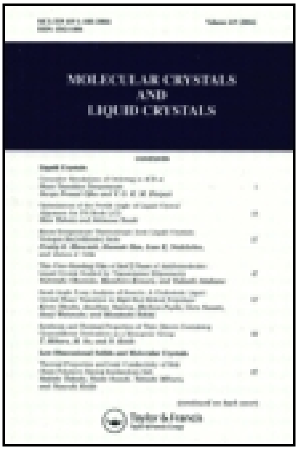

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Thirmotropic Smectic Liquid Crystals of Ionic Amphiphilic Compounds: A General Discussion

Vincenzo Busico [a], Angelo Ferraro [a] & Michele Vacatello [a]

[a] Dipartiomento de Chimica dell'Università, Via Mezzocannone, 4, 80134, Napoli, Italy

Version of record first published: 20 Apr 2011.

To cite this article: Vincenzo Busico, Angelo Ferraro & Michele Vacatello (1985): Thirmotropic Smectic Liquid Crystals of Ionic Amphiphilic Compounds: A General Discussion, Molecular Crystals and Liquid Crystals, 128:3-4, 243-261

To link to this article: http://dx.doi.org/10.1080/00268948508079494

Mol. Cryst. Liq. Cryst., 1985, Vol. 128, pp. 243–261
0026-8941/85/1284-0243/$20.00/0

Printed in the United States of America

Thermotropic Smectic Liquid Crystals of Ionic Amphiphilic Compounds: A General Discussion.

VINCENZO BUSICO, ANGELO FERRARO and MICHELE VACATELLO

Dipartimento di Chimica dell'Università, Via Mezzocannone, 4
80134 Napoli (Italy)

(*Received October 9, 1984*)

Starting from a reinvestigation of the long chain Na *n*-alkanoates in the molten state, the mesomorphism of amphiphilic molecules comprising an alkyl chain and an ionic endgroup is generally discussed.

Two different smectic mesophases of the 'neat' type can occur for these compounds: smectic I, viscous and birefringent, with regular layer stacking; smectic II (often described in the literature as a conventional liquid), fluid and optically isotropic, due to the small dimensions of the liquid crystalline domains, and with fluctuations in the interlayer distances, as indicated by its X-ray diffraction pattern.

Possible structural arrangements of the ionic end-groups in the smectic layers are presented, and the differences experimentally observed between short chain and long chain compounds explained in terms of a simple electrostatic model. In agreement with the experimental finding, the mesomorphic state is evaluated from the model to be stable relative to the isotropic state up to temperature well above those at which thermal decomposition occurs.

INTRODUCTION

This paper deals with thermotropic liquid crystals of molecules comprising an alkyl chain with an ionic end-group (general notation RAB).

Smectic liquid crystals of anhydrous alkali metal alkanoates are known at least since 1910, with the first published report of Vorlander.[1] Later systematic investigations were carried out by Luzzati and coworkers[2] and by Ubbelohde and coworkers.[3] The well-known lamellar model for the structure of these mesophases (Figure 1) is due to Luzzati ("les groupes polaires sont localisés en double couche dans des feuillets indéfinis, parallèles et équidistantes, séparés par

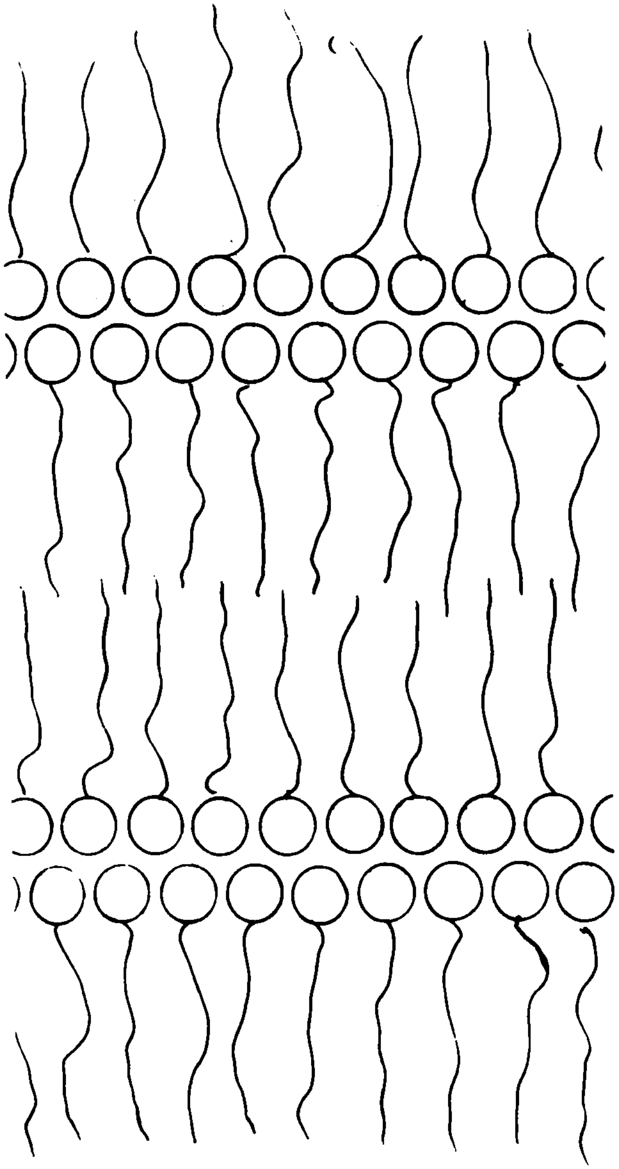

FIGURE 1 Schematic model of the structural arrangement of RAB molecules in the lamellar 'neat' mesophase (red. from ref. 2a)

les chaînes paraffiniques à l'état liquide").[2a] The textures, X-ray diffraction patterns and transport properties are typical of smectic A (or "neat") phases.[4-6] Clearing to conventional isotropic liquid is reported, on average, 30–100 K above the melting temperature,[2,3,7]

More recently, we found similar mesophases for two more classes of compounds: bis(*n*-alkylammonium) tetrahalogenozincates[8] and primary *n*-alkylammonium halides.[9]

Comparison of melting and clearing parameters for the latter compounds with literature data on the alkali metal alkanoates gives evidence of a common mesomorphic behavior qualitatively independent of the end-group[9] (Figure 2). On the other hand, our X-ray diffractometric investigation of the alkylammonium halides[9] revealed that the clear liquid itself is a smectic mesophase, structurally similar to the birefringent liquid but with considerable fluctuations in the interlayer distances and much smaller domains (unable to diffract visible

