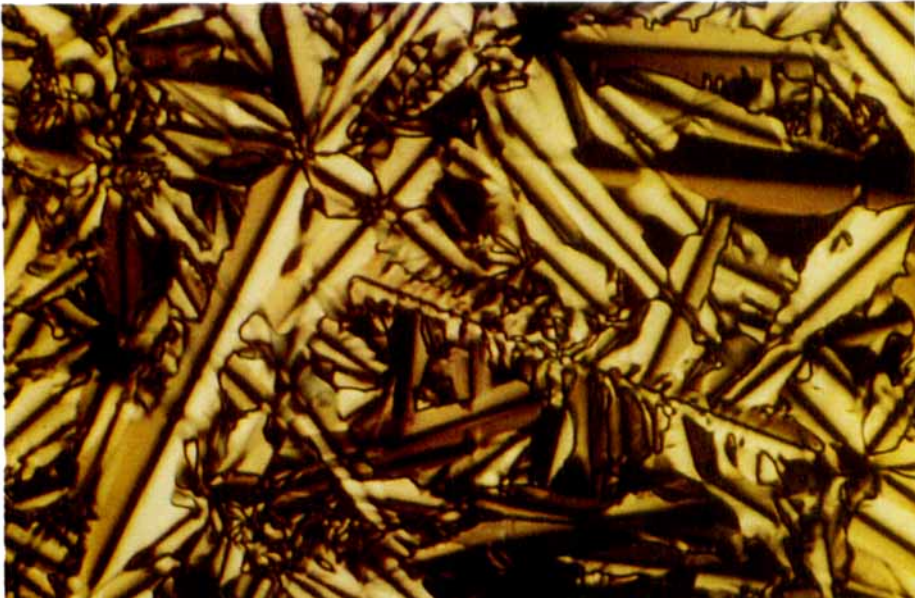
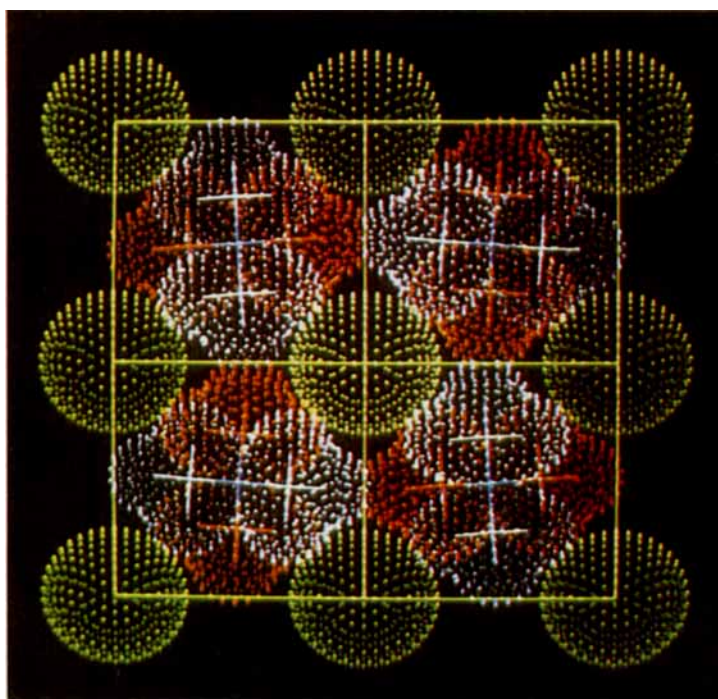


Figure 3. Lancet-like optical textures of $C_{12}C_{16}DMABr$ in the smectic S_T phase obtained by slow cooling from the isotropic melt: (a) at the clearing point and (b) at $128^\circ C$ (crossed polars, magnification $\times 180$).



