Smectic Mesophases from Dihydroxy Derivatives of Quaternary Alkylammonium Salts

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Abstract: A series of *N*,*N*-di(2-hydroxyethyl)-*N*-methyl-*N*-alkylammonium bromides (alkyl chain from dodecyl to octadecyl) was synthesized and characterized. Its thermotropic liquid-crystal behaviour was studied by differential scanning calorimetry, polarizing optical microscopy, infrared spectroscopy and X-ray diffraction. Two smectic phases were identified, an ordered smectic T and a disordered smectic A phase. Both phases result from an alternate periodic stacking of polar sublayers of ionic head groups and apolar sublayers of alkyl chains in a disordered conformation. In the low-temperature smectic T phase, the ionic head groups are arranged inside the polar sublayers in a particularly dense fashion, a tetragonal crystal lattice. In the high-temperature smectic A phase, the ionic head groups are arranged in a disordered fashion with normal packing density.

Keywords: amphiphiles • liquid crystals • quaternary ammonium salts • structure elucidation • thermotropism

Introduction

The liquid-crystal behaviour of several quaternary alkylammonium salts was first reported in the early eighties and reviewed in 1994 in a general article on amphiphilic liquid crystals.[1] Further work on the subject was carried out recently, dealing particularly with the structural characteristics of these compounds.[2–8] The interest in this type of liquid crystals arises from their facile preparation by simple interaction of tertiary amines with functionalized alkyl halides, leading to ammonium salts with a variety of functional groups (carboxy, hydroxy, cyano,…) attached to the quaternary centre through appropriate spacers. The structural analysis was primarily concerned with the effect on the liquid-crystal behaviour of functional groups that associate with one another through hydrogen or dipole interactions.[2–5]

The nature and temperature range of stability of the smectic phases observed were found to depend heavily upon the detailed molecular composition of the compounds. Thus, in systems without functional groups, as for instance in dialkyldimethylammonium bromides, the ionic species are submitted essentially to coulombic interactions; an ordered smectic T phase is then obtained, in which the ammonium and bromide ions, packed in single layers separated by the disordered alkyl chains, are arranged periodically according to a square two-dimensional crystal lattice.[6–7] On the other hand, in systems containing strongly interacting functional groups, as for instance in *N*-hydroxyalkyl or *N*-cyanoalkyl derivatives of alkyldimethylammonium bromides, the periodic arrangement of the ions is severely disturbed, and a disordered smectic A phase is obtained in which the molecules are packed in a loose, liquid-like fashion, with the ammonium and bromide ions arranged in double layers due to self-dimerization.[3–4]

As the chemical nature of the functional groups attached to the polar quaternary centre of the molecules appears to play a decisive role in the formation of liquid crystals, we thought it of interest to pursue the previous work with an investigation of additional examples of such N-substituted alkylammonium salts. In particular, we decided to consider salts carrying not only one but two interacting groups, in the hope of inducing the formation of supermolecular arrays or grids liable to strengthen the smectic layers.[9] The present work is concerned with quaternary *N*-methyl-*N*-alkylammonium bromides from dodecyl to octadecyl, *N*-substituted with two 2-hydroxyethyl groups as shown in Scheme 1 (referred to in the following as DH*n*).

Results and Discussion

Thermal and optical studies: The thermal stability of the DH*n* compounds was investigated by thermogravimetry. On heating dynamically at 10 °C min^{-1}, the compounds started to

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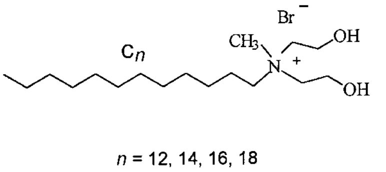


Scheme 1. Structure of DH*n*.

degrade thermally at temperatures above 180 °C. However, when a constant temperature was maintained, they proved to resist prolonged heating at 160 °C with weight losses smaller than about 1 %.

