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Structural compatibility of smectic sublayers: liquid crystals from oxynitrostilbene derivatives of dialkyldimethylammonium bromides

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A series of dialkyldimethylammonium bromides bearing a 4,4′-oxynitrostilbene calamitic core at the end of one of the alkyl chains was synthesized. Its thermotropic liquid crystal behaviour was examined using differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. An ordered smectic phase was identified in which the ionic ammonium bromide groups are arranged according to a square two-dimensional crystal lattice, and the oxynitrostilbene cores are tilted away from the layer normal by an angle of 54 degrees. This novel smectic structure is discussed in terms of structural compatibility of the smectic sublayers: the sublayers of the ionic groups and calamitic cores adapt their internal structure in order to become adequate for coherent superposition in a smectic structure.

1. Introduction

In ordered smectic liquid crystals obtained from calamitic mesogens, the molecular cores are laterally arranged according to hexagonal or pseudo-centred rectangular two-dimensional networks [1]. They are thus most densely packed as required by van der Waals interactions. In such an arrangement, each core is in close contact with six first neighbours, in compliance with the close-packing principles prevailing in the formation of molecular layers in organic crystals [2]. The cross-sectional area of the cores (without lateral substituents) is typically about 22 Å^2 [3].

With two-chain ionic amphiphiles deriving from dimethylammonium bromide, a new type of thermotropic ordered smectic phase (SmT) was recently identified, involving a totally different (tetragonal) arrangement of the molecules within the layers [4]. Confined to thin layers separated from one another by the alkyl chains in a disordered conformation, the bromide anions and ammonium cations are arranged according to a square lattice (with a unit cell area of 36·5 Å^2), in a manner similar to that found in the faces of the face-centred cubic crystals of alkali halides. This new type of ordering is due to the predominant rôle played here by the electrical forces among the ions. Being in equal numbers and standing in mutual contact at the corners and centres of a square two-dimensional network, the ammonium cations and bromide anions ensure a strict alternation in space of positive and negative charges as required by coulombic interactions.

We found it worth considering in the present work the composite case of smectogenic molecules containing an ammonium bromide pair of ions and a neutral calamitic end group at one and the same time. This raises indeed an interesting problem of structural compatibility of the smectic sublayers, the two species having different in-layer packing symmetries and cross-sectional areas. How can the sublayers of the two species adapt their internal structures to become adequate for coherent superposition in a common smectic structure? One possibility is that the ionic groups give up their tendency to organize, leaving the calamitic end groups free to arrange according to their own habits and abilities. A case of this kind was observed recently with cyanopropylalkyldimethylammonium bromides, carrying a cyano end group at the end of a short propyl chain; these compounds were indeed found to show a SmA phase, disordered in nature [5]. One other possibility is that the calamitic cores, whose cross-sectional area is only 22 Å^2, modify their organization by tilting away from the layer normal by an angle of $\cos^{-1}$ (22/36·5) = 53 degrees so as to cover in the smectic layers a surface

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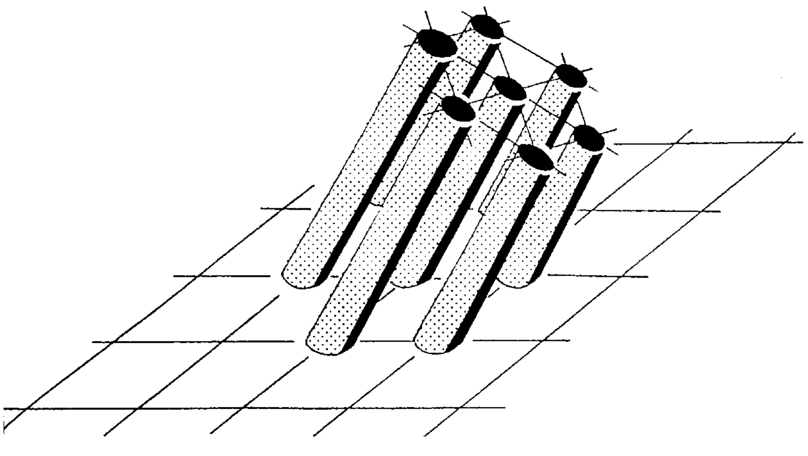
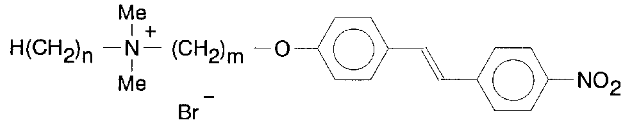