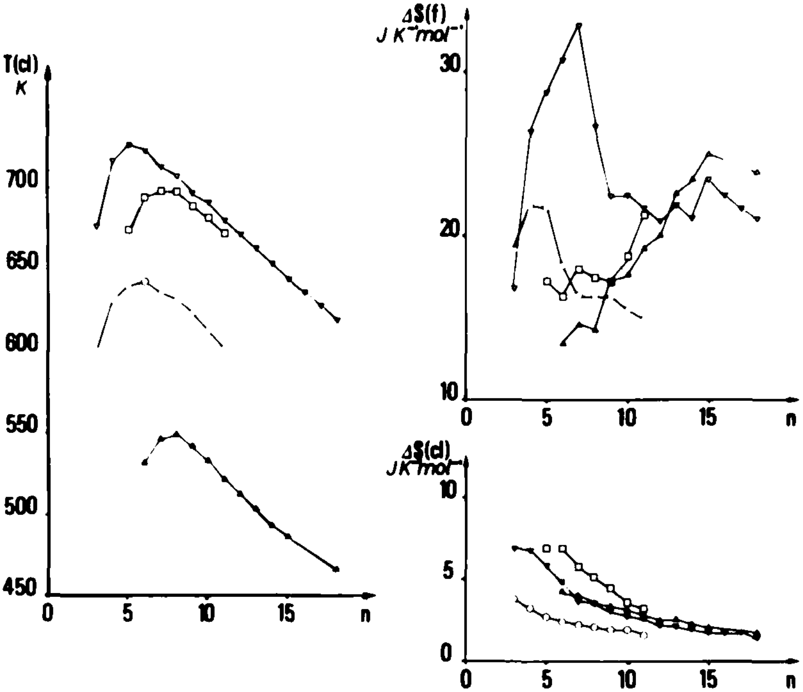

FIGURE 2 Clearing temperatures, T(cl); melting entropies, ΔS (f); clearing entropies, ΔS (cl) vs. the number, n of chain C atoms for primary *n*-alkylammonium chlorides (△), and for Na (○), K (▽) and Cs (□) *n*-alkanoates.

light). Ref. 9 describes thoroughly both mesophases, denominated with increasing temperature as Smectic I, Smectic II.

In a following paper,[10] we proved that molten lithium *n*-hexadecanoate (palmitate), reported to be a conventional isotropic liquid,[7g,11] is a smectic mesophase strictly analogous to Smectic II of the alkylammonium halides. As for the latter, the liquid phase remains anisotropic up to temperatures at which thermal decomposition begins.

In our opinion, a number of questions are raised by these results. First, is the anisotropy of the clear liquid a general fact for RAB compounds? If so, what is the extent of this anisotropy, and up to what temperatures is it maintained? Is there a general explanation for the trends in melting and clearing parameters of Figure 2? Finally, is the model of Figure 1 for the mesomorphic liquid qualitatively adequate and quantitatively improvable?

To answer the first question, we reinvestigated the classical Na alkanoates. In the literature, some evidence is found of a possible anisotropy of the clear liquid *a few degrees above the clearing temperature*. In a study of Na isovalerate,[3a] Ubbelohde et al. report that, "from X-ray photographs just above the clearing point, T_{cl} = 280°C, it was at first inferred that long spacing order was partly retained, even in the isotropic melt. However at somewhat higher temperature, about 290°C even those residual crescents vanished, leaving only a uniform halo typical of liquid structures". The apparent persistence of some long-range order for a few degrees above T_{cl} was attributed to wall effects on the sample sealed in a Lindemann capillary. In an investigation of longer chain compounds,[2b] Luzzati et al. report that "X-ray photographs taken at a temperature a few degrees above the melting point (they refer to the clearing transition) contain two or three fairly sharp bands ("bands floues" in another paper)[2a] corresponding to the Bragg spacing of neat soap. This observation suggests that the structure of the melt is quite similar to that of the neat phase." No data are given of the possible persistence of this anisotropy at higher temperatures.

In Figure 3, the melting and clearing temperatures of Na *n*-alkanoates are reported as a function of the number, n of C atoms in the alkyl chain. Data for compounds with $n > 19$ are not reported in the literature. However, the trends of Figure 3 suggest that, for compounds with $n >$ ca. 20, the clearing temperatures would be lower than the melting temperatures, and no birefringent neat mesophases should be observed. We synthesized the compounds with $n = 18$, 20, 22 and performed the X-ray characterization of their melts up to

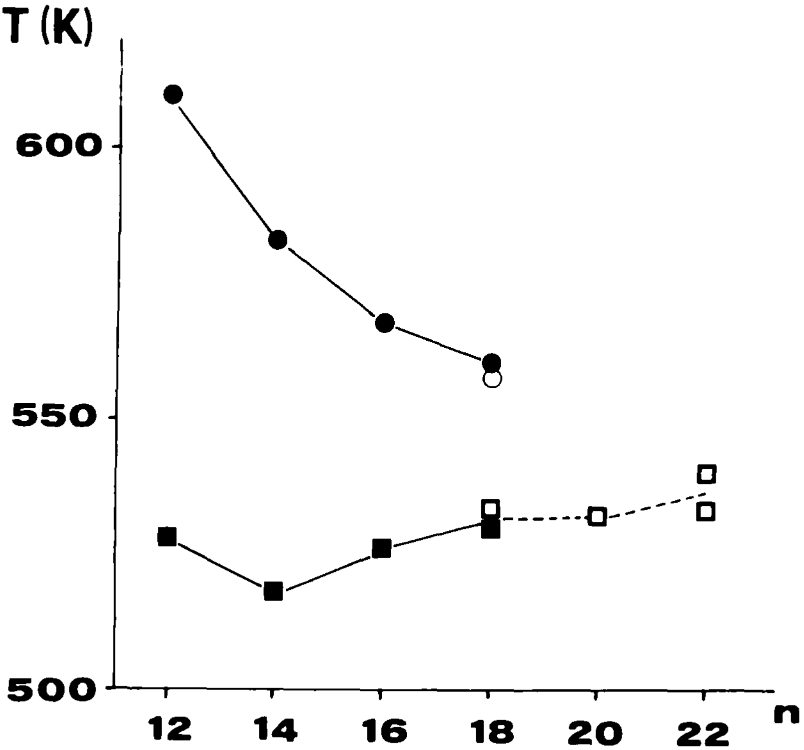

FIGURE 3 Melting (■, from ref. 2a; □, this work) and clearing (●, from ref. 2a; ○, this work) temperature vs. the number, n of chain C atoms for several long chain Na *n*-alkanoates.

