Crystal and liquid crystal behaviour of N-cyanoalkyl-N-alkyl-N,N-dimethylammonium bromides: Role of the dipole interactions of the cyano groups

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Crystal and liquid crystal behaviour of *N*-cyanoalkyl-*N*-alkyl-*N*,*N*-dimethylammonium bromides: Role of the dipole interactions of the cyano groups

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A homologous series of dialkyldimethylammonium bromides bearing a cyano group at the end of one of the alkyl chains was synthesized. The cyanoalkyl group ranges from monomethylene to hexamethylene and the cyano-free chain from dodecyl to octadecyl. The thermotropic liquid crystal behaviour of the series was investigated using differential scanning calorimetry, polarizing microscopy, and X-ray diffraction. The molar volume of four selected compounds was determined as a function of temperature using dilatometry. The low-temperature crystal phases were found to have a lamellar structure in which the ammonium bromide groups are arranged within the layers in two distinct planes, alternately separated by single layers of upright, interdigitated alkyl chains and double layers of cyanoalkyl chains coupled through the cyano end groups. The high-temperature smectic A phases were found to display a similar structure regarding the layering of the molecules, in which however the alkyl and cyanoalkyl chains have a disordered conformation. The rôle of the cyano end groups is discussed by comparing this smectic A structure with the known ordered smectic T structure of the cyano-free dialkyldimethylammonium bromides.

1. Introduction

Functionalization of alkyltrimethylammonium bromides [1] constitutes a facile method to synthesize an extensive variety of amphiphilic liquid crystalline materials [2]. The presence of functional groups, particularly of groups able to interact intermolecularly, is expected drastically to affect the overall packing geometry of the molecules in the crystalline as well as in the liquid crystalline state.

To study this subject, a series of *N*-cyanopropyl-*N*-alkyl-*N*,*N*-dimethylammonium bromides with alkyl chains from dodecyl to octadecyl was synthesized recently and the crystal and liquid crystal behaviour of the series was investigated by the usual experimental techniques: differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction [3]. A disordered smectic A phase was thus identified, involving smectic layers formed of two ionic planes alternately separated by sub-layers of cyanopropyl groups and disordered alkyl chains. This smectic phase was entirely different from the ordered smectic T phase described previously for the *N*,*N*-dialkyl-*N*,*N*-dimethylammonium bromides [4], which involved single layers of tetra-

gonally arranged ammonium and bromide ions separated by sub-layers of disordered alkyl chains. The presence of strongly interacting cyano groups not far from the ionic heads of the molecules was thus crucially affecting the spatial arrangement of the molecules and thereby the nature of the smectic phases produced.

The present work attempts to extend these results systematically to a homologous series of *N*-cyanoalkyl-*N*-alkyl-*N*,*N*-dimethylammonium bromides:
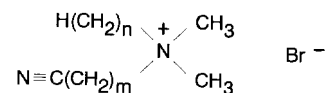
(designated in the following as *n*-*m*-CN), in which the length of the alkyl chains ranges from $n=12$ to $n=18$, and that of the spacer carrying the cyano group from $m=1$ to $m=6$.

2. Materials

Compounds *n*-*m*-CN with $m \geqslant 3$ were prepared as described previously [3] using the general quaternization reaction conditions described by Goerdler [5]:

$$CH_3(CH_2)_{n-1}NMe_2 + Br(CH_2)_mC{\equiv}N \rightarrow$$

$$CH_3(CH_2)_{n-1}N^{(+)}Me_2(CH_2)_mC{\equiv}N, Br^{(-)}$$
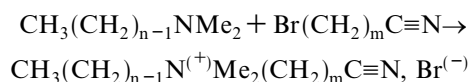
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Table 1.   Proton nuclear magnetic analysis of *n–m*–CN (chemical shifts in ppm).

Group	$m=1$	$m=3$	$m=4$	$m=5$	$m=6$
CH_3[a]	0·81 (t)	0·81 (t)	0·84 (t)	0·80 (t)	0·80 (t)
CH_2[a]	1·35 (m)	1·22 (m)	1·25 (m)	1·23 (m)	1·23 (m)
$\beta–CH_2$[a]	1·86 (m)	1·68 (m)	1·66 (m)	1·65 (m)	[b]
CH_3N	3·59 (s)	3·33 (s)	3·30 (s)	3·33 (s)	3·30 (s)
$\alpha–CH_2$[a]	3·75 (m)	3·43 (m)	3·41 (m)	3·42 (m)	3·41 (m)
$\alpha–CH_2$[c]	5·24 (s)	3·76 (m)	3·74 (m)	3·63 (m)	3·55 (m)
$\alpha–CH_2$[d]	5·24 (s)	2·68 (t)	2·58 (t)	2·42 (t)	2·33 (t)
$\beta–CH_2$[c]	—	2·21 (t)	1·93 (m)	1·82 (m)	[b]
$\beta–CH_2$[d]	—	2·21 (t)	1·80 (dd)	1·74 (dd)	—
$\gamma–CH_2$[c]	—	—	—	1·55 (m)	[b]
$\gamma–CH_2$[d]	—	—	—	1·55 (m)	[b]

[a] Of the main alkyl chain.
[b] Overlapping of absorption peaks.
[c] With respect to nitrogen.
[d] With respect to cyano group.