Figure 1. Rods placed at the nodes of a two-dimensional square network. When upright, the rods are laterally packed in a tetragonal fashion. When leaning over the diagonals of the square network, they are packed according to a centred rectangular two-dimensional lattice. When their tilt with respect to the plane normal is exactly 54·7 degrees, that is, when the rods lie along the body diagonals of the cubic lattice erected from the square network, then the rods are arranged laterally in a hexagonal fashion.

equal to the unit cell area (36·5 Å^2 [4]) of the square lattice of the ionic species. In doing so, that is, in tilting by an angle nearly identical to the angle (54·7 degrees) between the ⟨1 1 1⟩ diagonals and the ⟨001⟩ axis of a cubic lattice built upon the square network of the ionic species, the calamitic cores can, furthermore, pack laterally according to a hexagonal lattice, as is proper (see figure 1).

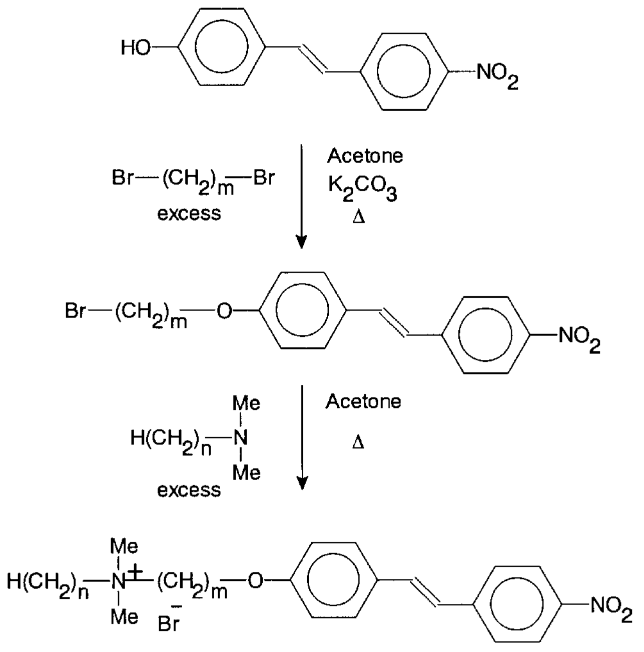
To investigate this question more thoroughly, we decided to synthesize and study a series of dialkyldimethylammonium bromides bearing a 4,4′-oxynitrostilbene moiety at the end of one of the alkyl chains [IUPAC nomenclature: dimethyl(ω-(4-((*E*)-2-(4-nitrophenyl)-1-ethenyl)phenoxy)alkyl)alkylammonium bromides; abbreviated in the following to *n,m*-ONSAB with *n* and *m* representing the number of methylene units in the alkyl chain and the spacer between the ammonium and oxynitrostilbene moieties, respectively]



We selected oxynitrostilbene as the end group for its particular length (about 13 Å) and its dipolar nature inducing a small negative charge at the nitro group and a positive charge at the ether group. We thought, indeed, that the tilted arrangement of the calamitic stems, if present, should then be enhanced by the coulombic attractions of the negative and positive charges of adjacent cores brought against one another as shown in figure 2.

2. Synthesis

To synthesize the *n,m*-ONSAB compounds we proceeded in two steps:



We first synthesized the 4,4′-(bromoalkoxy)nitrostilbene intermediates. A mixture of 4-hydroxy-4′-nitrostilbene (4·1 mmol) (Lancaster, used as received) and α,ω-dibromoalkane (4-molar excess) (Aldrich, *m*=6, 8 used as received, and *m*=10, 12 recrystallized from ethanol) were dissolved in 20 ml of acetone, and heated at reflux for 24 h in the presence of K_2CO_3 (36·2 mmol). After cooling, the insoluble inorganic salts were filtered off, the unreacted dibromoalkane was removed by extraction with heptane, and the disubstituted alkane was isolated by column chromatography (SiO_2 and CH_2Cl_2/hexane 1/1 v/v used as eluent). Yields: 74%, 67%, 64% and 62% for products with *m*=6, 8, 10 and 12, respectively. The ^{1}H NMR chemical shifts in $CDCl_3$ (AC 200 Bruker) of compound *m*=6 selected as an example were: 1·50 (m, 4, CH_2 of the alkyl chain), 1·85 (m, 4, βCH_2 of the alkyl chain), 3·45 (t, 2, CH_2Br), 4·00 (t, 2, CH_2O), 6·92 (dd, 2, ArH), 7·00 and 7·24 (dd, 1, 1, $CH{=}CH$), 7·49, 7·61 and 8·21 (dd, dd and dd, 2, 2 and 2, ArH).

We then synthesized the *n,m*-ONSAB products by quaternization of *N,N* dimethylamine with the above bromide intermediates. A mixture of each intermediate (1 mmol) with a 10-molar excess of *N,N* dimethylamine was dissolved in 20 ml of acetone, heated at 60°C for one hour, and finally left at room temperature for one day. Crystallizing easily, the 8,6-ONSAB, was purified by recrystallization from acetone. The other compounds were collected after complete evaporation of the solvent. After heptane extraction of the unreacted amine, the compounds were recrystallized from ethyl acetate, except for 12,12-ONSAB which was recrystallized from toluene. Yields: 77%, 78%, 84%, 66%, and 74% for 6,8-ONSAB, 6,12-ONSAB, 8,12-ONSAB, 10,12-ONSAB, and 12,12-ONSAB, respectively. Purity was checked by elemental analysis [6,8-ONSAB—calc: C63·9, H 8·0, O 8·9, N 4·8; found: C 64·2, H 8·1, O 8·6, N 5·0 per cent; 6,12-ONSAB—calc: C 65·8, H 8·6, O 8·1, N 4·4; found: C 66·1, H 8·6, O 7·8, N 4·5 per cent; 8,12-ONSAB—calc: C 66·6, H 8·8, O 7·8, N 4·1; found: C 67·0, H 8·9, O 7·4, N 4·3 per cent; 10,12-ONSAB—calc: C 67·5, H 9·1, O 7·2, N 4·0; found: C 67·7, H 9·1, O 7·1, N 4·2 per cent; 12,12-ONSAB—calc: C 67·8, H 9·3, O 7·1, N 3·8; found: C 68·4, H 9·3, O 6·8, N 4·0 per cent] and proton NMR in $CDCl_3$ [the chemical shifts of 8,6-ONSAB chosen as an example are: 0·85 (t, 3, CH_3 of the alkyl chain), 1·20–1·90 (m, 20, $(CH_2)_6$ and $(CH_2)_4$) 3·50 (m, 10, $N^+(CH_3)_2$ and $N^+(CH_2)_2$), 4·00 (t, 2, CH_2O), 6·92 (dd, 2, ArH), 7·00 and 7·24 (d, d, 1, 1, $CH{=}CH$), 7·49, 7·61 and 8·21 (dd, dd and dd, 2, 2 and 2, ArH)].

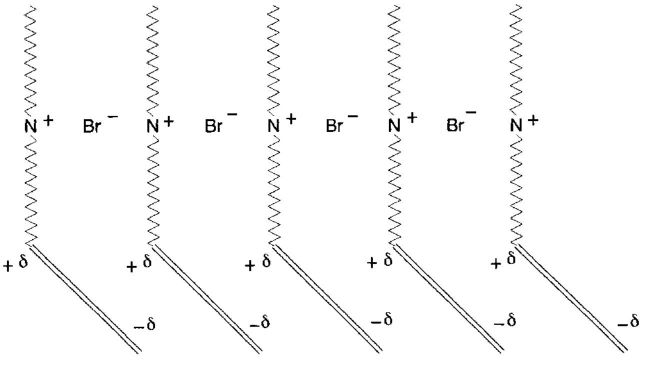


Figure 2. Schematic arrangement of the *n,m*-ONSAB molecules in layers. Wavy and double lines represent alkyl chains and calamitic moieties, respectively. Calamitic moieties are polarized due to intramolecular charge transfer. When the calamitic moieties are tilted away from the layer normal by about 54 degrees, then the negative charges come close to the positive charges.