570 K. From the results obtained, we start for a more general discussion of these highly interesting smectogens, in which possible answers to all other questions are attempted. As often happens for liquids, much of the discussion is devoted to semiquantitative evaluations of models, but emphasis is always given to the explanation of known experimental facts.

EXPERIMENTAL

Na *n*-octadecanoate, *n*-eicosanoate and *n*-docosanoate were synthesized reacting sodium sand with a slight excess of the proper *n*-alkanoic acid in toluene under reflux, as described in ref. 7c,e. The products were washed with dry acetone, recrystallized from acetone/2-propanol mixtures and dried under vacuum. The samples recovered from this preparation are rigorously anhydrous. Different syntheses were also attempted (see refs. 2a, 2b, 12, 13), all giving samples retaining some water and/or alcohol difficult to strip even under vacuum from molten specimens.

DSC curves of all samples were registered with a Mettler TA-3000 differential scanning calorimeter in the range 250–700 K. The temperature scale was calibrated with pure reference compounds. Transition enthalpies were measured by electronic integration using as a standard a sample of pure Indium (Δh_m = 28.4 Jg^{-1}).

X-ray photographs were taken on a flat plate camera equipped with a home-made variable temperature sample-holder (temperature control within ± 1.5K). The samples were sealed in 0.5 mm Lindemann capillaries. Ni-filtered CuKα radiation (λ = 1.5418 Å) was used throughout. The geometry of the apparatus, accurately calibrated with pure reference compounds, allowed to collect reflections corresponding to Bragg distances comprised between 2Å and 45Å. All the photographs were subjected to microdensitometric reading.

Optical observations were made with a Leitz polarizing microscope equipped with a Mettler FP-5 heating desk.

RESULTS

The thermal behavior of long chain Na *n*-alkanoates is known to be quite complex. Discussion of the polymorphism in the solid state is out of the scope of this paper. Our results on Na *n*-octadecanoate, anyway, substantially confirm those reported in ref. 13 by Pacor and Spier. As also remarked by these authors, we observed that traces of water and/or alcohol in the samples are able to induce additional high-enthalpy transitions in the range 340–400 K.

Melting and clearing parameters for the three Na salts prepared in this work, as obtained from heating DSC curves, are given in table 1. A clearing transition is observed only for Na *n*-octadecanoate and — as found in one case for *n*-pentadecylammonium chloride[14] — it occurs as a sharp peak with two unresolved maxima (Figure 4).

Microscopic observations in polarized light show that the melt of Na *n*-octadecanoate is birefringent below the clearing point, whereas molten Na *n*-eicosanoate and *n*-docosanoate, as well as *n*-octadecanoate above its clearing point, are dark when observed between crossed polaroids.

Microdensitometric traces of the X-ray photographs of the three Na salts in the molten state are reported in Figure 5. All show a

TABLE I

Melting and clearing temperatures, enthalpies and entropies for Na *n*-octadecanoate, *n*-eicosanoate and *n*-docosanoate from DSC heating scans.

n	T (K)		ΔH ($kJmol^{-1}$)	ΔS (JK^{-1} mol^{-1})
18	534	(f)	10.12	18.95
	557 559	(cl)	1.26	2.26
20	533	(f)	9.34	17.52
22	534 541	(f)	10.79	20.06

strong (001) reflection at low angles, corresponding to a Bragg distance listed in table 2. The half-width of the reflection for molten Na *n*-octadecanoate below the clearing point is comparable with that of the same line in the crystal, as is typical for a Smectic I phase.[9] In all other cases, the reflections are considerably broadened, but still intense at least up to 570 K. Therefore, for these compounds also the clear liquid is mesomorphic, a layer organization being retained. If we attribute the observed (001) line broadening to fluctuations in

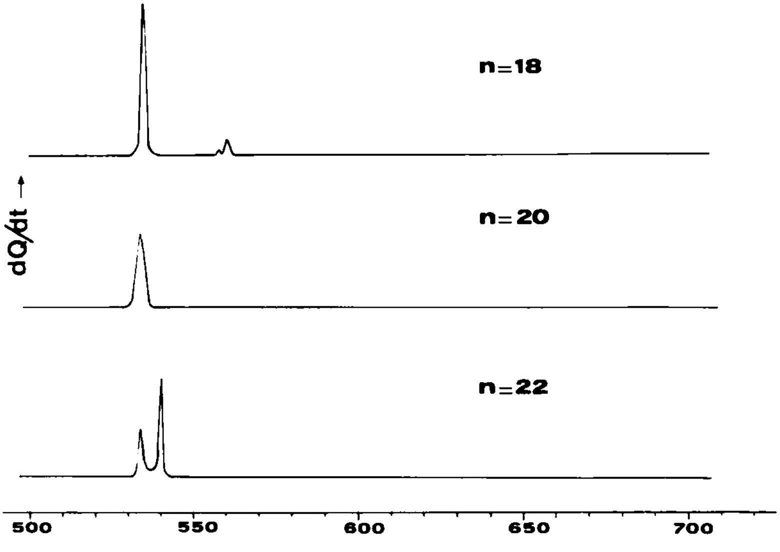

FIGURE 4 DSC heating curves in the temperature range 500–700 K for Na *n*-octadecanoate, *n*-eicosanoate and *n*-docosanoate.