(a)

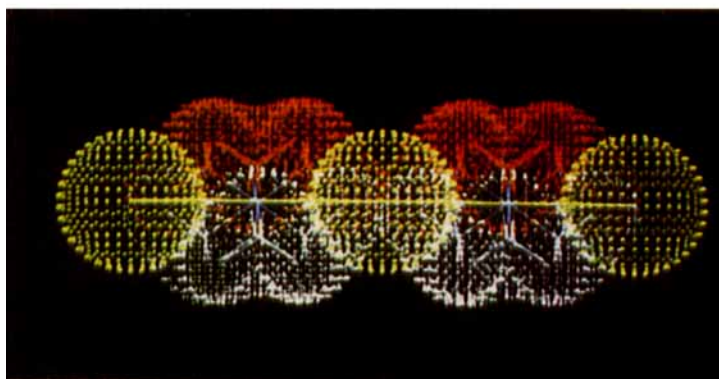
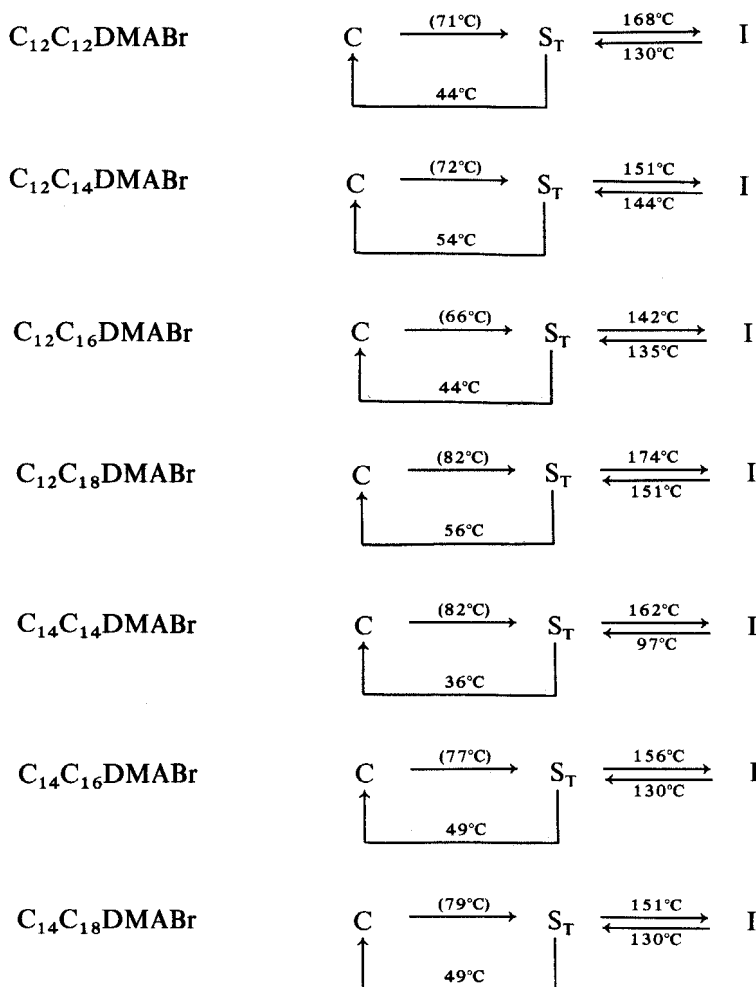
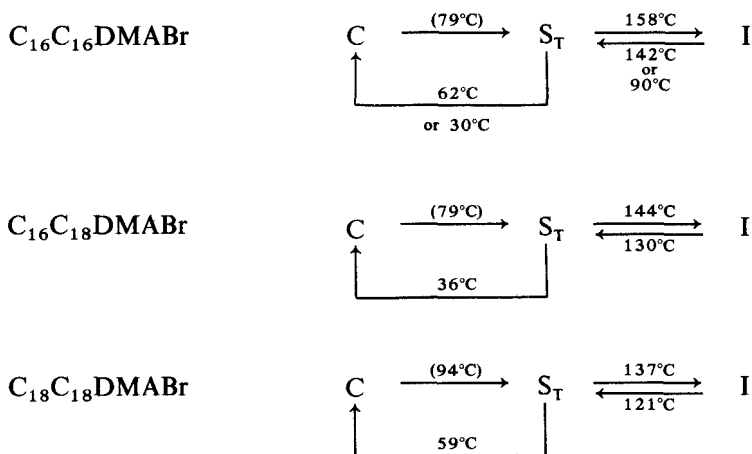