Their thermotropic polymorphism was first studied by polarizing optical microscopy. The textures observed in the temperature range from ambient to 160 °C revealed a series of phase transitions. As confirmed later by X-ray diffraction, the first transition (undetected for DH12) corresponds to a polymorphic transformation in the crystalline state, similar to that reported previously for the homologous series of *n*-alkylammonium halides.[10] Upon heating above the second transition temperature, the DH*n* compounds transformed into a viscous birefringent mass with chaotic and confused textures. It was only above the third transition temperature that well-developed focal-conic textures could be observed (Figure 1 top), pointing to the presence of smectic A phases. Upon cooling, these textures developed striations (Figure 1 bottom) attesting to the presence of an ordered smectic phase, actually of a smectic T phase as established by X-ray diffraction.

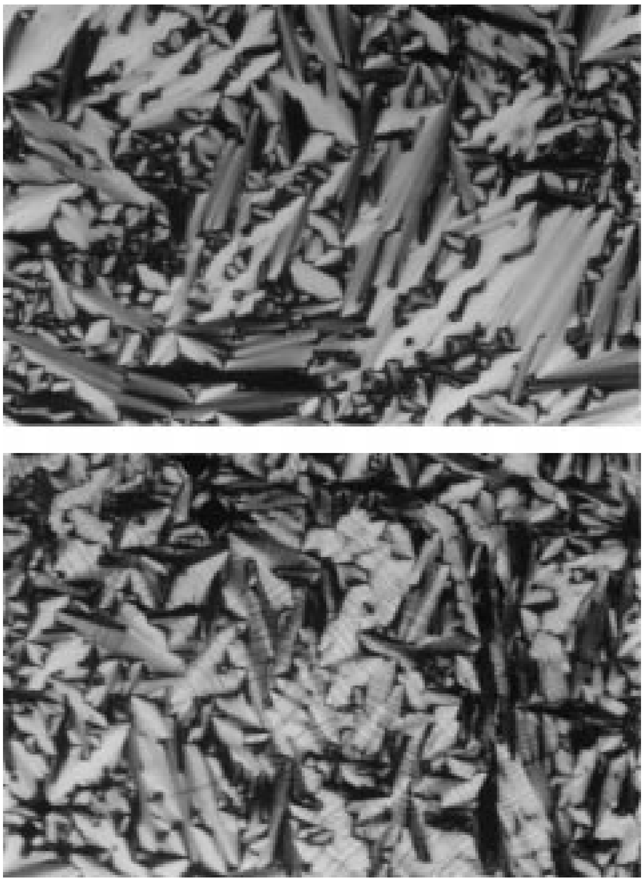
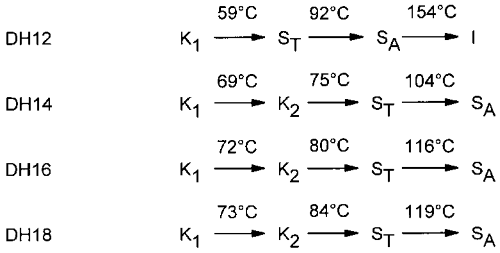


Figure 1. Optical textures of the DH12 compound in the smectic A (top) and the smectic T (bottom) phases, obtained by slow cooling from the isotropic melt.



$$\text{DH12} \quad K_1 \xrightarrow{59^{\circ}\text{C}} S_T \xrightarrow{92^{\circ}\text{C}} S_A \xrightarrow{154^{\circ}\text{C}} I$$

$$\text{DH14} \quad K_1 \xrightarrow{69^{\circ}\text{C}} K_2 \xrightarrow{75^{\circ}\text{C}} S_T \xrightarrow{104^{\circ}\text{C}} S_A$$

$$\text{DH16} \quad K_1 \xrightarrow{72^{\circ}\text{C}} K_2 \xrightarrow{80^{\circ}\text{C}} S_T \xrightarrow{116^{\circ}\text{C}} S_A$$

$$\text{DH18} \quad K_1 \xrightarrow{73^{\circ}\text{C}} K_2 \xrightarrow{84^{\circ}\text{C}} S_T \xrightarrow{119^{\circ}\text{C}} S_A$$

Scheme 2. Thermotropic polymorphism of the DH*n* compounds.