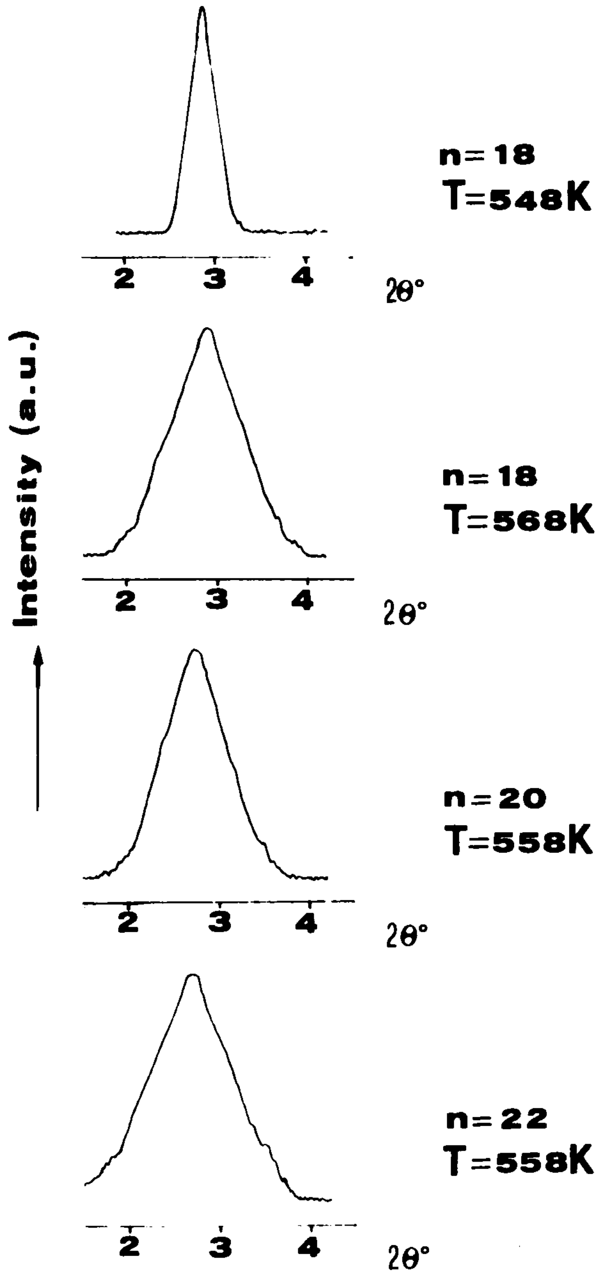

FIGURE 5 X-ray diffraction profiles for the 'neat' mesophases of Na *n*-octadecanoate, *n*-eicosanoate and *n*-docosanoate.

TABLE II

Long spacing, c and monodimensional paracrystallinity factor, g for the 'neat' - type mesophases of Na *n*-octadecanoate, *n*-eicosanoate and *n*-docosanoate.

n	T (K)	c (Å)	g
18	548	30.8	
	568	30.3	0.12
20	558	31.9	0.14
22	558	32.5	0.14

the interlayer distances analogous to paracrystalline distortions of the second kind, a monodimensional paracrystallinity factor, g can be calculated[9] from the X-ray patterns, which is also given in table 2. The obtained g values coincide with those found for the Smectic II phases of the alkylammonium chlorides of comparable chain length. We can conclude that Na *n*-octadecanoate melts to a Smectic I - type mesophase, which changes to a Smectic II - type mesophase at the clearing point; on the other hand, as expected from Figure 3, Na *n*-eicosanoate and *n*-docosanoate melt directly to a Smectic II - type mesophase.

Due to the high melting points of the Na salts, using our X-ray apparatus it was not possible to characterize the clear liquids at temperatures higher than ca. 20 K above the clearing (melting) point. In addition, thermal decomposition is anyway a serious drawback for measurements at higher temperatures.

On the other hand, the diffracted intensity of the (001) reflection for the Smectic II phase of Li *n*-alkanoates, which melt at considerably lower temperatures, remains practically unchanged within 60K above the melting temperature.[10]

DISCUSSION

As for the Li homologues[10] and for the alkylammonium halides,[9] the clear melt of long chain Na alkanoates is mesophasic. It is thus confirmed that RAB compounds are able to give two different smectic phases: one viscous and birefrigent, with regular layer stacking and large domains; another fluid and optically isotropic due to the small size of the smectic domains, and with fluctuations in the interlayer distances, as shown by the broadening of the (001) reflection and the absence of (001) lines with l > 1 in its X-ray patterns. We suggest the new general denominations of Smectic I, Smectic II respectively, also to stress the difference between such mesophases and those of rigid mesogens with high axial ratios. For the latter, indeed, the reasons for the stability of the mesomorphic state are mainly entropic, whereas for RAB compounds they can be found in the tendency of the ionic end-groups to aggregate in layers in order to minimize their electrostatic energy.[9,10] In ref. 9, we also explained in a qualitative way why, in contrast to aqueous solutions, other structural arrangements such as micelles or vesicles are ruled out in the absence of a solvent.

A quantitative evaluation of the stability of the mesomorphic relative to the isotropic state would require a detailed knowledge of the structure of both states. For RAB molecules, possible models can be proposed.

From the most recent investigations on the isotropic melts of *n*-alkanes[15,16] and of simple AB - type salts,[17] a reasonable model for the isotropic melt appears that of unperturbed alkyl chains each ending with an ion pair. At least from a given chain length up, we can assume each ion pair isolated from the others, since it would be diluted in a hydrocarbon liquid with low dielectric constant.

For the model of the mesomorphic state, we start from the scheme of Figure 1, in which double ionic layers are postulated, but no information is given concerning the relative positions of the anions and cations.[2] From ^{23}Na - NMR data on short chain Na *n*-alkanoates and through two successive interpretations[6,18] Jonas et al. propose the 'quasi-crystalline' model of Figure 6, supporting their view with the fact that a similar arrangement of the ions is found in the crystalline layer structures of K *n*-decanoate[19] and K *n*-hexadecanoate.[20] Actually, the same arrangement was proposed by two of us[9] for the plastic phase of the primary *n*-alkylammonium chlorides; a possible unit cell is sketched in Figure 7. This model can be tested with a simple check. From X-ray diffractometric and density measurements, Ubbelohde et al.[3] and Luzzati et al.[2] calculated, for the Smectic I phases of several alkali metal alkanoates, the values of average cross section, S of each chain in its basel layer listed in table 3 (the data of ref. 3, wrong by a factor 2 in the original paper, have been corrected). The table gives also the S values found for the same compounds in their crystalline layer structures.[2,3] It is seen that if, for short chain compounds, the S values for Smectic I are only 10–20% higher than those for the crystal, for long chain compounds they are almost twice those for the crystal. This means that the model of Figure

TABLE III

Cross-sections, S of the *n*-alkyl chains in the basal layers of Na and K *n*-alkanoates in the room-temperature crystalline bilayer structures and in the Smectic I mesophases (data from ref. 2,3)

	Compound	S (Å^2)-Smectic I	S (Å^2)-Crystal
(a) RCOONa	*n*-Butanoate	24	22
	2-methyl-butanoate	29	29
	n-Dodecanoate	36	24
	n-Tetradecanoate	38	23
	n-Hexadecanoate	40	23
	n-Octadecanoate	42	25
(b) RCOOK	*n*-Octanoate	33.3	25.3
	n-Decanoate	34.6	25.4
	n-Dodecanoate	35.7	25.5
	n-Tetradecanoate	37.0	25.4
	n-Hexadecanoate	39.6	25.1
	n-Octadecanoate	41.7	25.0

7 for the ion packing in the mesomorphic state, if not unreasonable for short chain compounds, is unrealistic for long chain ones. The same limits apply also to Figure 1. In Figure 8, we sketch a possible 'quasi-crystalline' model for the ionic planes in the mesomorphic liquid with S values twice those for the crystal: a *single* ionic layer with chains pointing alternatively in opposite directions.