3. Thermal behaviour

We investigated the thermal stability of the *n,m*-ONSAB compounds using thermogravimetry (Setaram TGA 92, nitrogen flow, heating rate of 10°C × min^{-1}).

Although readily degrading above temperatures of about 200°C, these proved to withstand heating for 5 hours at 125°C without weight loss. They thus appeared perfectly suitable for the thermal studies planned in this work, especially for the rather lengthy (typically a few hours) X-ray experiments at high temperature.

We then studied their thermotropic phase behaviour by differential scanning calorimetry (Perkin-Elmer DSC 7, heating and cooling rates of 5°C min^{-1}) and polarizing optical microscopy (Leitz Orthoplan, Mettler FP 82 hot stage). The DSC thermograms recorded on heating and subsequent cooling in the range from 25 to 125°C showed the presence of rather sharp peaks indicative of first order transitions. The fluid character of the samples at high temperatures and their focal-conic textures suggested the presence of smectic liquid crystal phases. With compounds 12,6-ONSAB and 12,8-ONSAB, the transition from the smectic to the crystalline state was found to proceed, as usual, with a few degrees of hysteresis. Compound 8,6-ONSAB passes on heating directly into the isotropic liquid state; however, on cooling from the melt, it shows a monotropic smectic phase before turning into a crystal (or a highly ordered smectic phase). Compounds 12,10-ONSAB and 12,12-ONSAB exhibit one enantiotropic smectic phase; like compound 8,6-ONSAB, they show on cooling one additional (monotropic) smectic phase followed by a crystalline (or a highly ordered smectic) phase. These observations are summarized as follows (Cr, Sm and I stand for crystal, smectic and isotropic liquid; X and X′ stand for highly ordered smectic or crystal phases; temperatures in °C) (see also figure 3):

8-6	Cr 117 (X 46 Sm 80) I
12-6	Cr 38 Sm 120 I
12-8	Cr 66 Sm 122 I
12-10	Cr 88 (X61 X′82) Sm 120 I
12-12	Cr 63 (X59) Sm 95 I

4. Smectic phase structure

Finally, we investigated the structure of the smectic phase (see above polymorphic scheme) using X-ray diffraction (Guinier focusing camera, Cu-K_{α_1} radiation). Similar to those for the SmT ordered smectic phase of dialkyldimethylammonium bromides described previously [4], the X-ray patterns recorded (figure 4) suggest the same (tetragonal) ordering of the molecules within the smectic layers.

In the small angle region, the patterns contain three sharp Bragg reflections corresponding to spacings in the

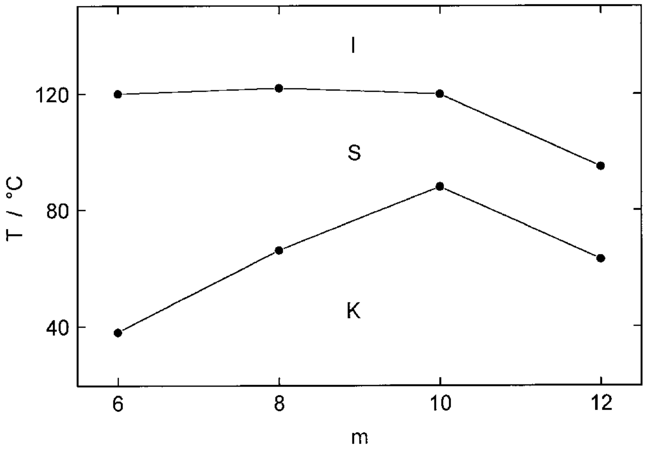


Figure 3. Phase diagram of compounds 12,*m*-ONSAB, determined upon heating (I: isotropic liquid; Sm: smectic phase; Cr: crystalline state).