The compounds were then analysed by differential scanning calorimetry. The DSC thermograms showed the presence, at the same temperatures as detected by optical microscopy, of sharp peaks indicative of first-order phase transitions. The phase transitions observed upon heating from room temperature up to 160 °C are summarized in Scheme 2 (symbols K, S_T, S_A, and I stand respectively for crystal, smectic T, smectic A, and isotropic liquid). The enthalpy involved in the transition from K_2 to S_T, related to the melting of the alkyl chains, was rather significant as usual (of the order of 50 J g^{-1}), while that involved in the transition from S_T to S_A, connected with the disordering of the polar heads, was much smaller (of the order of 3 to 5 J g^{-1}).

Abstract in Greek:

Περίληψις

Παρασκευάσθηκε και υποβλήθηκε σε μελέτες χαρακτηρισμού σειρά βρωμιούχων *N,N*-δι(*2*-υδροξυαιθυλο-*N*-μεθυλο-*N*-αλκυλαμμωνιακών αλάτων με αλκυλομάδες δώδεκα έως δεκαοκτώ ατόμων άνθρακος. Η υγροκρυσταλλική τους συμπεριφορά μελετήθηκε με διαφορική θερμιδομετρία σαρώσεως, πολωτική οπτική μικροσκοπία, φασματοσκοπία υπερύθρου και περίθλαση ακτίνων Χ. Πιστοποιήθηκαν δύο σμηγματικές φάσεις, και συγκεκριμένα μία οργανωμένη σμηγματική Τ και μία μη οργανωμένη σμηγματική Α φάση. Αμφότερες οι φάσεις είναι αποτέλεσμα εναλλασσόμενης περιοδικής διευθέτησης των πολικών υποστοιβάδων που αποτελούνται από ιοντικές ομάδες και των μη πολικών υποστοιβάδων των αλκυλομάδων σε μη οργανωμένη διαμόρφωση. Στην σμηγματική φάση Τ που εμφανίζεται σε χαμηλές θερμοκρασίες, οι ιοντικές ομάδες διευθετούνται μέσα στις πολικές υποστοιβάδες κατά ιδιαιτέρως πυκνό τρόπο, σε τετραγωνικό κρυσταλλικό πλέγμα με δύο μόρια ανά μοναδιαία κυψελίδα. Στην σμηγματική φάση Α που εμφανίζεται σε υψηλότερες θερμοκρασίες, οι ιοντικές ομάδες διατάσσονται κατά μη οργανωμένο τρόπο με φυσιολογική πυκνότητα διευθέτησης.

Without going into details, it is useful to note that, upon cooling, the reverse phase transitions between S_T and K, and more significantly between S_A and S_T, all took place with a hysteresis of about 20 °C, revealing the importance of nucleation in both processes. It is of interest to add that the K_2 crystalline form is not observed with DH12, quite probably because the compound is hydrated, as established by infrared spectroscopy.

Infrared spectroscopy: The FT-IR spectra of the DH*n* compounds (from tetradecyl to octadecyl) in the K_1 crystal phase show a rather sharp stretching band at 3294 cm^{-1}

(having a width at half intensity of $\nu_{1/2} \approx 100\,\text{cm}^{-1}$), which is consistent with a polymer-type association of the OH groups through hydrogen bonding.[11] The OH stretching band of the DH12 compound is significantly broader and weaker, pointing to water absorption (difficult to avoid completely under usual experimental conditions, due to hygroscopicity); this conclusion is supported by an additional broad peak at about $1640\,\text{cm}^{-1}$.

Hydrogen bonding of the Br^- anions with the OH groups may likewise be inferred from the presence, as a shoulder, of a peak at $3320\,\text{cm}^{-1}$.[12] It is worth noting that this particular peak continues to exist even in extremely dilute solutions in apolar solvents, where the ionically undissociated molecules are separated by large distances, meaning that the OH groups continue to interact appreciably with the bromide anions; the presence of a weak stretching band at about $3680\,\text{cm}^{-1}$, related to free OH groups, indicates that, on the other hand, the OH groups no longer interact with one another intermolecularly.

In the spectrum of the K_2 crystal phase, the OH stretching band is slightly broadened ($\nu_{1/2} \approx 140\,\text{cm}^{-1}$) and shifted upscale to $3297\,\text{cm}^{-1}$, indicating some lengthening of the hydrogen bonds between the OH groups. However, the band (shoulder) at $3320\,\text{cm}^{-1}$, which is connected with the hydrogen bonding of the bromide anions, remains at exactly the same position, as established using the second-order derivative of the spectra.