We suggest that, with increasing chain length, the structural arrangement in the smectic layers changes from a limiting structure not far from that of Figure 7 towards a limiting structure not far from that of Figure 8. In all cases, *in a first approximation* (see further), the conformational disorder of the alkyl chains can be considered complete.[2,3,9,10]

Now that we have derived possible structural models for both the mesomorphic and the isotropic liquid, we can try to evaluate quantitatively the difference in their stability. The basic idea is that , since the conformational entropy of the alkyl chains is substantially the same in both states, and the residual translational and orientational entropy of the mesomorphic liquid expected to be low (it is on average 1–10 J K^{-1} mol^{-1} for Smectic A),[21] the electrostatic energy alone would account mainly for this difference.

Figure 9 gives preliminary results of a calculation performed in this laboratory (the details of which will be given in a following paper).[22] Square ionic layers of composition A^+B^- (the ions A^+,B^- represented by point charges) were grown through bidimensional trans-

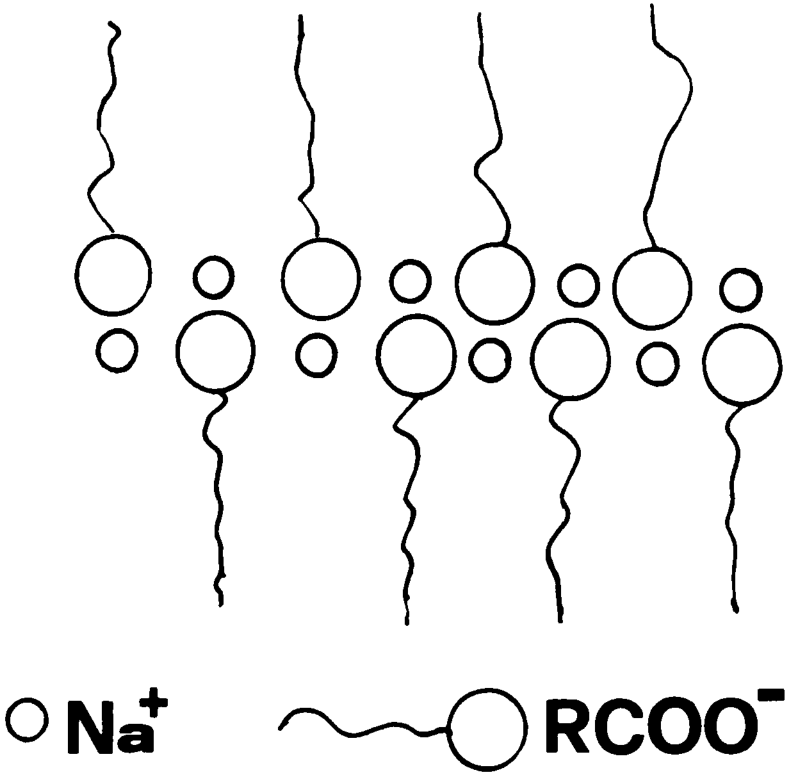

FIGURE 6 'Quasi crystalline' model of the ion packing in the 'neat' mesophases of Na *n*-alcanoates(ref. 18).

lation of the unit cells represented in Figures 7, 8; the cell parameters (table 4) were chosen in order to reproduce approximately the ion packing in the ionic layers of *n*-alkylammonium chlorides in the plastic tetragonal modification.[9] The Coulomb energy of the layers per mole of A^+B^- was calculated, and plotted as a function of the layer side length in Figure 9. From the plots, it can be seen that, as expected, with increasing layer side length the molar Coulomb energy reaches a limiting value. This is ca. 250 kJ for the double layer of Figure 7, ca. 200 kJ for the single layer of Figure 8 lower than the value of the Coulomb energy per mole of isolated ion pairs (represented by the circle in Figure 9). Though these values (as well as the structural models for which they were calculated) might be only a first approximation of the real ones and are obviously dependent on the cell parameters and on which ions are considered, we believe that they give the correct order of magnitude for the relative stability of the

