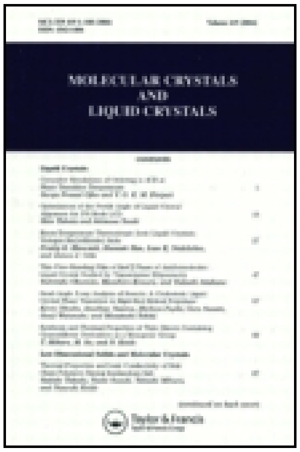

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Mesomorphic Character of Quaternary Ammonium Salts Affected by Secondary Hydrogen Bonding Interactions

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Mesomorphic Character of Quaternary Ammonium Salts Affected by Secondary Hydrogen Bonding Interactions

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In the present study we investigate the effect of hydrogen bonding secondary interactions on the crystalline and liquid crystalline phases of quaternary ammonium salts functionalized by a hydroxyl or a carboxylic group attached at the polar head through an appropriate spacer. The observed liquid crystalline phases have resulted from the interplay of the effects of the long aliphatic chain, $n = 12$, 14, 16, 18, the length of the spacer $m = 1$, 3, 4, 5, 6 and certainly of hydrogen bonding interactions. The smectic liquid character of these quaternaries was established by optical microscopy, differential scanning calorimetry and X-ray diffraction studies.

Keywords: Amphiphilic quaternary ammonium salts; smectic liquid crystalline phases; X-ray diffraction; thermal analysis

1. INTRODUCTION

Amphiphilic quaternary ammonium salts exhibit mesomorphic properties, as it is usual with amphiphilic molecules, and their liquid crystalline character has been investigated in a series of papers [1–8]. The subject on the physical aspects of amphiphilic mesogens has been reviewed by Busico *et al.* [9] and Skoulios and Guillon [10] while a third review [11] discusses the diversified classes of amphiphilic compounds that exhibit liquid crystalline phases. Following the initial studies on ionic amphiphiles, which exhibit liquid crystalline behaviour, the subject has been extended to non-ionic amphiphiles including carbohydrate amphiphiles [12, 13] and amphiphiles whose mesomorphic character was induced by hydrogen bonding interactions [14, 15]. The liquid crystalline behavior was attributed to the segregation [10, 11] of the hydrophilic moieties from the lipophilic alkyl chains leading to the formation of hydrophilic and lipophilic sublayers.

Among the polar groups of amphiphilic molecules, the quaternary ammonium group can extensively be modified by the introduction of various functionalities through a suitable spacer. Thus groups such as carboxy-, hydroxy- or nitrile which can themselves modify the liquid crystalline character of quaternary ammonium salts, also share the property of inducing intermolecular association. The first two groups by hydrogen bonding and the second by dipole–dipole interaction. The effect of the nitrile group on the liquid crystalline character of quaternary amphiphiles has recently been systematically investigated by our group [16, 17].

In the present study we investigate the effect of hydrogen bonding interaction on the liquid crystalline character of quaternary ammonium salts functionalized by the introduction, through the appropriate spacer, of a hydroxy- or a carboxylic group at the quaternary nitrogen. The observed liquid crystalline textures resulted from an interplay of the effects of the long aliphatic chain, $n = 12$, 14, 16, 18, the spacer $m = 1$, 2, 3, 5, 6, (Scheme) and certainly on hydrogen bonding interaction. The characterization of these compounds was performed by optical microscopy, differential scanning calorimetry and X-ray diffraction studies.

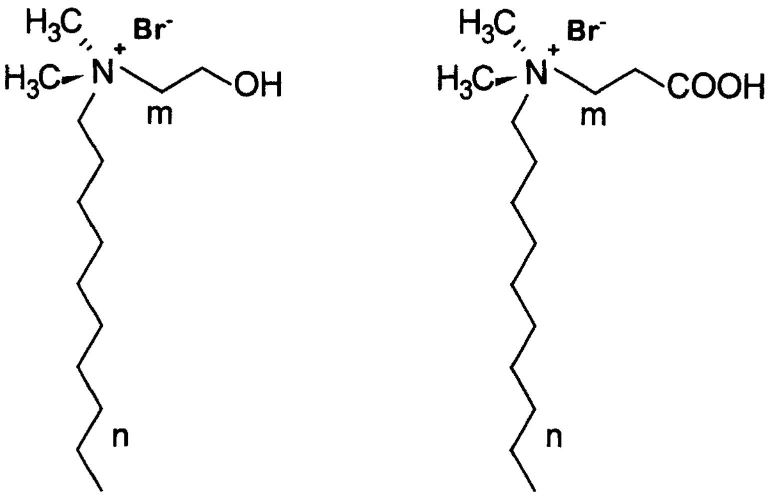
2. EXPERIMENTAL

The compounds were prepared by the quaternization of the appropriate tertiary amines under the experimental conditions described by Goerdler [18], following the general quaternization procedure:

$$\mathrm{CH_3(CH_2)_{n-1}NMe_2 + Br(CH_2)_mX \rightarrow CH_3(CH_2)_{n-1}}$$
$$\mathrm{N^{(+)}Me_2(CH_2)_m X, Br^{(-)}}$$
$$\mathrm{Where\ X = OH, COOH}$$

1. Synthesis of Hydroxylated Quaternary Ammonium Salts (n-m-OH).

Hydroxylated quaternaries with $n = 12, 14, 16, 18$ and $m = 2, 3$ were prepared by the reaction of the respective 1-bromoalkanes with dimethylaminoethylalcohol or dimethylaminopropyl alcohol according to the General Procedure A.



n-m-OH

n-m-COOH

where:

n = length of the long alkyl chain and
m = length of the spacer.

SCHEME

General Procedure (A)

To 0.01 mol of the appropriate tertiary aminoalcohol dissolved in ethylacetate, 0.011 mol of 1-bromoalkane was added and the reaction mixture was allowed under stirring for several hours. The precipitated material was recrystallized from ethylacetate and dried extensively over phosphorous pentoxide.

Hydroxylated quaternaries with $n = 12, 14, 16, 18$ and $m = 6$ were prepared by the reaction of *n*-alkyldimethylamines with 1-bromohexanol as described in the general Procedure A.

2. Synthesis of Carboxylated Quaternary Ammonium Salts (*n*-*m*-COOH)
Carboxylated quaternaries with $n = 12, 14, 16, 18$ and $m = 1$.

General Procedure (B)

To 0.01 mol of *n*-alkyldimethylamine dissolved in methanol, 0.011 mol of the sodium salt of bromoacetic acid was added and the mixture was allowed under stirring, at room temperature, for several days. Subsequently the reaction mixture was reacted with 48% hydrobromic acid and the precipitated material was collected and recrystallized from a mixture of ethanol:ethylacetate (3:7).

3. Synthesis of carboxylated quaternaries with $n = 12$, 14, 16, 18 and $m = 5$.

These quaternaries were prepared following the General Procedure A by reacting *n*-alkyldimethylamines with 6-bromohexanoic acid.

The Chemical structure and the purity of the materials was established by elemental analysis (Tabs. I and II) and proton NMR (AC 250 Bruker Spectrometer operating at 215, 13 MHz). The assignment of the peaks was based on intensities and chemical shifts in $CDCl_3$ and were referred to external TMS (Tabs. III and IV). The shorter the alkyl chain the higher is the hydroscopicity and therefore the quaternaries should have to be handled with care.

Thermogravimetry experiments were performed employing a Mettler TC 10A instrument coupled with TA processor an M3 balance while phase transitions were investigated with a Perkin-Elmer DSC-7 calorimeter at heating and cooling rates of 5°C $\min^{-1}$.

Polarized optical microscopic studies were performed with Leitz Orthoplan Microscope equipped with a Mettler FP82 hot stage.

X-ray diffraction studies experiments were performed using a home-made Guinier camera equipped with a bend quartz monochromator ($K\alpha_1$, radiation from an INEL-XRG- 2500 X-ray generator) and an INEL-CPS-120 curved position-sensitive detector which permitted measurement of both the angular position and the intensity of the Bragg reflections. Samples were

TABLE I Experimental and calculated (in parenthesis) elemental analysis data for *n*-*m*-OH quaternary ammonium salts

n	*m*	*C*	*H*	*N*
12	2	56.78 (56.88)	10.74 (10.89)	4.14 (4.11)
14	2	58.99 (59.08)	11.02 (11.12)	3.82 (3.80)
16	2	60.80 (60.90)	11.25 (11.24)	3.42 (3.55)
18	2	62.52 (62.69)	11.47 (11.59)	3.32 (3.32)
12	3	57.81 (57.53)	10.94 (10.89)	3.91 (3.97)
14	3	59.77 (59.97)	11.21 (11.15)	3.63 (3.68)
16	3	61.51 (61.74)	11.36 (11.35)	3.22 (3.43)
18	3	62.91 (63.28)	11.60 (11.54)	3.18 (3.21)
12	6	60.20 (60.88)	11.15 (11.26)	3.50 (3.55)
14	6	62.19 (62.52)	11.47 (11.47)	3.29 (3.31)
16	6	63.30 (63.98)	11.55 (11.63)	2.95 (3.11)
18	6	64.94 (65.23)	11.81 (11.81)	2.76 (2.93)