Upon melting into the smectic T and then into the smectic A phase, the OH stretching band widens out significantly ($\nu_{1/2} \approx 200$ then $240\,\text{cm}^{-1}$) and shifts still further away (to 3310 then to $3320\,\text{cm}^{-1}$), as illustrated in Figure 2. Although ending, in the smectic A phase, by overlapping with the band associated with the hydrogen bonding of the Br anions, this band is nevertheless still connected (at least in part) with the hydrogen bonding of the OH groups with each other, since no free OH groups could be detected (for instance, by a band at about $3680\,\text{cm}^{-1}$). The considerable change in position and width of this band at the transition from the crystal into the smectic T phase corresponds, however, only to small changes in the length of the hydrogen bonds (of about 0.1 Å)[13] and to a minor alteration of their strength. Despite a possible rearrangement of the hydrogen-bonding pattern in the course of the polymorphic process, the molecules in the liquid-crystal phases, even in the least ordered smectic A phase, are quite probably self-assembled as they certainly are in the crystal forms.

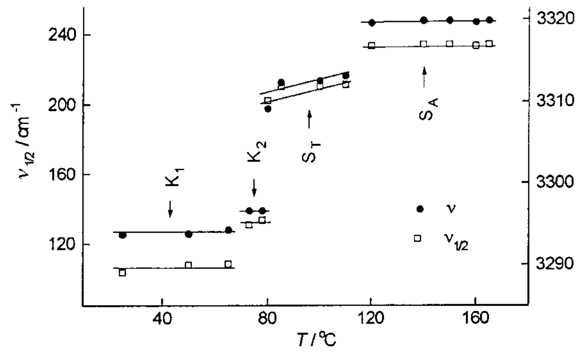


Figure 2. Temperature dependence of the frequency $\tilde{\nu}$ and width at half intensity $\nu_{1/2}$ of the hydrogen-bonded OH stretching band of DH16 in the crystal K_1, crystal K_2, smectic T and smectic A phases.

The peaks observed in the range from 700 to $1400\,\text{cm}^{-1}$ provide valuable information about the conformation and packing of the alkyl chains. The doubling in the K_1 crystal phase of the methylene rocking-mode band at 719 and $726\,\text{cm}^{-1}$ and the scissoring-mode band at 1465 and $1474\,\text{cm}^{-1}$ indicates an all-*trans* conformation of chains packed in an orthorhombic crystal lattice.[14–15] Moreover, the presence of bands at 1345, 1164, 1085, 965, and $885\,\text{cm}^{-1}$, assigned to *end-gauche* conformations, and of bands at 1363 and $1301\,\text{cm}^{-1}$, assigned to kinks, reveals some distortion of the free ends of the alkyl chains,[14] which are tilted with respect to the polar sublayers (see also X-ray results).

The splitting of the methylene rocking and scissoring bands observed in K_1 disappears in the K_2 crystal phase, while single bands emerge at 1467 and $721\,\text{cm}^{-1}$, suggesting that the alkyl chains are now packed less tightly, in a way similar to that observed in the hexagonal high-temperature crystal form of linear paraffins.[14–15] As for the broadening of the bands associated with the *end-gauche* conformations, it clearly suggests that the chain ends are more distorted in K_2 than in K_1, because of the less constrained packing of the alkyl chains.

Above the transition of the crystal to the smectic T phase, the replacement of the bands related to a crystalline state of the alkyl chains by a band at $1352\,\text{cm}^{-1}$ related to *double-gauche* conformations clearly indicates that the alkyl chains have now melted. The presence of a rather strong band at $720\,\text{cm}^{-1}$ suggests, however, the existence in the alkyl chains of sequences of more than four methylene groups all bonded in a *trans* conformation;[16] this will be discussed below in connection with the three-dimensional positional correlations of the polar sublayers. It is only in the range of stability of the smectic A phases that the alkyl chains finally melt completely, as revealed by the broadening and weakening of this latter band, which, in addition, shifts to $718\,\text{cm}^{-1}$.