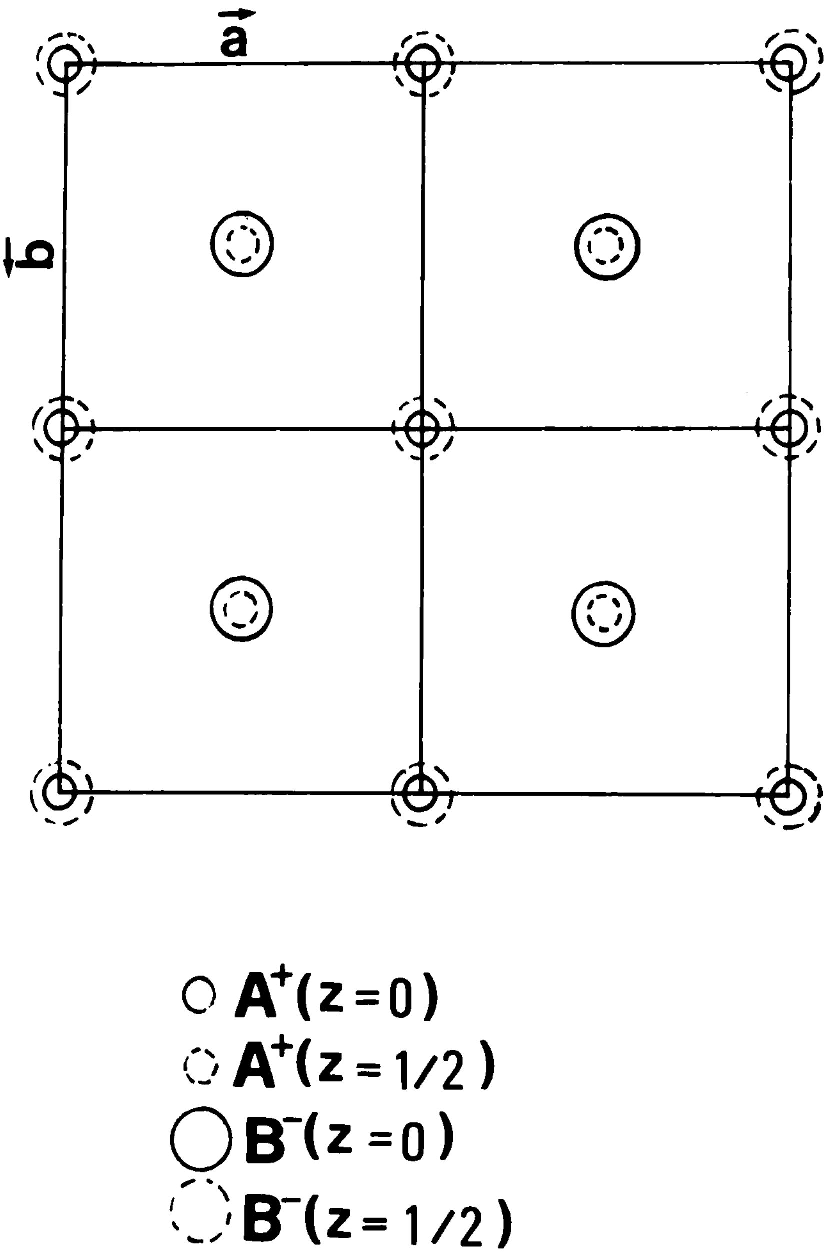

FIGURE 7 Double-layer 'quasi crystalline' model of the ion packing in the 'neat' mesophases of RAB compounds (see also table 4).

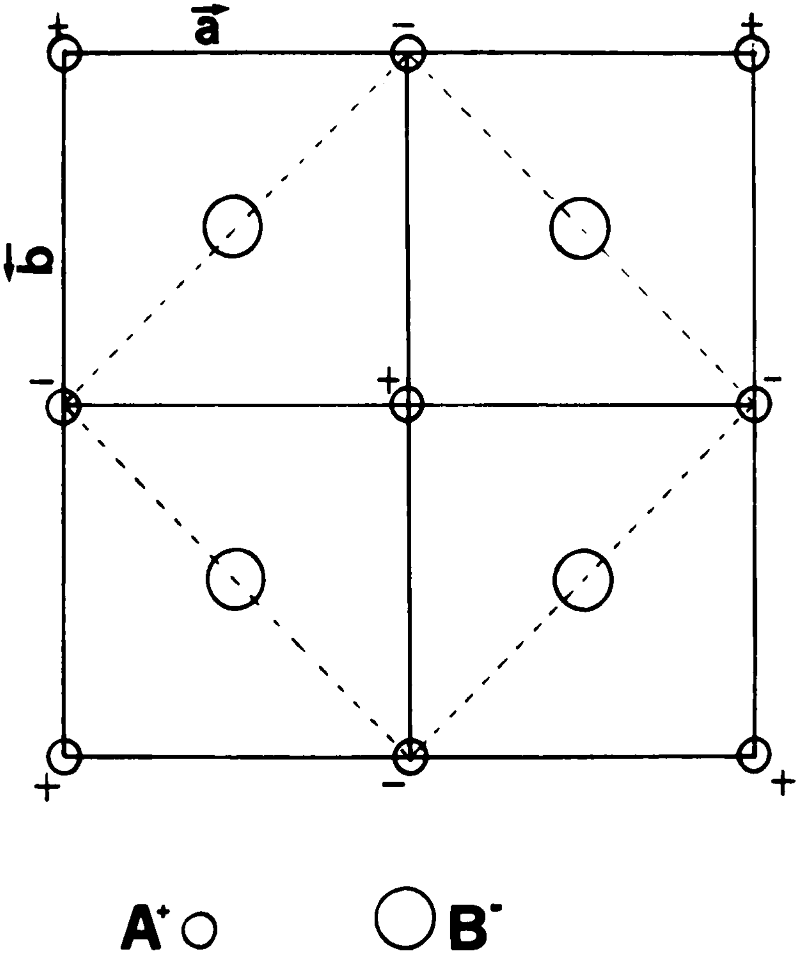

FIGURE 8 Single-layer 'quasi crystalline' model of the ion packing in the 'neat' mesophases of RAB compounds (see also table 4); + :upward chain; - :downward chain. The average cross section, S of a chain in its basal layer is shown by the dashed line.

mesomorphic and of the isotropic liquid for RAB compounds. If so, it is easily explained why, at ordinary temperatures, a true isotropic liquid has never been observed for RAB, at least from a given chain length up (see further): with a residual translational and orientational entropy for the mesomorphic state of the order of R, temperatures of the order of 10^4K would be necessary to stabilize the true isotropic state.

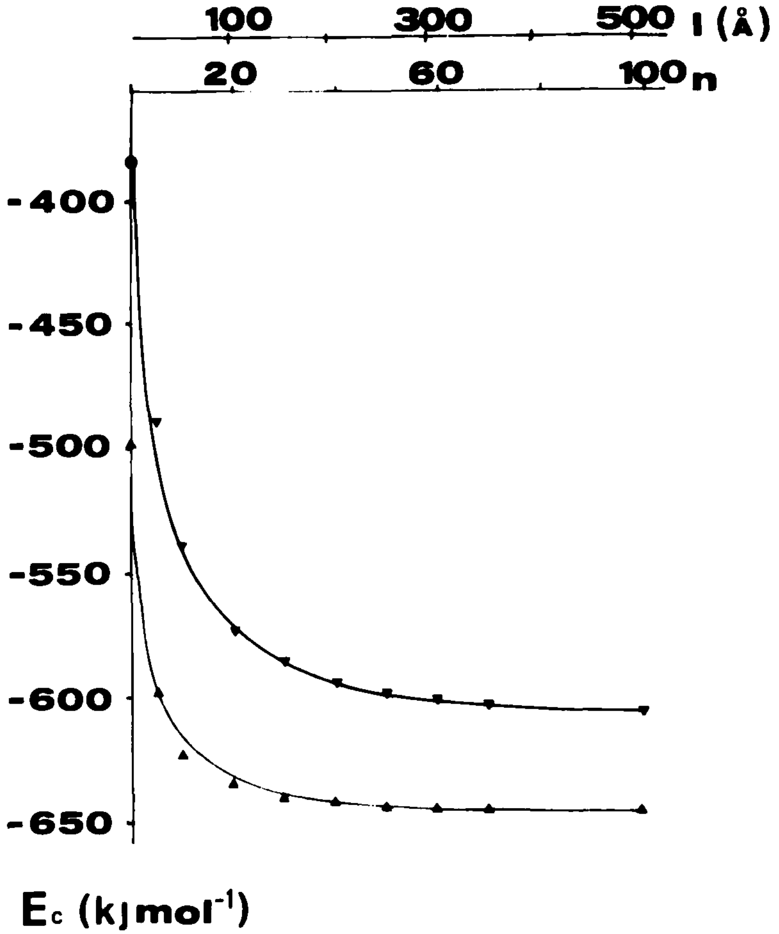

FIGURE 9 Coulomb energy, E_c per mole of ion pair A^+B^- vs. layer side length, l and number, n of unit cells along the layer side for a square ionic double layer (Δ, fig. 7) and single layer (∇, fig. 8). For the unit cell parameters, see table 4. The E_c value for an isolated A^+B^- ion pair is represented by the full circle (●).