Alkyldimethylamines ($12 \leqslant n \leqslant 18$) were obtained from Hoechst, and bromoalkylnitriles ($2 \leqslant m \leqslant 6$) from Aldrich. In ethyl acetate solution, 0·01 mol of amine was added to 0·011 mol of nitrile, and quaternization was conducted with stirring at room temperature for several hours, and sometimes days. The precipitated material was recrystallized twice from ethyl acetate.

Compounds with $m=1$ were prepared according to the quaternization reaction:

$$CH_3(CH_2)_{n-1}Br + Me_2NCH_2C\equiv N \rightarrow$$

$$CH_3(CH_2)_{n-1}N^{(+)}Me_2CH_2C\equiv N, \, Br^{(-)}$$
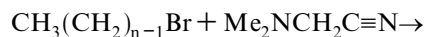
Bromoalkanes ($12 \leqslant n \leqslant 18$) and *N,N*-dimethylamino-acetonitrile were obtained from Aldrich.

The synthesis of compounds *n-m*-CN with $m=2$ proved unsuccessful. The direct reaction of bromoalkane with dimethylaminopropionitrile led essentially to by-products. And the reaction of *N,N*-dimethylalkyl-amine with 2-bromopropionitrile led to spontaneous dehydrobromination due to the presence of amine which acts as an effective nucleophile [6].

The chemical structures of the quaternary ammonium bromides synthesized were checked by proton NMR (AC 250 Bruker Spectrometer operating at 215·13 MHz). The assignment of the peaks was based on intensities, and chemical shifts in $CDCl_3$ were referred to external TMS (table 1). The compounds were also checked by elemental analysis (table 2); the purity of the compounds was found satisfactory, bearing in mind problems arising from reactants co-crystallizing with products during purification and the fact that the *n-m*-CN materials are hygroscopic. In the latter connection it is important to note that the shorter the alkyl chains the more the quaternary salts were found to be hygroscopic, demanding special care in handling.

Table 2.   Elemental analyses of *n–m*–CN in per cent; (calculated values in parenthesis).

n	*m*	C	H	N	Br
12	1	56·9 (57·7)	10·6 (10·0)	8·5 (8·4)	—
14	1	59·5 (59·8)	10·2 (10·3)	7·7 (7·8)	21·1 (22·1)
16	1	60·5 (61·7)	10·4 (10·6)	7·2 (7·2)	19·7 (20·5)
18	1	63·1 (63·3)	10·8 (10·9)	6·3 (6·7)	17·4 (19·1)
12	3	59·5 (59·8)	10·5 (10·3)	7·6 (7·8)	21·5 (22·1)
14	3	61·6 (61·7)	10·8 (10·6)	7·0 (7·2)	20·2 (20·5)
16	3	63·3 (63·3)	11·1 (10·9)	6·5 (6·7)	18·5 (19·1)
18	3	64·6 (64·7)	11·1 (11·1)	6·2 (6·3)	17·6 (17·9)
12	4	59·0 (60·8)	10·9 (10·5)	7·0 (7·5)	20·8 (21·3)
14	4	61·3 (62·5)	10·9 (10·7)	6·6 (6·9)	19·3 (20·0)
16	4	63·9 (64·0)	11·0 (11·0)	6·3 (6·5)	18·3 (18·2)
18	4	64·9 (65·3)	11·3 (11·2)	5·8 (6·1)	17·2 (17·4)
12	5	60·4 (61·7)	10·9 (10·6)	6·9 (7·2)	20·1 (20·5)
14	5	62·7 (63·3)	11·6 (10·9)	6·2 (6·7)	—
16	5	64·5 (64·7)	11·0 (11·1)	5·9 (6·3)	16·8 (17·9)
18	5	65·8 (65·9)	12·0 (11·3)	5·7 (5·9)	—
12	6	61·8 (62·5)	11·2 (10·7)	6·8 (6·9)	—
14	6	64·4 (64·0)	11·2 (11·0)	6·2 (6·5)	17·8 (18·5)
16	6	65·1 (65·3)	11·2 (11·2)	5·9 (6·1)	17·3 (17·4)
18	6	66·5 (66·5)	11·3 (11·4)	5·6 (5·7)	15·5 (16·4)