X-ray investigation of the crystal phases: The X-ray patterns of the crystal phases contain a great number of sharp reflections located both at small and wide angles, showing the existence of well-developed three-dimensional lattices. The equidistant small-angle reflections indicate that the molecules are arranged in a lamellar fashion, as commonly observed with long-chain amphiphilic derivatives. The structure consists of an alternate and periodic superposition of two types of sublayer, consisting of the ionic head groups of the molecules and of the alkyl chains. In both K_1 and K_2 crystal forms, the lamellar periods measured from the small-angle reflections are independent of temperature and grow linearly with the number n of carbon atoms in the alkyl chains (Figure 3), according to equations: d_{K1} [Å] $= 8.5_{\pm 1.6} + 0.89_{\pm 0.10}n$ and d_{K2} [Å] $= 9.8_{\pm 1.4} + 1.03_{\pm 0.09}n$ (deduced from a least-squares linear fit of the experimental data).

The y intercepts of the d vs. n straight lines provide an estimate of the thickness of the polar sublayers. The small difference between the two values, 8.5 Å for K_1 and 9.8 Å for K_2, is no doubt related to small changes in the detailed

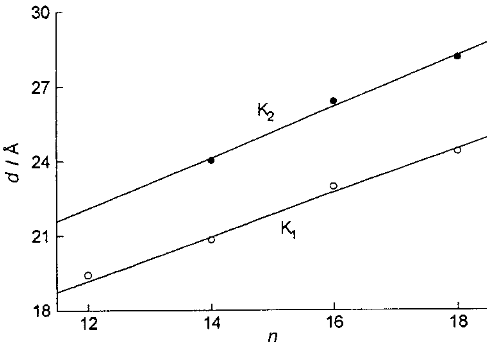


Figure 3. Lamellar periods of the crystal K_1 and K_2 phases as a function of the number *n* of carbon atoms in the alkyl chains.

internal structure of the sublayers and of the hydrogen-bonding pattern of the polar head groups, a theory supported by evidence from infrared spectroscopy. As for the slopes, they represent the increase in thickness of the lamellae for an elongation of the alkyl chains by one methylene group. They are much smaller than half the length of one zigzag in a fully extended paraffin chain (2.54/2 = 1.27 Å),[17–18] suggesting that the alkyl chains are not only arranged head-to-tail and interdigitated to form single layers, but also tilted with respect to the layer normal. Estimated from the experimental data, the tilt angles, $\cos^{-1}$(slope/1.27), are of about $46_{\pm 6}$ and $36_{\pm 6}$°, respectively.

X-ray investigation of the smectic T phases: The diffraction patterns of the S_T liquid-crystal phase contain up to five equidistant and sharp reflections in the small-angle region, consistent with a smectic layering. Independent of temperature, the smectic periods measured, like the lamellar periods of the crystal, grow linearly with the number of carbon atoms in the alkyl chains (Figure 4), according to the equation: $d\,[\text{Å}] = 9.8_{\pm 1.4} + 1.16_{\pm 0.08}n$. The abnormally high value of the spacing of the DH12 compound is very likely connected with the presence of small amounts of water in the samples, a conjecture supported by infrared spectroscopy. Quite interestingly, the thickness of the polar sublayers ($d_0 = 9.8$ Å) is equal to that of the K_2 crystal phase, implying that the internal structure of the polar sublayers ought also to be similar in both structures. However, this conclusion is evidently unfounded, because, in the first place, it overlooks the fact that the hydrogen-bonding pattern of the polar head groups changes appreciably at the transition from K_2 to S_T (evidence from infrared spectroscopy), and, furthermore, it does not take into consideration a possible rearrangement of the polar groups inside the layers at constant thickness.

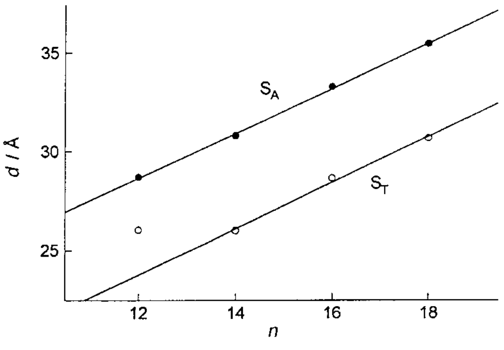


Figure 4. Lamellar periods of the smectic T and smectic A phases as a function of the number *n* of carbon atoms in the alkyl chains.