ratio 1 : 1/2 : 1/3 : 1/4, i.e. characteristic of a lamellar structure. Temperature independent, the measured smectic periods, *d*, depend on the mesogen under study, more precisely, on the total number, $n+m$, of carbon atoms in the alkyl chains. As shown in figure 5, the $n+m$ dependence of *d* is linear, obeying equation:

$$d/\text{Å} = 20{\cdot}47 + 1{\cdot}567\ (n+m)$$

(determined by a linear least square fit method, $R=0{\cdot}9995$, standard errors on slope and *Y*-intercept: 0·028 and 0·56 Å, respectively). In the wide angle region, the X-ray patterns contain a diffuse ring at 4·5 Å, corresponding to the lateral, in-layer correlations of the non-ionic parts of the molecules, and two rather sharp Bragg reflections at 4·35 and 3·07 Å, corresponding to the $2^{1/2}$ and $4^{1/2}$ reflections from a square two-dimensional crystal lattice describing the packing of the ionic species. Temperature independent, the square lattice parameter found, $a=6{\cdot}15$ Å, is the same for all the compounds studied and is very close to that (6·04 Å) measured for the SmT phase of dialkyldimethylammonium bromides [4]. The molecular area, that is, the surface covered in the layers by the ammonium bromide groups, is thus: $S=a^2=(6{\cdot}15\,\text{Å})^2=37{\cdot}8\,\text{Å}^2$.

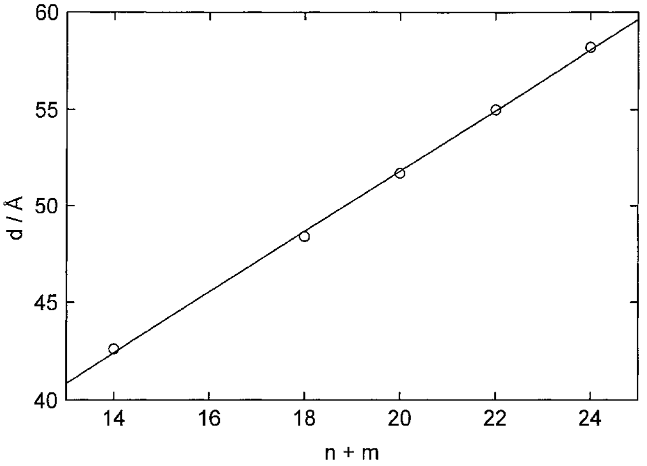


Figure 5. Linear variation of the period of the *n*,*m*-ONSAB compounds in the smectic state at 100°C as a function of the total number $(n+m)$ of carbon atoms in the alkyl chains.

The lateral tetragonal packing mode of the ionic species being thus established, it is important now to discuss the arrangement of the whole molecules in the smectic layers and, particularly, to decide whether the smectic structure is single or double layered. This may be done by analysing the linear dependence of the smectic period *d* on the number $(n+m)$ of carbon atoms in the alkyl chains. Indeed, the volume of one molecule is equal to $V=V_0+(n+m)\ V_{\text{CH2}}$ (where V_{CH2} and V_0 are the respective volumes of one methylene group and of