3.   Thermal behaviour
3.1. *Thermal stability*

Upon heating, the compounds *n-m*-CN start to degrade thermally at temperatures depending on the length of the alkyl chains. Their thermal stability was studied by thermogravimetry (Mettler TC10A instrument coupled with TA processor and M3 balance). Compounds with $n=16$ start to degrade at about 150°C when $m=3$, 4, 5, 6 and at about 110°C when $m=1$ (figure 1). Compounds with $m=3$ seem to degrade slightly more rapidly when alkyl chains are shorter (figure 2). Experiments performed at a constant temperature as a function of time showed the samples (except
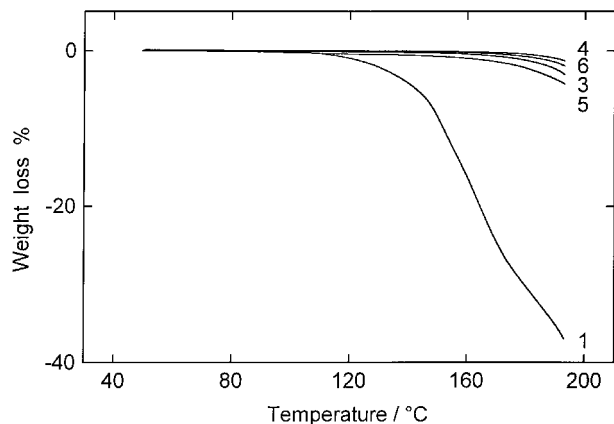
Figure 1. Thermal degradation of the compounds 16-*m*-CN as a function of *m*. Numerals in the plot represent the number of methylene groups in the cyanoalkyl chains.
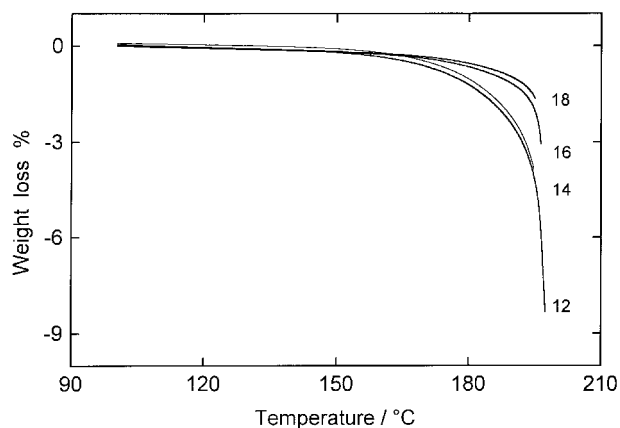

Figure 2. Thermal degradation of the compounds *n*-3-CN as a function of *n*. Numerals in the plot represent the number of methylene groups in the alkyl chains.

for compounds with $m=1$, which degrade readily at low temperatures) to withstand prolonged heating at 150°C with weight losses smaller than a few per cent.

3.2. *Thermotropic polymorphism*

The thermotropic polymorphism of the compounds *n-m*-CN was studied by differential scanning calorimetry (Perkin-Elmer DSC 7, heating and cooling rates of 2·5, 5, or 10°C min⁻¹) and polarizing optical microscopy (Leitz Orthoplan, Mettler FP82 hot stage). The DSC thermograms, registered in the temperature range from 0°C (or −50°C for certain compounds that were difficult to crystallize) to 150°C for compounds with $m \geqslant 3$ and 120°C for compounds with $m=1$, showed the presence of sharp peaks indicative of first order phase transitions. The fluidity of the samples at high temperature and their optical textures (oily streaks or exceptionally well developed spherulitic focal-conic domains) suggested the

presence of smectic A liquid crystalline phases, similar to those reported recently for compounds *n-m*-CN with $m=3$ [3]; the results collected are summarized in table 3. It is worth noting that recrystallization always occurred with a strong hysteresis due to nucleation. (In the particular case of compound 12-5-CN, hysteresis was so pronounced that recrystallization was never observed, even on cooling down to −80°C.)

It is important to note the significant rôle of hygroscopicity in the thermotropic behaviour of the *n-m*-CN compounds. This is particularly clear with compounds 14-4-CN and 18-4-CN for which the hygroscopicity is the most pronounced. Handled without precaution, these compounds do not pass directly from the crystalline to the smectic state, but undergo a eutectic melting, signalled by the presence in the DSC thermograms of two distinct, but connected peaks (one sharp peak at the eutectic temperature and an asymmetrical one at the *solidus* temperature: see ref. [7]). This phenomenon becomes less marked as the heating and cooling cycles proceed, vanishing completely after the third cycle of heating when the specimens are completely dry.

3.3. *Temperature dependence of molar volume*

The temperature dependence of the molar volume of compounds 12-3-CN, 18-5-CN, and 18-6-CN was studied by dilatometry. Measurements were performed with a home-made dilatometer. Changes in volume were investigated as a function of temperature (heating steps of 0·2°C every minute) in the range from 35 to 70°C for 12-3-CN, and from 35 to 110°C for 18-5-CN and 18-6-CN. As already reported for compound 18-3-CN (see figure 2 in ref. [3]), specific volumes grow with temperature, jumping suddenly at the phase transition from the crystal to the liquid crystal, due to the melting of the paraffin chains. A least-squares linear fit of the data leads to the values included in table 4 for the temperature dependence of the molar volume.

For the volume measurements to be meaningful, it is crucial to submit samples to careful degassing (several heating and cooling cycles under vacuum from the crystalline to the smectic state). Being hygroscopic, the samples considered in this work liberated appreciable amounts of water in the degassing treatment (condensing onto the internal walls of the dilatometer capillaries and thus perfectly visible). As a result, the absolute values of the molar volumes measured were rather inaccurate ($\pm 2\%$), preventing a direct measure of the molar volume of the methylene groups (through the slope of the linear dependence of molar volume on $n+m$), but yet allowing a reasonable estimate of the molecular areas in the layer planes (see below).