In the wide-angle region, the X-ray patterns contain, on the one hand, a diffuse band at about 4.5 Å, indicative of the liquid-like conformation of the alkyl chains,[19,20] and, on the other hand, several sharp reflections consistent with the existence of a three-dimensional tetragonal crystal lattice (Table 1) of cell parameters $a = b = 6.96$ Å and $c = d$. The alkyl chains being disordered, this lattice can only describe the periodic arrangement of the ammonium bromide groups in three-dimensional space. Although soft and flowing readily, the S_T phase is, therefore, from a formal point of view, a genuine crystal exhibiting three-dimensional positional order.[21] Independent of temperature, the *a* parameter of the tetragonal lattice is exactly the same for all the DH*n* compounds studied, meaning that the packing of the ammonium bromide groups inside the polar sublayers is totally independent of the length of the alkyl chains.

Table 1. Observed and calculated spacings [Å] of the wide-angle reflections of the DH*n* compounds in the smectic T state at 90 °C.

	DH12		DH14		DH16		DH18	
hkl	d_{obs}	d_{calcd}	d_{obs}	d_{calcd}	d_{obs}	d_{calcd}	d_{obs}	d_{calcd}
110	4.92	4.92	4.92	4.92	4.91	4.92	4.91	4.92
111	4.83	4.82	4.83	4.83	4.84	4.85	4.84	4.86
200	–	–	3.47	3.48	3.47	3.48	3.47	3.48
201	–	–	3.44	3.45	3.43	3.45	3.43	3.46
210	–	–	3.07	3.11	–	–	–	–

To get a deeper insight into the arrangement of the ionic head groups inside the polar sublayers, it is useful to specify the number *Z* of molecules per tetragonal unit cell. This can be done very easily by means of the linear dependence of the smectic period *d* on the number *n* of carbon atoms in the alkyl chains: $d = ZV_0/a^2 + (ZV_{CH_2}/a^2)n$. This equation originates in the fact that the volume a^2d of the tetragonal unit cell is equal to *Z* times the volume *V* of one molecule, which, for its part, is equal to $V_0 + nV_{CH_2}$, where V_{CH_2} is the volume of one methylene group and V_0 that of one polar head. From the measured slope of the *d* vs. *n* straight line ($ZV_{CH_2}/a^2 = 1.16_{\pm 0.08}$ Å) and from the known value of V_{CH_2} (27.8 Å^3 at 90 °C),[22] it is then easy to calculate $Z = 2.0_{\pm 0.1}$. Each tetragonal unit cell therefore contains exactly two molecules. Considering that the area available in the square basis of the lattice ($a^2 = 48.4$ Å^2) is significantly smaller than twice the lateral extension of one polar head (about 37 Å^2, inferred from the area covered by a single quaternary ammonium group in the layers of the smectic T phase of dialkyldimethylammonium bromides),[6] one arrives at once at the conclusion that the ammonium and bromide ions inside the polar sublayers are not juxtaposed in single layers, but superposed on top of one another to form double layers as shown in Figure 5, with the positive and negative ions alternating in space to minimize electric repulsion.

As for the hydroxyethyl substituents of the ammonium groups, they are quite probably located in the core of the polar

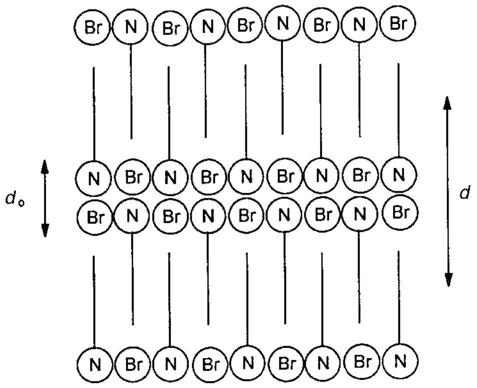


Figure 5. Schematic view of the molecular arrangement in the smectic T layers. The positive ammonium and negative bromide anions are alternating within the polar sublayers to minimize the coulombic repulsion. Although disordered, the alkyl chains (represented for clarity by straight lines) are probably interdigitated to some extent.