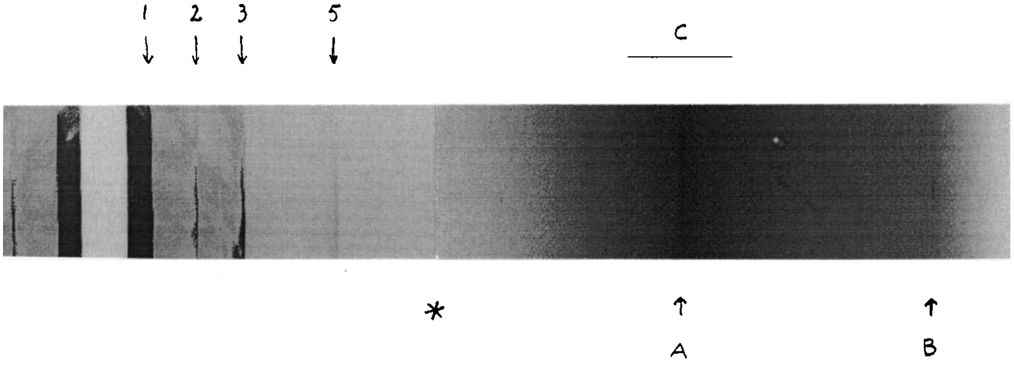


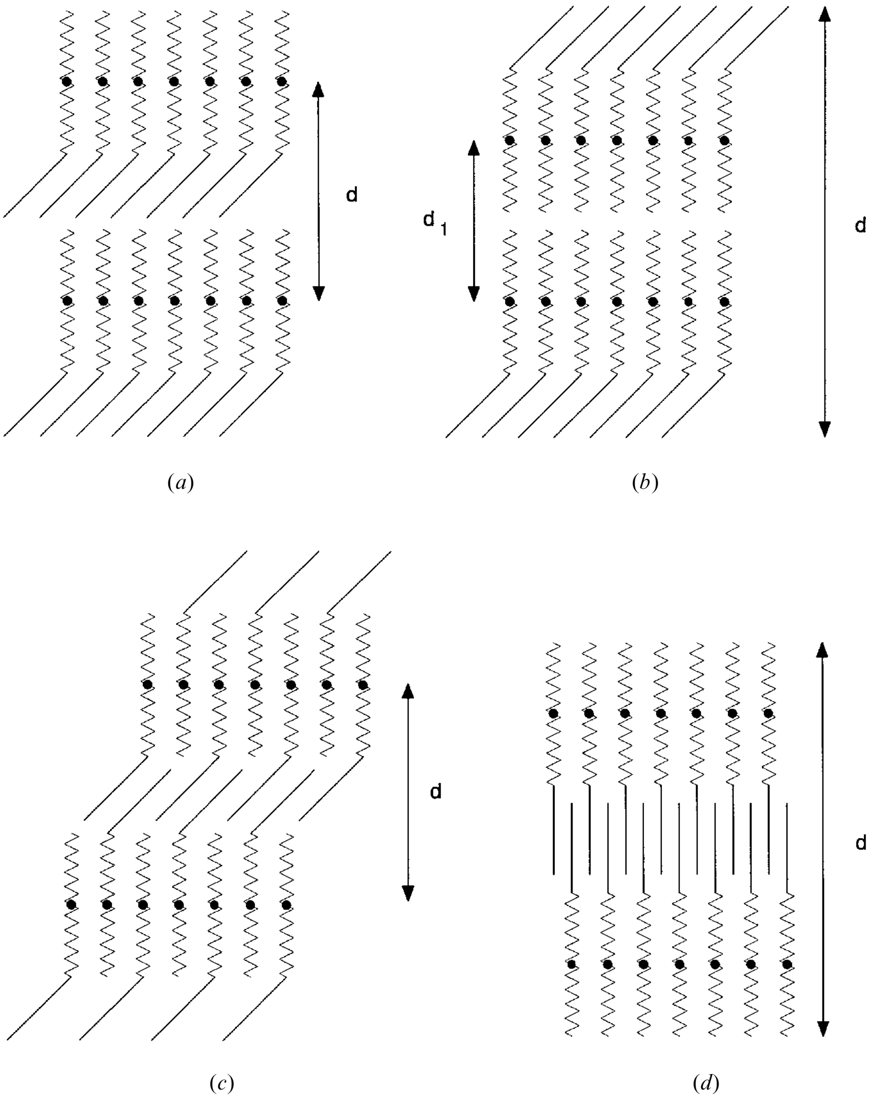
Figure 4. Powder X-ray diffraction pattern for 12,10-ONSAB in the smectic phase at 100°C (Guinier camera with a sample to film distance of 125 mm). 1, 2, 3, 5: sharp, small angle Bragg harmonics of the smectic layering; C: diffuse ring of molten alkyl chains; A, B: sharp, wide angle Bragg reflections of the tetragonal lateral packing of the ions. For clear reproduction of this pattern, its small angle and wide angle regions were scanned separately and their contrast and brightness were optimized independently. The star shows where the two images were joined.

one molecule deprived of all its methylene groups including those of the methyl end-groups of the alkyl chains). On the other hand, it is equal to Sd/ε (where ε is 1 or 2 depending on whether the smectic layers contain one (figures 6(*a*) and 6(*c*) or two (figures 6(*b*) and 6(*d*) ionic planes). The $(n+m)$ dependence of d may then be written as:

$$d = V/S = \varepsilon V_0/S + \varepsilon(n+m)V_{\mathrm{CH2}}/S$$

From the known value of V_{CH2} (=28 Å^3 at 100°C [6]) and from the slope ($\varepsilon V_{\mathrm{CH2}}/S = 1{\cdot}567$ Å) of the straight line d versus $(n+m)$ measured experimentally (figure 5), we can thus immediately deduce $\varepsilon = \mathrm{slope} \times (S/V_{\mathrm{CH2}}) = 1{\cdot}567 \times (37{\cdot}8/28) = 2{\cdot}1 \cong 2$ and conclude that, regarding the ionic species, the smectic structure is bilayered.