Table 3. Thermotropic polymorphism of compounds *n–m*–CN. Cr, Sm, and I stand for crystal, smectic liquid crystal, and isotropic melt; temperatures are given in °C.

m	*n* = 12	*n* = 14	*n* = 16	*n* = 18
1	Cr 59 Sm	Cr 73 Sm	Cr 77 Sm	Cr 75 Sm
3	Cr 49 Sm 97 I	Cr 72 Sm	Cr 78 Sm	Cr 80 Sm
4	Cr 21 Sm 76 I	Cr 48 Sm 96 I	Cr 63 Sm	Cr 67 Sm
5	Cr 28 Sm 51 I	Cr 34 Sm 75 I	Cr 47 Sm 123 I	Cr 60 Sm
6	Cr 29 I	Cr 53 I	Cr 60 I	Cr 70 Sm

Table 4. Temperature dependence of the molar volume $V = V_0 (1 + \beta \times T)$ of *n–m*–CN in the crystalline and smectic phases.

Phase	Compound	$V_0 / cm^3\ mol^{-1}$	$\beta \times 10^4 / °C^{-1}$
Crystal	18–3–CN	389	4·1
	18–6–CN	458	3·7
Smectic	12–3–CN	332	6·8
	18–3–CN	413	6·9
	18–5–CN	466	6·7
	18–6–CN	477	6·6

Figure 3. Lamellar period of the crystal (Cr) phase of the compounds *n–m*-CN at room temperature as a function of the number *n* of carbon atoms in the alkyl chains. Numerals in the plot represent the number of methylene groups in the cyanoalkyl chains. The dotted line connects data corresponding to imperfectly dried samples.

4. Structural behaviour

The structural behaviour of the *n-m*-CN compounds synthesized was investigated by X-ray diffraction. The crystalline nature of the Cr phases at low temperature and the smectic nature of the A phases at high temperature (see table 3) could thus be fully confirmed. Experiments were performed using a home-made Guinier camera equipped with a bent quartz monochromator (K_{α_1} radiation from an INEL-XRG-2500 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 their temperature was controlled (within better than 0·1°C) by an INSTEC hot stage.

4.1. *Crystal structure*

The X-ray patterns of the Cr phases (see table 3) were in many respects identical with those reported previously for compounds *n*-3-CN [3]. They contain quite a few, occasionally up to eight, equidistant sharp reflections in the small-angle region, characteristic of a lamellar arrangement of the molecules, and numerous sharp reflections in the wide-angle region, indicative of a well developed three-dimensional crystal ordering. Independent of temperature within experimental accuracy, the lamellar periods grow with the number *n* or *m* of carbon atoms in the alkyl chains in a very coherent way (figure 3), suggesting that, even if not strictly identical, the molecular arrangements of all the compounds studied are closely related to one another. Before dis-
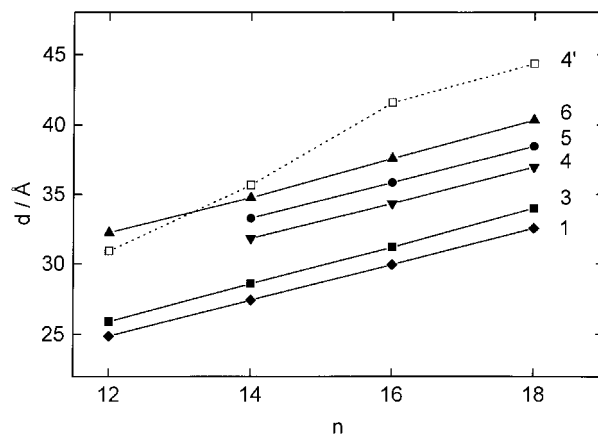
cussing this further, it is of interest to note again the important rôle played by hygroscopicity in the structural behaviour of the *n-m*-CN compounds in the crystalline state. This is particularly clear with the compounds *n*-4-CN (4′ in figure 3) which, when imperfectly dried, exhibit lamellar structures with significantly altered lamellar periods, varying irregularly with *n*. (Anhydrous samples may be obtained by careful vacuum-drying at 65°C in Lindemann capillaries which are then immediately sealed off.)

Inspection of figure 3 shows that the lamellar periods grow linearly with length *n* of the cyano-free alkyl chains. The corresponding straight lines are parallel to one another and shift upwards when *m* increases (*Y*-intercepts and slopes are given in table 5). The packing mode of the cyano-free alkyl chains (in single or double layers) and their tilt with regard to the layer normal must therefore be the same for all the compounds studied, independently of their individual length.