Figure 8. Top view (a) and side view (b) of the tetragonal, two dimensional arrangement of the ionic species of C_xC_yDMABr in the smectic S_T phase, as obtained (from the known unit cell, bond distances and atomic radii) by molecular modelling (Sybyl software from Tripos). Bromide anions in green, hidden ammonium cations in blue, methyl(ene) groups above the lattice plane in white, and methyl(ene) groups below the lattice plane in red.

unambiguously (see parentheses in polymorphic schemes below). As for the transition between the liquid-crystalline and the isotropic liquid state, it was generally well defined, showing little hysteresis (about a few degrees of supercooling) as is customary; the corresponding transition enthalpy ranges from 4.2 to 12.6 Jg⁻¹. In the special case of C₁₆C₁₆DMABr, however, the occurrence of the liquid crystal from the isotropic melt occasionally took place with a very large hysteresis (down to about 90°C), probably brought about by undue heating of the material well above the clearing point and hence partial thermal degradation. A similar hysteresis was also observed for C₁₄C₁₄DMABr.

The liquid-crystalline nature of the samples in the temperature range between the melting of the crystals and the clearing point is characterized by the fluidity of the samples and by optical textures such as those shown in figure 3. It is noteworthy that liquid crystals were only observed with compounds containing sufficiently long alkyl chains, starting from C₁₂C₁₂DMABr. Compounds with shorter chains either crystallize directly upon cooling from the melt or remain in the isotropic liquid state down to room temperature. The experimental observations are summarized in the following polymorphic schemes:





4. Crystal structure

Detailed knowledge of the crystal (as opposed to liquid crystal) structures of the C_xC_yDMABr compounds was outside the scope of this work. Thus the C_xC_yDMABr compounds were analysed only briefly and superficially, in order to identify their crystalline nature at room temperature and establish the basic features of their lamellar structure. The technique used for this purpose was X-ray diffraction (Guinier focusing camera, bent quartz monochromator, $Cu-K_{\alpha 1}$ radiation from a Philips PW 1009 X-ray generator, purpose built electrical oven). The diffraction patterns registered contain a number of Bragg reflections located both at small and wide angles, all very sharp and perfectly consistent with the existence of well-developed three dimensional crystals.

In the special case of the symmetrical compounds, for which the alkyl chains are identical, the X-ray patterns are generally simple, containing in the small angle region a single set of reflections with reciprocal spacings in the ratio 1 : 2 : 3 : 4. They indicate the presence of a unique crystalline form, the three dimensional structure of which is clearly lamellar, as usually observed with long rod-like or thread-like molecules. Without going more deeply into details, it suffices to note that the measured lamellar periods are very close to the lengths of the individual alkyl chains (half of the molecules), pointing to lamellar arrangements either of upright dialkyl molecules bent double or fully extended molecules tilted at an angle of about 60° with respect to the layer normal, or alternatively to interdigitated, upright, fully extended molecules with the ionic groups in lateral register.

In the more general case of the non-symmetrical compounds, in which the alkyl chains are unequal in length, the X-ray patterns are usually rather complex. They contain more than one set of equidistant, small angle reflections, indicating the presence of several coexisting lamellar systems, in compliance with the above reported DSC observations.

5. Liquid crystal structure

The exact nature of the liquid-crystalline phase observed with C_xC_yDMABr at high temperature immediately turned out to be smectic and this was analysed systematically by X-ray diffraction. The diffraction patterns registered (see figure 4) contain, in the small angle region, from three to five sharp Bragg reflections, the reciprocal spacings of

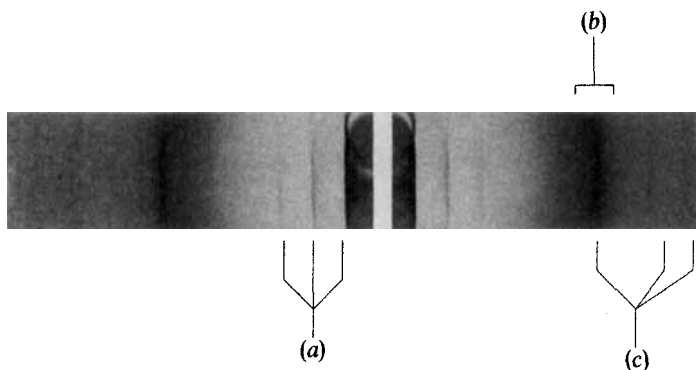


Figure 4. X-ray diffraction pattern for C_xC_y DMABr in the smectic S_T phase at 100°C (Guinier camera with a sample to film distance of 125 mm): (a) sharp, small angle reflections of the smectic layering, (b) diffuse ring of the molten alkyl chains, and (c) sharp, wide angle reflections of the tetragonal lateral packing of the ions.