For a given layer, it is seen from Figure 9 that the limiting value of molar Coulomb energy is approached for layer side lengths of the order of 200–300 Å; smaller layers become rapidly much less stable. Since typical values of molar clearing enthalpies for RAB compounds are in the range 1–5 kJ mol^{-1},[7,9] 200–300 Å would appear as the lower limit for the layer side length in Smectic II. This figure is totally adequate to explain why Smectic II is not birefringent (visible light

TABLE IV

Unit cell parameters and fractional coordinates of the ions for the calculations of electrostatic energy (see text and Figure 9)

Double layer, S = 26 Å^2 (fig. 7):	$\bar{a} = \bar{b} = 5.10$ Å; $\bar{c} = 3.60$ Å ($\bar{c}$ is not a repetition axis) $\alpha = \beta = \gamma = 90°$ A_1^+ (0,0,0); A_2^+ (1/2,1/2,1) B_1^- (0,0,1); B_2^- (1/2,1/2,0)
Single layer, S = 52 Å^2 (fig. 8):	$\bar{a} = \bar{b} = 5.10$ Å; $\gamma = 90°$ A^+ (0,0); B^- (1/2,1/2)

has wavelengths in the range 4000–7000 Å) but able to give strong Bragg diffractions in its X-ray patterns.

We have now to explain the variations in ion packing when changing from short chain to long chain compounds. The experimental evidence is that the longer the alkyl chain, the higher is the area, S per chain in the layers (table 3) and - according to our models - the Coulomb energy per mole of ion pairs (Figure 9).

In this context, the first step is to recall that the conformational statistics of an alkyl chain in a layer environment is perturbed by excluded volume interactions with the neighboring chains with a resulting loss of conformational entropy.[23] The entropic reduction decreases with increasing cross-section, S of the chain in its basal layer;[23] from experimental measurements on model compounds from this laboratory, it can be estimated as ca. 0.3 R per mole of CH_2 when S = 26 Å^2,[24] ca. 0.1 R when S = 36 Å^2 [25] (the melting entropy of *n*-alkanes being 1.2 R per mole of CH_2).[26] This means that an alkyl chain in a layer environment will exert a 'lateral pressure'[27] in order to increase its cross-section in the basal layer and - correspondingly - its conformational entropy. For each chain, the total entropic gain which can be obtained increases with increasing chain length.

According to our models of Smectic I, Smectic II, an increase in electrostatic energy must be compensated by a chain in these phases to increase its cross-section S; such an increase can be shown to be proportional to the S increase,[22] but is independent of chain length. This would explain why longer chains can obtain higher S values, as shown by table 3.

An internal check of our hypotheses can be made. Table 3 reports for Na and K *n*-octadecanoates an increase in S from ca. 25 Å^2 in the crystalline state to 42 Å^2 in the Smectic I phase. From Figure 9, a corresponding increase in electrostatic energy of the order of 20 kJ mol^{-1} can be estimated (it would be ca. 40 kJ mol^{-1} from 26 Å^2 to 52 Å^2). As for all known RAB compounds, the crystalline phases which melt have conformationally disordered alkyl chains. With a residual conformational entropy of the chains of the order of 0.3 R per mole of CH_2 at S = 25 Å^2 and virtually zero at S = 42 Å^2,[24,25] the entropic gain of the *n*-octadecyl chain following the ionic lattice expansion would be ca. 4.8 R. At the melting point (T_m = 534 K for Na *n*-octadecanoate (table 1); 542 K for K *n*-octadecanoate),[7f] it would be $T\Delta S_{conf}$ = 21 kJmol^{-1}, identical to the postulated increase in electrostatic energy. We should also expect measured melting enthalpies of the same order of magnitude. The experimental melting enthalpy of Na *n*-octadecanoate is 10.1 kJmol^{-1} (table 1), that of K *n*-octadecanoate 11.8 kJmol^{-1};[7f] unfortunately these values, which would be anyway in an order-of-magnitude agreement with our calculations, must be used with same care because the crystalline phases which melt are not lamellar, but super-reticular ribbon phases.[2a-2c] On the other hand, the experimental melting enthalpy of *n*-octadecylammonium chloride from a crystalline lamellar to a Smectic I phase is 23.8 kJ mol^{-1}.[9]

No values of S like those of table III for Smectic I are available for Smectic II. From the observed collapse in interlayer distances[9] and increase in molar volumes[3a,12] at the Smectic I → Smectic II transition, anyway, an increase in S is to be desumed for each compound following this transition.

At this point, an overall picture of melting and clearing transitions for RAB compounds capable to explain the observed trends of Figure 2 can be drawn. Compounds with very short or very long chains deserve special attention, and will be considered separately.

As also remarked elsewhere,[9] melting mainly implies the bidimensional disordering of the ionic layers from the crystalline to the liquid crystalline organization. The conformational disordering of the alkyl chains indeed takes place at lower temperature (polymorphic transitions in the solid state), apart from the residual entropy of which we have discussed. Therefore, we should expect for the melting parameters a substantial independence of chain length, as confirmed by Figure 2. Actually, liberation of residual conformational entropy allowed by the gradual increase of S in Smectic I with increasing chain length should imply a corresponding slight increase in molar melting enthalpies and entropies, as also seen from Figure 2. The absolute values of molar melting enthalpies for each series of compounds depend on the nature and structure of the ionic layers in the crystalline and liquid crystalline states; it is interesting, anyway, to observe that their order of magnitude is the same for all RAB compounds, and not much different from that for AB-type salts without conformationally flexible bonds.[28]

The increase in S with increasing chain length (table III) implies that Smectic I is gradually less organized the longer are the molecules. A corresponding decrease in the dimension of the layers is also indicated by microscopic observations on Na *n*-alkanoates, showing that the size of the domains in Smectic I drops continuously from the *n*-butanoate (20–100 μm) to the *n*-heptanoate (7 μm).[3,4,18] This means that, within each series of compounds, the difference between Smectic I and Smectic II phases tend to vanish with increasing chain length, and this indeed is suggested by the trends of the clearing enthalpies and entropies of Figure 2.