To obtain some information about the molecular arrangement of the cyano-free alkyl chains in the crystal, it is useful to calculate their tilt angle and their molecular

Table 5. Variation of the lamellar period ($d = d_0 + \delta \times n$) of the crystal (Cr) phase at room temperature with the number n of carbon atoms in the alkyl chains and the number m of methylene groups in the cyanoalkyl chains. Tilt angle θ_2 of the alkyl chains (supposed to be arranged in double layers) with respect to the layer normal.

m	$d_0/\text{Å}$ ± 0.5	$\delta/\text{Å}$ ± 0.05	θ_2/deg ± 1
1	9.5	1.28	60
3	9.8	1.35	58
4	13.8	1.29	60
5	15.1	1.30	59
6	15.9	1.36	58

area. Their tilt may be estimated from a comparison of the slope of the $d_m(n)$ straight lines ($1.32 \pm 0.05\,\text{Å}$, see table 5) with the known elongation (per methylene group) of linear paraffin chains in a fully extended, all-*trans*-conformation ($2.54/2 = 1.27 \pm 0.03\,\text{Å}$ [8, 9]). It is thus easy to ascertain that, if arranged in single layers, the alkyl chains must stand upright within the layers [$\theta_1 \cong \cos(\text{slope}/1.27) \cong 0$], and if arranged in double layers, they must be tilted away from the layer normal by an angle $\theta_2 \cong \cos(\text{slope}/2.54)$ of about 60 degrees (table 5 and figure 4).

As for the molecular area S, it may easily be calculated from the slope $2\mathscr{V}_{CH2}/S$ of the $d_m(n)$ straight lines ($1.32 \pm 0.05\,\text{Å}$, table 5) using the known value of the volume of one methylene group in the crystalline state ($\mathscr{V}_{CH2} = 25 \pm 1\,\text{Å}^3$ at room temperature [10]). Indeed, the volume of two molecules: $2\mathscr{V} = 2\mathscr{V}_m + n \times 2\mathscr{V}_{CH2}$ (where $\mathscr{V}_m$ is the volume of one molecule deprived of all the methylene groups of the cyano-free alkyl chain, including that of the methyl end group) is equal to $S \times d$ (where d is the lamellar period and S the surface covered

by two molecules in the layers of the crystal) and, therefore, the equation of the $d_m(n)$ straight lines is:

$$d = 2\mathscr{V}/S = 2\mathscr{V}_m/S + (2\mathscr{V}_{CH2}/S)n$$

The value found for S is $38 \pm 1\,\text{Å}^2$, that is, exactly twice the known cross-sectional area of linear paraffin molecules in the crystalline state ($2 \times 18.5\,\text{Å}^2$ [8]). Unless utterly coincidental, this means that of the two structural models shown in figure 4, only the single-layered one must be retained here. Standing upright and set side by side in a head to tail configuration, the alkyl chains are arranged in single layers covered on both faces by the ammonium and bromide ions (figure 4 left).

As for the Y-intercept of the $d_m(n)$ straight lines (figure 3 and table 5), it represents the thickness of the cyanoalkyldimethylammonium bromide sub-layers. Apparently, this varies linearly with the number m of methylene groups in the cyanoalkyl chains (figure 5) (the case of $m = 3$ will be discussed below). The corresponding slope ($1.3 \pm 0.1\,\text{Å}$) turns out to be identical to that of the $d_m(n)$ lines themselves. As the cyanoalkyl and the cyano-free alkyl chains (connected in pairs in the ammonium groups) cover the same area in the layers, this identity simply means that in both cyano and cyano-free chains the methylene groups have exactly the same molar volume, as expected. Although it might be tempting to interpret the identity of the slopes of the $d_{n=0}(m)$ and $d_m(n)$ lines as an indication of a similar packing in single layers for the two chains, this would be incorrect for two reasons: first, the cyano–alkyl chains are strongly coupled through the dipolar cyano end-groups [11], and hence arranged necessarily in double layers, and second, the cyanoalkyl chains considered ($m \leqslant 6$) are perhaps too short to be safely discussed in terms of clear-cut linear conformations. It is of interest to note
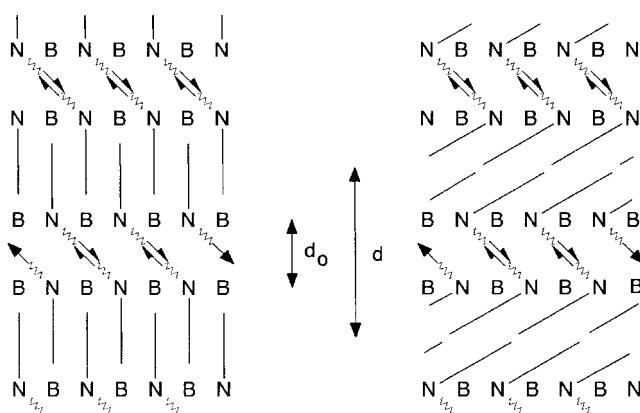