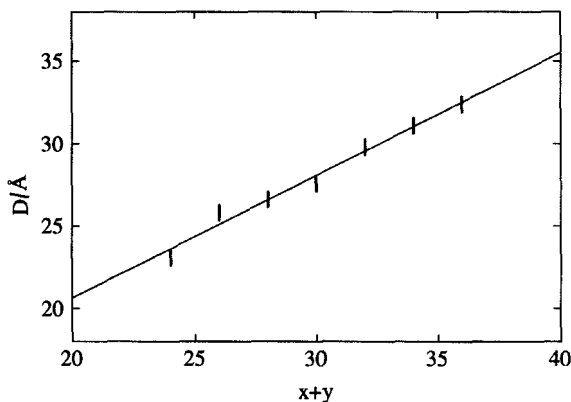


Figure 5. Smectic period at 100°C as a function of total number of carbon atoms in the alkyl chains.

which are in the ratio 1 : 2 : 3 : 4 : 5. Within experimental accuracy, the smectic periods measured, D , are independent of temperature; however, they depend considerably upon the mesogen at hand, and more precisely upon its total number of carbon atoms, whatever the individual length (x or y) of the two alkyl chains. As shown in figure 5, the $x + y$ dependence of D is conclusively linear. The straight line going through the points has been determined by a least square fit method ($R = 0.992$) and obeys the equation

$$D(\text{\AA}) = 0.745(x + y) + 5.72.$$

The standard errors on the slope and Y-intercept of the line are 0.043 \AA and 1.31 \AA , respectively. It is of interest to note at this point that the intensity of the smectic reflections decreases slowly as the Bragg angle increases up to at least the fifth harmonic, suggesting that the strongly diffracting ionic species, particularly the heavy bromine atoms, are confined to thin layers, typically less than about 5 \AA in thickness, in agreement with the value of the Y-intercept of D versus $x + y$, which actually corresponds to the thickness of the ionic layers.

In the wide angle region, the X-ray patterns (see figure 4) contain a diffuse ring at 4.5 \AA , identical to that shown by liquid paraffins, revealing the molten state of the alkyl chains as repeatedly reported for lyotropic [7] and thermotropic liquid crystals [8]. This disordered conformation of the long alkyl chains helps us understand why compounds with the same total number of carbon atoms in their molecules but with alkyl chains of different lengths (as for instance $C_{12}C_{16}$ DMABr and $C_{14}C_{14}$ DMABr, or $C_{12}C_{18}$ DMABr and $C_{14}C_{16}$ DMABr, or $C_{16}C_{16}$ DMABr and $C_{14}C_{18}$ DMABr) are characterized very precisely by the same, single smectic period.

Interestingly, the X-ray patterns contain in the wide angle region three additional rather sharp Bragg reflections (see figure 4), indicative of the ordered arrangement of the ionic ammonium bromide groups within the smectic layers. Much to our surprise, the reciprocal spacings of the sharp reflections ($1/4.27$; $1/3.03$; and $1/2.71 \text{ \AA}^{-1}$, respectively) happen to be in the characteristic ratios $\sqrt{2}:\sqrt{4}:\sqrt{5}$, which indicates a two dimensional tetragonal arrangement of the molecules. The lattice parameter found, $a = 6.04 \text{ \AA}$, is exactly the same for all the compounds studied and also independent of temperature.