sublayers, with the hydroxy groups arranged tetragonally (Figure 6) and hydrogen bonded as much with one another as with the neighbouring bromide anions. Inferred from a variety of molecular modelling tests (Hyperchem software) and also supported by infrared spectroscopy, this structure turns out to be remarkably dense. In many respects, it resembles that of crystalline pentaerythritol $C(CH_2OH)_4$, in which molecules are also arranged in layers with a tetragonal pattern of hydrogen bonds.[23] The volume of one polar head, equal to $a^2d_0/2 = 237.2$ Å^3, corresponds to a density of $1.4_{\pm0.15}$ g cm^{-3}. Unexpectedly high at first sight, this density is, however, consistent with that of pentaerythritol (1.40 g cm^{-3})[23] or tetramethylammonium bromide (1.57 g cm^{-3}).[24]

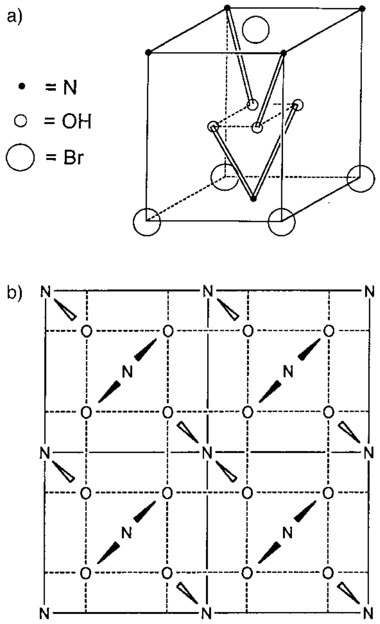


Figure 6. a) Arrangement of the ionic species and hydroxyethyl substituents (double lines) in that portion of the polar sublayer of the smectic T phase which is contained in one tetragonal unit cell; b) top view of the molecular arrangement in four contiguous square unit cells of the polar sublayers of the smectic T phase. Bromide cations (at the same positions as ammonium cations) are omitted for clarity. The average plane of the dihydroxyethyl substituents (represented by full or empty arrows, depending on whether the ammonium cation is located on the upper or lower face of the polar sublayer) are oriented alternately along the two diagonals of the square lattice. Located in the median plane of the polar sublayers, the hydroxy groups are hydrogen-bonded as much with themselves as with the bromide anions. Although plausible, it is difficult to propose any specific hydrogen-bonding pattern permitting description of the polar sublayers in terms of extended supermolecular arrays or grids.

The area of the square unit cell (48.4 Å^2) is about twice the usual cross-sectional area of linear alkyl chains in a disordered conformation ($\approx$24 Å^2).[22] It seems, therefore, that there is enough lateral space in the paraffin layers for the alkyl chains to interdigitate, at least to some extent, in an alternate up and down configuration, without unduly losing the disordered but yet substantially elongated conformation suggested by infrared spectroscopy. Incidentally, such an interdigitation might be the very reason why the superposed smectic layers are in fact found to be positionally correlated, leading to the three-dimensional crystal observed by X-ray diffraction.

X-ray investigation of the smectic A phases: The diffraction patterns of the S_A liquid-crystal phase contain only one sharp small-angle reflection related to the smectic layering, suggesting that the position of the strongly diffracting bromide anions in the polar sublayers of S_A are not as well defined as in the case of S_T. In the wide-angle region, the patterns contain only a diffuse band at 4.5 Å, indicating that not only the alkyl chains but also the polar head groups are arranged in a disorderly fashion.