Figure 4. Possible structural models for *n-m*-CN in the crystalline state. Alkyl chains are represented by straight lines, cyanoalkyl chains by zig zag lines, and coupled cyano end groups by arrows. N and B stand for ammonium and bromide ions, respectively.
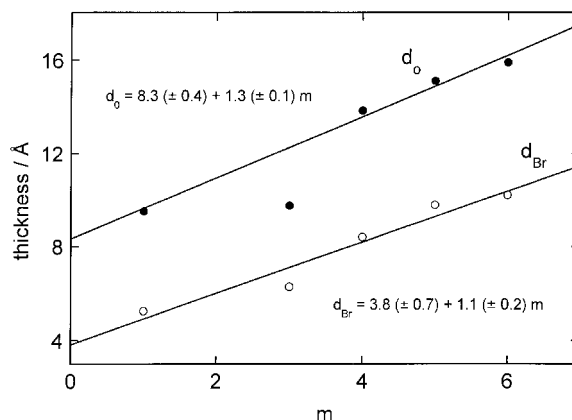

Figure 5. Thickness d_0 of the cyanoalkyldimethylammonium bromide sub-layers and spacing of bromide planes d_{Br} in the crystal (Cr) phase of the compounds *n-m*-CN at room temperature as a function of the number m of methylene groups in the cyanoalkyl chains.

in this context the singular behaviour of the compounds *n-m*-CN with $m=3$, whose cyanoalkyl sub-layer is abnormally thin (figure 5). Apparently, the packing of the cyanoalkyl chains is particularly compact here, probably due to a special conformation brought about by their specific length and the particular distance of their anchoring sites onto the ionic layers. At any rate, the *n*-3-CN compounds also have an altogether special behaviour in that they are less hygroscopic and less waxy in appearance.

The structural model proposed involves sub-layers of cyanoalkyl chains covered on both surfaces by dimethyl-ammonium and bromide ions, and separated from one another by single layers of upright, fully extended alkyl chains set side by side in a head to tail configuration (figure 4 left). This model was fully confirmed by the intensity distribution of the small-angle reflections observed in the X-ray patterns. The intensity of the successive Bragg harmonics does not decline monotonically (as would have been the case if the dominant bromide anions were confined to single planes), but oscillates, suggesting that the bromide anions are in fact located in two distinct planes within the crystalline layers. Moreover, for a given series of compounds with the same cyanoalkyl chain, the intensity distribution follows a unique master curve (see figure 6), showing that the cyanoalkyl sub-layers have indeed a constant thickness. Simple crystallographic considerations (see footnote quoted as ref. 13 in [3]) show that the intensity varies with the reciprocal spacing ($s=2\sin\theta/\lambda$) of the reflections as $\cos^2(\pi\, d_{Br}s)/s^2$ where d_{Br} is the spacing of the bromine planes. From the reciprocal spacing of the first minimum in the intensity curve ($s_{min}=1/2d_{Br}$), it is then quite easy to get a measure of d_{Br}. In this way, d_{Br}

was found to increase linearly with *m* (figure 5), going parallel to the d_0 line; its small downward shift is due to the location of the centres of the bromide anions (of diameter 3·9 Å) not exactly at the surface but within the sub-layers.

4.2. *Smectic structure*

The X-ray patterns of the smectic phases (see table 3) are identical with those reported previously for compounds *n*-3-CN, indicating a smectic A structure [3]. They contain one sharp reflection in the small-angle region, related to the smectic period (followed in the particular case of $m=1$ by a second, very faint harmonic), and a diffuse band in the wide-angle region at 4·5 Å, indicative of the disordered conformation of the molecules within the layers.

The smectic periods measured vary with temperature as well as with the number *n* or *m* of carbon atoms in the alkyl or cyanoalkyl chains in a very coherent way (figures 7 and 8), suggesting that the smectic structure is the same for all the homologues considered. Comparable to those measured for the crystal at low temperature, these periods suggest furthermore that the smectic structure is in many respects similar to that of the crystalline Cr phase, particularly with regard to the location of the ionic groups in two distinct planes, and to the location of the alkyl and cyanoalkyl chains (predominantly) in separate sub-layers. Indeed, if the ionic groups were arranged in single instead of two separate planes within the smectic layers (i.e. if the alkyl and cyanoalkyl chains should for some reason be mixed within the same layers), then of course the smectic periods should be about half the corresponding lamellar periods of the crystal, which is definitely not the case. The structure of the smectic phase has nevertheless two important characteristics of its own: the liquid-like
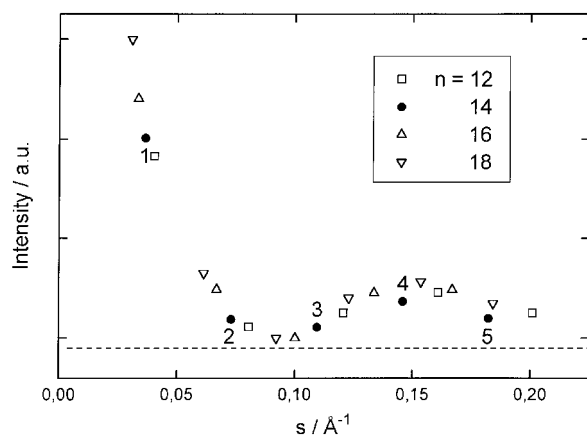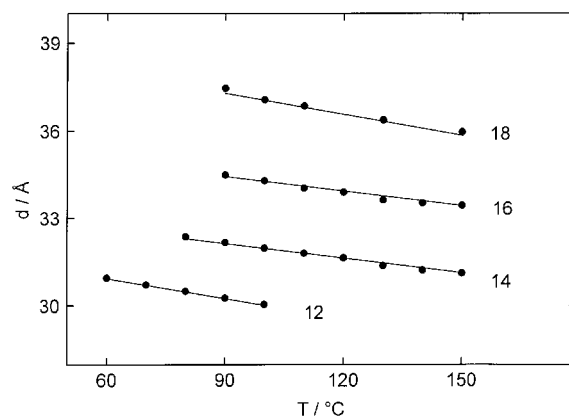