If our model is correct, Smectic II is really a peculiar mesophase. It would be the most disordered known smectic phase (fluid and optically isotropic, with irregular layer stacking, layer size of the order of 200–300 Å, and rapid exchange of molecules between different layers, as would appear from recent NMR studies),[18] and, at the same time, the most stable one (apart from Smectic I) relative to the isotropic liquid.

We conclude this discussion with a few considerations about RAB compounds with very short ($n < \sim 4$) or very long ($n > \sim 20$) chains. For the latter, the observed trends suggest that they should melt directly to Smectic II mesophases, as already observed in this work for Na *n*-alkanoates with n = 20, 22. Some information can also be obtained from the characterization of ionomer melts, in which ion clustering is observed, possibly in the lamellar geometry.[29] For the melts of compounds with very short chains, on the other hand, no mesomorphic behavior should be expected until the hydrocarbon part occupies the majority of the molar volume, so differentiating the resulting liquid phases from those of totally ionic compounds, obviously non-mesogenic.

References

1. D. Vorlander, *Ber. dt. Chem. Gesell.*, **43**, 3120 (1910).
2. a. A. E. Skoulios and V. Luzzati, *Acta Cryst.*, **14**, 278 (1961); b. A. Skoulios and V. Luzzati, *Nature*, **183**, 1310 (1959); c. B. Gallot and Skoulios. *Koll. Z.u.Z. Polym.*, **210**, 143 (1966); d. B. Gallot and A. Skoulios, *Koll. Z.u.Z. Polym.*, **209**, 164 (1966).
3. a. J. J. Duruz and A. R. Ubbelohde, *Proc. R. Soc. Lond.*, **A330**, 1 (1972); b. A. R. Ubbelohde, H. J. Michels and J. J. Duruz, *Nature*, **228**, 50 (1970); c. A. R. Ubbelohde, *Nature*, **244**, 487 (1973).

4. J. Bonekamp, B. Hegemann and J. Jonas, *Mol. Cryst. Liq. Cryst.*, **87**, 13 (1982).
5. M. Wolfe, J. Bonekamp and J. Jonas, *J. Chem. Phys.*, **70**, 3993 (1979).
6. J. E. Bonekamp, T. Eguchi, S. Plesko and J. Jonas, *J. Chem. Phys.*, **79** 1203 (1983).
7. a. P. Ferloni, M. Sanesi and P. Franzosini, *Z. Naturforsch.*, **30a**, 1447 (1975); b. M. Sanesi, P. Ferloni and P. Franzosini, ibid. **32a**, 1173 (1977); c. P. Ferloni, M. Zangen and P. Franzosini, ibid. **32a**, 627 (1977); d. M. Sanesi, P. Ferloni, M. Zangen and P. Franzosini, ibid. **32a**, 285 (1977); e. P. Ferloni, G. Spinolo, M. Zangen and P. Franzosini, ibid. **32a**, 329 (1977); f. A. Cingolani, G. Spinolo, M. Sanesi and P. Franzosini, ibid. **35a**, 757 (1980); g. P. Franzosini, M. Sanesi, A. Cingolani and P. Ferloni, ibid **35a**, 98 (1980).
8. V. Busico, D. Castaldo and M. Vacatello, *Mol. Cryst. Liq. Cryst.*, **78**, 221 (1981).
9. V. Busico, P. Cernicchiaro, P. Corradini and M. Vacatello, *J. Phys. Chem.*, **87**, 1631 (1983).
10. V. Busico, A. Ferraro and M. Vacatello, *J. Phys. Chem.*, **88**, 4055 (1984).
11. M. J. Vold, H. Funakoshi and R. D. Vold, *J. Phys. Chem.*, **80**, 16 (1976).
12. D. P. Benton, P. G. Howe and I. E. Puddington, *Can. J. Chem.*, **33**, 1384 (1955); ibid **33**, 1798 (1955).
13. P. Pacor and H. L. Spier, *J. Am. Oil Chem Soc.*, **45**, 338 (1968).
14. V. Busico, P. Corradini and M. Vacatello, *J. Phys. Chem.*, **86**, 1033 (1982).
15. M. Vacatello, G. Avitabile, P. Corradini and A. Tuzi, *J. Chem Phys.*, **73**, 548 (1980).
16. R. G. Kirste, W. A. Kruse and K. Ibel, *Polymer*, **16**, 120 (1975).
17. a. K. Ichikawa, *J. Chem. Soc. Farad. II*, **113** (1979); b. D. W. James and W. H. Leong, *J. Chem Phys.*, **51**, 640 (1969); c. D. Harold-Smith, *J. Chem. Phys.*, **59**, 4771 (1973).
18. S. Plesko, M. L. Phillips, R. Cassell and J. Jonas, *J. Chem Phys.*, **80**, 5806 (1984).
19. V. Vand, T. R. Lomer and A. Lang, *Acta Cryst.*, **2**, 214 (1949).
20. E. L. V. Lewis and T. R. Lomer, *Acta Cryst.*, **B25**, 702 (1969).
21. H. Helker and R. Hatz, *Handbook of Liquid Crystals*, Verlag Chemie (Weinheim), 1980.
22 V. Busico, P. Corradini, G. Guerra and P. Severino, *Gazz. Chim. Ital.*, *115*, 17 (1985).
23. V. Busico and M. Vacatello, *Mol. Cryst. Liq. Cryst.*, **97**, 195 (1983).
24. M. Vacatello and P. Corradini, *Gazz. Chim. Ital.*, **103**, 1027 (1973); ibid. **104**, 773 (1974).
25. a. E, Landi and M. Vacatello, *Thermoc. Acta*, **12**, 141 (1975); b. E. Landi and M. Vacatello, *Thermoc. Acta* **13**, 441 (1975).
26. A. Bondi, *Chem. Rev.*, **67**, 565 (1967).
27. S. Marcelja, *Biochim. Biophys. Acta*, **367**, 165 (1974).
28. A. R. Ubbelohde, *Melting and Crystal Structure*, Clarendon Press, Oxford (UK), 1965, Chapter 7.
29. E. J. Roche, R. S. Stein, T. P. Russell and J. W. McKnight, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 1497 (1980).