The smectic periods measured grow linearly with the number of carbon atoms in the alkyl chains (Figure 4), according to the equation d [Å] $= 15.0_{\pm0.4} + 1.14_{\pm0.02}n$. From the slope of the $d = 2V/S = 2V_0/S + (2V_{CH_2}/S)n$ straight line, the area S covered in the plane of the smectic layers by a pair of molecules may be easily determined as previously, from the known volume of one methylene group (28.4 Å^3 at 120 °C).[22] The value found ($S = 49.8$ Å^2) is only slightly larger than that in the S_T phase, despite the molten state of the polar sublayers. Quite interesting, however, is the $5_{\pm2}$ Å increase of the thickness of the polar sublayers at the S_T to S_A phase transition, leading to a density in the smectic A phase of the order of only 0.9 g cm^{-3}. Though lacking in precision, this notable expansion, which is directly related to the melting of the polar heads, gives a clear idea of the importance of the packing constraints that are relieved in the melting process.

Conclusion

Ordered smectic T phases have up to the present time been observed only with quaternary dialkyldimethylammonium bromides, whose ionic head groups are devoid of strongly interacting *N*-substituents. Alkyldimethylammonium compounds carrying one single such hydroxyalkyl, cyanoalkyl or carboxyalkyl *N*-substituent, on the other hand, have been found to produce only disordered smectic A phases because of the hydrogen-bonding or dipolar interactions which disturb the packing of the polar heads. In the present work, a series of alkylmethylammonium bromides carrying two hydrogen-bonding hydroxyethyl groups were synthesized, which turned out to exhibit an ordered smectic T phase and also a smectic A phase at higher temperatures. The presence in these latter compounds of the ordered T phase is clearly imputable to the hydrogen-bond network developed inside the polar sublayers between the hydroxy groups themselves on the one hand, and between the hydroxy groups and the bromide anions on the other; this network appears to fit perfectly with the tetragonal arrangement of the ionic quaternary ammonium groups. Although no direct evidence of any specific hydrogen-bonding pattern could be collected in the present work, it is, however, tempting to discuss the observed smectic T structure in terms of supermolecular assemblies (arrays or grids) of ionic groups.

Experimental Section

Materials: A bromoalkyl derivative (0.01 mol) was added to *N*-methyldiethanolamine (0.01 mol) (Aldrich) dissolved in ethyl acetate, and quaternization was conducted during stirring at room temperature for several days. The precipitated material was recrystallized twice from ethyl acetate. Purity of compounds was checked by elemental analysis [DH12: calcd C 55.43, H 10.40, N 3.80; found: C 55.66, H 10.54, N 3.76; DH14: calcd C 57.56, H 10.68, N 3.53; found: C 57.84, H 10.82, N 3.49; DH16: calcd C 59.42, H 10.92, N 3.30; found: C 59.70, H 11.06, N 3.25; DH18: calcd C 61.04, H 11.14, N 3.09; found: C 61.23, H 11.28, N 3.05] and ^{1}H NMR (AC250 Bruker spectrometer, 250 MHz, $CDCl_3$, 25 °C, TMS) [$\delta = 0.86$ (t, 3H, CH_3), 1.28 (m, 2(n – 3)H, CH_2), 1.72 (m, 2H, α-CH_2), 3.31 (s, 3H, CH_3N), 3.52 (m, 3H, α-CH_2), 3.71 (m, 2H, $C\mathbf{H}_2CH_2OH$), 4.09 (t, 2H, $CH_2C\mathbf{H}_2OH$), 4.78 (br, 1H, OH)].

Characterization techniques: Thermogravimetric experiments were performed with a heating rate of 10 °C min^{-1} by means of a Mettler TC10A instrument coupled with a TA processor and a M3 balance. Phase transitions were investigated with heating and cooling rates of 5 °C min^{-1}, in a Perkin–Elmer DSC-7 calorimeter. Optical microscopy observations were made with a Leitz Orthoplan polarizing microscope coupled with a Mettler FP82 hot stage. FT-IR studies were performed with a Nicolet Magna 550 spectrometer coupled with a VLT-2 variable temperature cell (Research & Industrial Instruments Company). X-ray diffraction experiments were performed with a home-made Guinier camera equipped with a bent quartz monochromator ($K_{\alpha 1}$ radiation from an INEL X-ray generator) and an INEL-CPS-120 curved position-sensitive detector permitting measurement of both the angular position and the intensity of the Bragg reflections. Samples were held in sealed Lindemann capillaries and temperature was controlled (to < 0.1 °C) by an INSTEC hot stage.

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