This arrangement of the ionic species is clearly supported by the intensity distribution of the small angle smectic reflections observed. It is useful to recall that in the case of the dialkyldimethylammonium bromides discussed previously [4], the intensity distribution was shown to decrease slowly as the Bragg angle increased up to at least the fifth harmonic (see figure 7), in conformity with the fact that the strongly diffracting ionic species, particularly the heavy bromine atoms, are confined to thin layers (about 5 Å thick). In the case of the compounds 12,*m*-ONSAB, the intensity distribution observed is conclusively different (see figure 7): the first harmonic is always much stronger than the following ones, and the ratio of the intensities of the second over the third harmonic decreases when m increases, passing from above unity for $m=6$, to unity for $m=8$, to below unity for $m=10$ and 12. Such a behaviour is in compliance with the ionic species being located in two distinct planes (figures 6(*b*) and 6(*d*)) separated by a double



(*a*) (*b*) (*c*) (*d*)

Figure 6. Schematic representation of possible smectic structures of *n*,*m*-ONSAB. The ionic groups (full circles) are arranged in single (*a* and *c*) or double (*b* and *d*) layers. Inside each molecular layer built on each side of the ionic planes, molecules are oriented in a parallel (*a*, *b* and *d*) or antiparallel (*c*) fashion. Inside each smectic layer, molecular layers are superposed over one another in a parallel (*a*) or antiparallel (*b* and *d*) fashion. The aromatic cores (straight lines) are arranged in single (*a*, *c* and *d*) or double (*b*) layers. The dependence of the smectic period on the length of the alkyl chains (figure 5) and the distribution of the smectic Bragg reflections (figure 7) exclude models (*a*) and (*c*). Smaller than twice the cross-sectional area of extended alkyl chains (2 × 22 Å^2), the square unit cell area measured experimentally (37·8 Å^2) excludes model d.

layer of dodecyl chains of thickness $d_1 = 18{\cdot}8$ Å. The value of d_1 can easily be deduced from the observed $(n+m)$ dependence of the smectic period: $d/\text{Å} = 20{\cdot}47 + 1{\cdot}567\ (n+m)$. Indeed, for $n=12$, the spacing $d_1 = 12 \times 1{\cdot}567 = 18{\cdot}8$ Å. The intensity distribution $I(s)$ $(s = 2\sin\theta/\lambda)$ for a smectic structure containing two planes of strongly diffracting atoms (here the bromine atoms) separated by a distance d_1 is proportional to $[\cos(\pi d_1 s)/s]^2$. Thus $I_2/I_3 = [3\cos(\pi d_1 2/d)/2\cos(\pi d_1 3/d)]^2$. It follows that $I_2/I_3 = 1{\cdot}65$, $1{\cdot}01$, $0{\cdot}678$, $0{\cdot}275$ for $m = 6$, 8, 10, 12.

It is important to add that the double layered arrangement of the molecules does not only apply to the ionic species, but also to the aromatic cores. The alternative model, involving mono-layers of interdigitated calamitic cores arranged head to tail (figure 6 (*d*)), is totally unacceptable here, because the available molecular area in the smectic planes ($37{\cdot}8$ Å^2), determined by the ionic species, is much smaller than twice the cross-sectional area of the cores ($\approx 2 \times 22$ Å^2). Arranged in double layers, the aromatic cores are then tilted with respect to the smectic planes (figure 6 (*b*)) by an angle of $\cos^{-1}(22/37{\cdot}8) \cong 54$ degrees. They are allowed therefore to arrange laterally according to a hexagonal lattice (see figure 1).