The molecular area S , i.e. the surface covered by each molecule in the layers, may be calculated in two distinct ways. The first makes use of the linear dependence of the smectic period upon the number ($x + y$) of carbon atoms in the alkyl chains. Indeed, the volume V of one molecule may, for simple geometrical reasons, be taken as equal to the product DS . With the reasonable assumption of additivity of the partial volumes of the constituent parts of the molecules, this volume may, on the other hand, be taken as equal also to $V_0 + (x + y)V_{\text{CH}_2}$ where V_{CH_2} and V_0 are the respective volumes of one methylene group and of one molecule deprived of all its methylene groups (including those in the methyl end-groups of the alkyl chains)

$$D = V/S = V_0/S + (x + y)V_{\text{CH}_2}/S.$$

The linear dependence of D upon $x + y$, observed experimentally (see figure 5), means that V_0 , V_{CH_2} , and S do not depend on the molecular weight of the material. From the measured slope of the straight line, $V_{\text{CH}_2}/S = 0.745 \pm 0.043 \text{ \AA}$, and the value of $V_{\text{CH}_2} = 28 \text{ \AA}^3$ at 100°C [9], we immediately obtain for the molecular area S the value of $37.6 \pm 2.2 \text{ \AA}^2$, in perfect compliance with what is known of the lateral packing areas of disordered alkyl chains in smectic structures of amphiphiles [7, 8]. The second way to evaluate S makes use of the tetragonal cell parameter measured from the wide angle Bragg reflections. The area of one square unit cell: $a^2 = (6.04 \text{ \AA})^2 = 36.5 \text{ \AA}^2$, is in excellent agreement with the molecular area just quoted, and proves the presence of only one molecule per square unit cell.

The overall smectic ordering of the molecules being this generally elucidated, attention is now focused on the lateral packing mode of the ionic species within the layers. With one molecule per unit cell, the space group symmetry of the system is either $p4$ or $p4m$, the more symmetrical being $p4m$. Quite evidently, the positions of the bromide and ammonium ions are at the corners and centres of the square lattice respectively. Identical to that found in the faces of the face-centred cubic lattice of alkali halides (see chapter on *Crystal Lattices* in [10]), such an arrangement ensures perfect alternation in space of the positive and negative charges, as required by thermodynamics for systems with coulombic interactions.

To visualize this structural model, the electron density distribution in the square unit cell was calculated from the (visually estimated) intensities of the sharp, wide angle reflections, with the following structure factors (taken all positive): $F(11) \cong +4$,

$F(20) \cong +2$, $F(21) \cong +1$. As shown in figure 6, the heavy bromide anions located at the corners of the square lattice are spherical, whereas the tetramethyl(ene)ammonium cations located at the centre are square in shape, as expected for tetrahedral objects viewed in projection. It is important to note that the ammonium tetrahedrons are oriented with two opposite edges parallel to the lattice plane and axes, and with the methyl(ene) groups lying directly above and below the median lines of the square lattice (see figure 7).

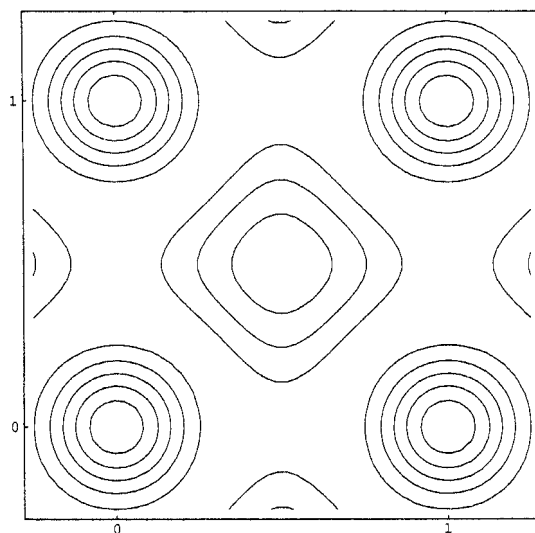


Figure 6. Electron density distribution in the plane of the tetragonal, two dimensional lattice of the S_T mesophases of C_xC_yDMABr as inferred from X-ray diffraction data. The heavy bromide anions at the corners look spherical, while the tetrahedral tetramethyl(ene)ammonium cations at the centre look square.