Figure 6. Intensity distribution of the small-angle X-ray reflections of the crystal (Cr) phase of the compounds *n*-1-CN at room temperature as a function of increasing reciprocal spacing ($s=2\sin\theta/\lambda$). Numerals in the plot represent the order of the reflections.

Figure 7. Thermal variation of the smectic period of *n*-3-CN. Numerals in the plot represent the number *n* of carbon atoms in the cyano-free alkyl chains.
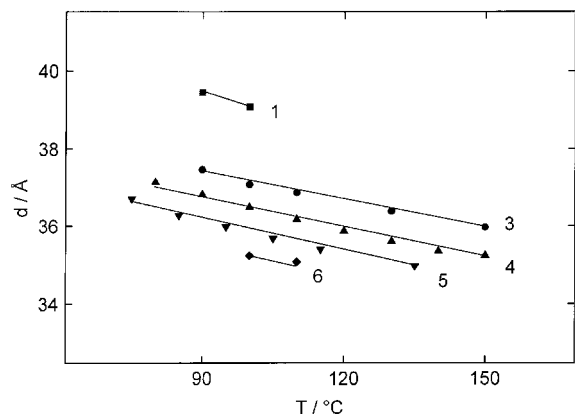
Figure 8. Thermal variation of the smectic period of 18-*m*-CN. Numerals in the plot represent the number *m* of methylene groups in the cyanoalkyl chains.
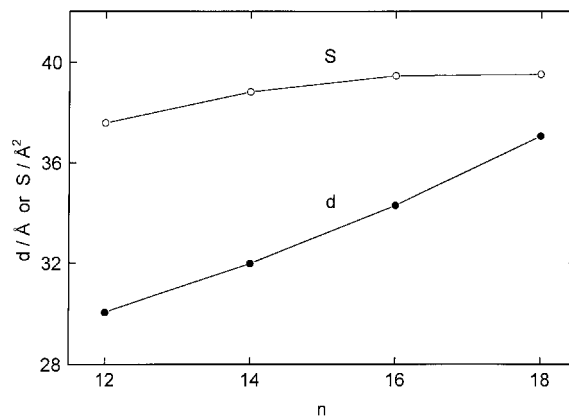
Figure 9. Smectic period *d* and molecular area *S* of the compounds *n*-3-CN at 100°C as a function of the number *n* of carbon atoms in the alkyl chains.
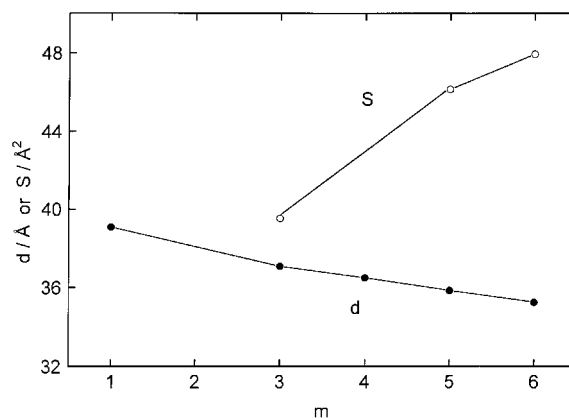
Figure 10. Smectic period *d* and molecular area *S* of the compounds 18-*m*-CN at 100°C as a function of the number *m* of methylene groups in the cyanoalkyl chains.

conformation of the molecules and the disordered packing of the ionic groups. The first results in the presence of a diffuse band in the wide-angle region of the X-ray diffraction patterns; the second causes some overlap of the electron density distribution of the bromide anions along the layer normal—more especially as the lateral spreading of the molecules increases significantly with *m* (see below), tending to maintain the thickness of the cyanoalkyl sub-layers at low values—producing an apparent thickening of the scattering layers and hence causing an important attenuation of the high Bragg harmonics, as effectively observed.