5. Concluding remarks

We started the present work with the implicit assumption that the interactions of the oxynitrostilbene parts of the *n*,*m*-ONSAB smectogenic molecules are not so strong as to outbalance the coulombic forces among the ionic ammonium bromide groups and thus stand against their natural tendency to arrange within their sublayers in an ordered tetragonal fashion. Using X-ray diffraction, we have found that the *n*,*m*-ONSAB compounds do effectively exhibit an ordered smectic phase of tetragonal symmetry.

From the measured parameter of the square lattice we found that the area covered by the ammonium bromide groups in the smectic layers ($37{\cdot}8$ Å^2) was by far smaller than twice the cross-sectional area of the aromatic cores (2×22 Å^2); we thus concluded that the aromatic cores cannot adopt an interdigitated upright arrangement in single layers, but must be strongly tilted away from the layer normal. By analysing the intensity distribution of the smectic reflections and the variation of the smectic period as a function of the length of the alkyl chains, we showed that each smectic layer contains a double layer of tilted aromatic cores and two layers of ammonium bromide groups separated from one another by layers of alkyl chains in a disordered conformation, as illustrated in figure 6 (*b*).

It is worth noting parenthetically that, at the beginning of this work, we thought optimistically that the electrical repulsions of the surface charges of the molecular layers (see figure 2) might very well favour a parallel (see figure 6 (*a*)) over an antiparallel (see figure 6 (*b*) stacking of the layers, letting us anticipate a possibility for building a ferroelectric system with the polarization vector normal to the smectic layers. As just mentioned, however, such is not the case. Probably, the polarization of the oxynitrostilbene cores is too weak to counterbalance the van der Waals attractions of the like sublayers.

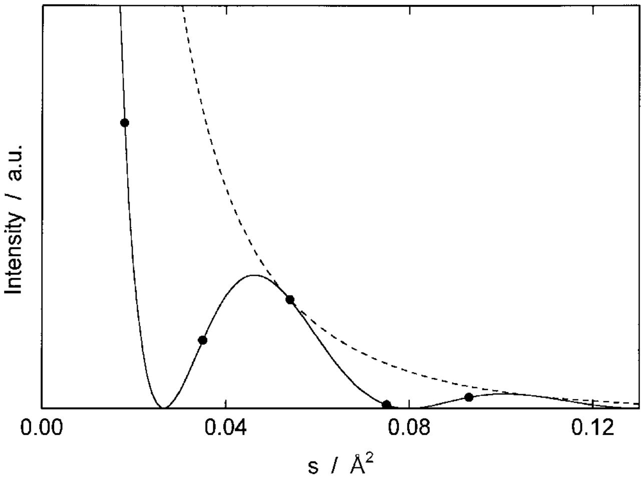


Figure 7. Intensity distribution of X-rays scattered in the small angle region from single (dashed line) or double planes of ions (solid line) according to functions $(\sin\pi bs/\pi bs)^2/4\pi s^2$ or $(\cos\pi d_1 s)^2\ (\sin\pi bs/\pi bs)^2/4\pi s^2$, respectively. In these functions, $s\ (=2\sin\theta/\lambda)$ is the reciprocal Bragg spacing; b and d_1 represent the thickness of one ionic layer (5 Å [4]) and the separation of the double layers. The factor $4\pi s^2$ accounts for the isotropic symmetry of the scattering from powder samples. Black dots on the solid line correspond to the first five harmonics of 12,10-ONSAB in the smectic state.

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References

[1] Gray, G. W., and Goodby, J. W., 1984, *Smectic Liquid Crystals* (Glasgow: Leonard Hill).
[2] Kitaigorodskii, A. I., 1961, *Organic Chemical Crystallography* (New York: Consultants Bureau Enterprises).
[3] Seurin, P., Guillon, D., and Skoulios, A., 1981, *Mol. Cryst. liq. Cryst.*, **71**, 51.
[4] Alami, E., Levy, H., Zana, R., Weber, P., and Skoulios, A., 1993, *Liq. Cryst.*, **13**, 201.
[5] Arkas, M., Yannakopoulou, K., Paleos, C., Weber, P., and Skoulios, A., 1995, *Liq. Cryst.*, **18**, 563.
[6] Guillon, D., Skoulios, A., and Benattar, J. J., 1986, *J. Phys., Paris*, **47**, 133.