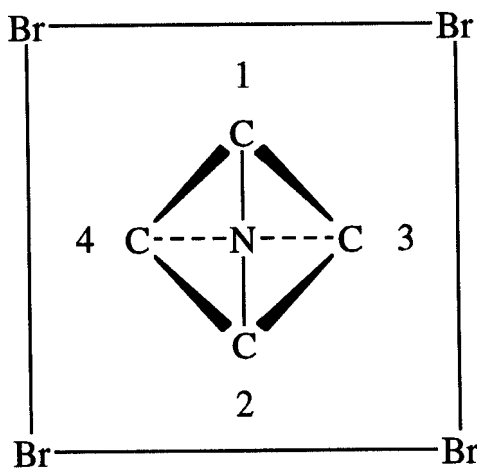


Figure 7. Schematic representation of the two dimensional arrangement of the ionic species in the square lattice. The tetrahedral ammonium cation is oriented with two opposite edges (12 and 34) parallel to the lattice plane and to the sides of the square unit cell. Carbon atoms 1 and 2 are above, while atoms 3 and 4 are below the plane of the lattice.

However satisfactory it may be from the standpoint of electrical interactions, this model certainly needs further inspection as regards the compactness of the molecular arrangement. For this purpose, due consideration must be taken of the effective intermolecular packing radii of the ions and atomic groups involved: 1.95 Å for Br⁻, 3.47 Å for (CH₃)₄N⁺, 2.0 Å for CH₃ compared to CH₄ (see section on *Sizes of Atoms, Molecules and Ions* in [11]). Evidently, the sum of the van der Waals radii of the ammonium cations and bromide anions (5.42 Å) exceeds by 1.15 Å their centre-to-centre distance ($6.04/\sqrt{2}=4.27$ Å); the bromine atoms hence penetrate appreciably the equivalent sphere of the tetramethyl(ene) ammonium groups. Taking, however, account of the position of the methyl(ene) groups (deduced from the standard nitrogen/carbon bond length of 1.48 Å), standing out of the lattice plane at a distance of 0.86 Å (see figure 7), with a centre-to-centre distance from the bromine atoms of 3.62 Å, we see at once that, in fact, the bromide anions are in close contact with the methyl(ene) groups, fitting just into the hollows between them. Finally, it is worth noting that the methyl(ene) groups stand exactly within the limits of the square unit cells (see figure 8).

To complete this description, it is useful to discuss briefly the arrangement of the disordered alkyl chains stemming outwards from the ionic layers. The molecular area calculated previously ($S \cong 37$ Å²) is compatible with the presence of one chain per unit cell on each side of the lattice plane. This can be achieved either by letting the two chains of each molecule extend in opposite directions, on both sides of the lattice planes, or by bending the molecules round their ionic midpoint and letting the paired chains point alternately up and down, or else by permitting, for entropic reasons, a random mixing of double bent and extended molecules. With the experimental data available it is, of course, difficult to decide definitely the exact location of the alkyl chains. However, if the chains were arranged in pairs, the orientation of the ammonium tetrahedra parallel to the tetragonal axes should, for obvious steric reasons, alternate from cell to cell as shown in figure 8.

6. Conclusion

The main result reported in this article is the existence of a new ordered smectic mesophase, in which the lateral packing of the molecules within the layers is tetragonal in symmetry. We believe this is the first reported instance of tetragonal packing in a smectic layer.

Until now, the smectic mesophases reported in the literature have always involved hexagonal, rectangular or oblique two dimensional ordered lattices for the lateral packing of the molecules within the layers. The presence of such lattices is in perfect compliance with the requirements of closest packing of elongated aromatic molecules subject to van der Waals or dipolar attractions and short range hard core repulsions (see chapter on *Typical Structures* in [12]). For a given symmetry, layers of maximum density are indeed obtained only when each molecule is in direct contact with six neighbours.

The occurrence of smectic layers with tetragonal symmetry is, in our opinion, clearly related to the special chemical nature of the mesogens considered. With ionic groups, the molecules interact predominantly through coulombic forces, which are markedly stronger than van der Waals or dipolar forces. Charges of the same sign tend to stand as far as possible from one another, while charges of opposite signs tend to stand in close contact. As a result, two dimensional, ionic systems are arranged according to a square crystal lattice, which is the only one to ensure strict alternation of positive and negative charges in equal numbers.

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