Inspection of figures 7 and 8 shows that the smectic period decreases slightly as a function of increasing temperature, with a relative thermal expansion coefficient of about $6 \times 10^{-4} \, \text{K}^{-1}$, in accordance with what is usually observed in smectic A liquid crystals. Even more interestingly it shows (see also table 6), first, that the spacing grows appreciably with the number *n* of carbon atoms in the alkyl chains (which is quite a normal phenomenon as it simply reflects the fact that the alkyl chain sub-layers increase in volume and so become thicker) and second, that it decreases with increasing *m*, which is rather unexpected. To understand this behaviour it suffices to note that the molecular area *S*, that is, the area covered in the smectic layers by the dimethylammonium bromide groups, grows only slightly with the length of the cyano-free alkyl chains (figure 9), while it grows considerably (figure 10) with the length of the cynoalkyl chains. Indeed, on spreading out laterally, the smectic layers inevitably become thinner. The molecular areas may easily be calculated from $d = 2\nu/S = 2\nu_m/S + (2\nu_{CH2}/S) \, n$ (see above: §4.1) using the values measured for *d* (table 6) and ν (table 4) (some of the values of ν were estimated by interpolation/extrapolation on the basis of $\nu_{CH2} = 28 \cdot 0 \, \text{Å}^3$ at 100°C

Table 6. Smectic periods (in Å) of the compounds *n*–*m*–CN measured at 100°C (other temperatures are indicated in parentheses) as a function of the number *n* of carbon atoms in the alkyl chains and the number *m* of methylene groups in the cyanoalkyl chains.

n	*m*=1	*m*=3	*m*=4	*m*=5	*m*=6
12	28·2	30·0	29·6(75)	28·9(80)	28·4(29)
14	31·0	32·0	31·6	33·8(55)	31·9(48)
16	34·8	34·3	33·9	33·5	35·3(61)
18	39·1	37·1	36·5	35·8	35·2

[12]). The strong *m* dependence of *S* is probably related to the geometrical constraints imposed upon the ionic species by the strongly coupled cyanoalkyl spacers, this effect being all the more important because the spacers are short. Incidentally, it is of interest to note the temperature dependence of the molecular area (figure 11) which, increasing upon heating, causes the observed thinning of the smectic layers.
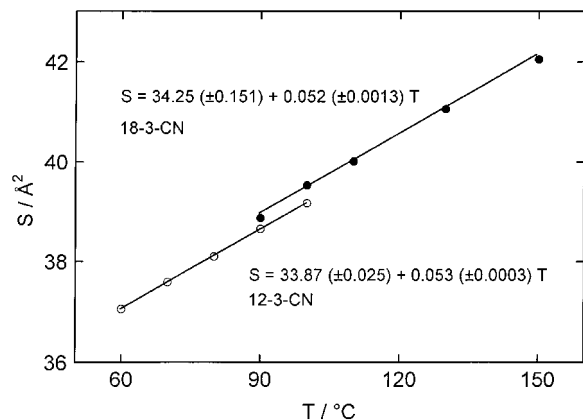
Figure 11. Temperature dependence of the molecular area in the smectic phase of 18-3-CN (full circles) and 12-3-CN (open circles).

5.   Discussion

The observations and data presented in this work entirely confirm those reported previously for the *n*-3-CN series [3], extending them convincingly to a set of homologous series of *n-m*-CN compounds with *m* ranging from 1 to 6. The crystal and smectic structures observed consist of layers of cyanoalkyl chains, covered on both faces by dimethylammonium bromide groups and separated from one another by layers of cyano-free alkyl chains. In the crystal form, the molecular parts, that is, the ionic groups together with the alkyl and cyanoalkyl chains, are located in separate sub-layers and all assembled in a regular, three-dimensionally periodical fashion, with the alkyl chains standing upright in single layers in a head to tail configuration (figure 4 left). In the smectic form, the molecular parts, though assembled in similar sub-layers to those in the crystal, are arranged in a disordered, liquid-like fashion.

To discuss these results it is useful to recall the behaviour of two homologous series of ammonium bromide derivatives studied not so long ago, different from, but closely related to *n-m*-CN: the *N,N*-dialkyl-*N,N*-dimethylammonium bromides [4] and the alkane-diyl-*α,ω*-bis-(dimethylalkylammonium bromides) [13]. The first series (denoted as H) corresponds to the compounds *n-m*-CN deprived of their cyano end group, the second (denoted as D) may be considered as the dimers of H. Compounds H exhibit at high temperature an ordered smectic structure entirely different from that described here for *n-m*-CN; this structure involves single layers of tetragonally arranged ammonium bromide groups separated by disordered alkyl chains (pointing randomly up and down when different in length). The difference is of course related to the presence in the *n-*

m-CN series of the cyano end groups which compel the molecules to join in pairs and so to pack in double, instead of single, layers. As for compounds D, they do not exhibit smectic phases at all, but pass directly from the crystalline into the isotropic liquid state. Evidently, this is simply due to the fact that the paraffin spacers of D are attached at both ends to the ammonium cations. They can thus adopt only a reduced pattern of conformations and gain little entropy upon the transition from the crystal to the smectic state. As a result, the melting takes place at rather high temperatures (>120°C [13]), above the stability range expected (see table 3) for a smectic phase.

Another structural difference between the *n-m*-CN and the H homologous series lies in the packing mode of the ionic groups in the smectic state. In the first series the ionic groups are assembled in a disordered fashion, whereas in the second they are regularly packed according to a two-dimensional square lattice. This is obviously related to the severe geometrical constraints introduced in *n-m*-CN by the coupling of the cyanoalkyl spacers.

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