TABLE II Experimental and calculated (in parenthesis) elemental analysis data for *n*-*m*-COOH quaternary ammonium salts

		C	*H*	*N*
12	1	54.56 (54.39)	9.81 (9.72)	3.82 (3.97)
14	1	56.84 (56.84)	10.15 (10.09)	3.53 (3.68)
16	1	58.86 (58.80)	10.48 (10.38)	3.31 (3.43)
18	1	61.34 (60.52)	10.99 (10.64)	3.16 (3.20)
12	5	58.83 (58.81)	10.43 (10.36)	3.40 (3.43)
14	5	60.59 (60.53)	10.69 (10.62)	3.19 (3.21)
16	5	62.18 (62.05)	10.93 (10.85)	3.00 (3.01)
18	5	63.47 (63.39)	11.14 (11.05)	2.83 (2.84)

TABLE III NMR chemical shifts of *n*-*m*-OH in ppm

	m = *2*	*m* = *3*	*m* = *6*
CH_3[a]	0.77 (t)	0.79 (t)	0.85 (t)
CH_2[a]	1,20 (m)	1,31 (m)	1,28 (m)
β-CH_2[a]	1,64 (m)	1,74 (m)	1,73 (m)
CH_3N	3,30 (s)	3,31 (s)	3,31 (s)
α-CH_2[a]	3.46 (m)	3,42 (m)	3,42 (m)
α-CH_2[b]	3,64 (m)	3,74 (m)	3,57 (m)
α-CH_2[c]	4,04 (b)	3,74 (m)	3,57 (m)
OH	4.93 (t)	4,40 (b)	–
β-CH_2[b]	–	2,05 (m)	1.73 (m)
β-CH_2[c]	–	–	1.56 (m)
γCH_2[b]	–	–	1,44 (m)
γCH_2[c]	–	–	1,44 (m)

[a] Main alkyl chain.

[b] Side chain with respect to the nitrogen.

[c] Side chain with respect to the hydroxy group.

TABLE IV NMR chemical shifts of *n*-*m*-COOH in ppm

	m = *1*	*m* = *5*
CH_3[a]	0,83 (t)	0,87 (t)
CH_2[a]	1,39 (m)	1,31 (m)
β-CH_2[a]	1,82 (m)	1,72 (m)
CH_3N	3,36 (s)	3,30 (s)
α-CH_2[a]	3,62 (m)	3,44 (m)
α-CH_2[b]	4,96 (s)	3,59 (m)
α-CH_2[δ]	4,96 (s)	2,43 (t)
β-CH_2[δ]	–	1,72 (m)
β-CH_2[b]	–	1,82 (m)
γ-CH_2[b]	–	1,48 (m)

[a] Main alkyl chain.

[b] Side chain with respect to the nitrogen.

[c] Side chain with respect to the carboxy group.

held in sealed Lindermann capillaries and the temperature was controlled by an INSTEC hot-stage.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Quaternaries

Quaternaries functionalized with the hydroxy group were easily prepared by the usual quaternization procedure [18] employing polar but aprotic solvents. However only two series of the carboxylated quaternary homologues were synthesized since quaternization was not successful in the reaction of the tertiary amines with β-bromopropanoic, γ-bromobutanoic, or δ-bromopentanoic acids. When the first acid or its corresponding sodium salt was allowed to react under the well-known quaternization conditions, elimination did occurred. This elimination was attributed to the presence of a bromine atom at the β-position relative to the electron withdrawing carboxy group, following an analogous mechanism which was proposed, several years ago, for the reaction of organic halides with piperidine [19, 20]. The hydrogen bromide produced was reacted, *in situ*, with the tertiary amine affording, as established, the corresponding ammonium salt. For γ-bromobutanoic and δ-bromopentanoic acids, with the bromine at the γ or δ position relative to the carboxy group, hydrogen bromide was formed through a simultaneous formation of a cyclic lactone by an internal SN2 reaction [21].

3.2. Thermal Studies

3.2.1. Thermal Stability

Hydroxylated quaternaries (n-m-OH) with $n = 12$, 14, 16, 18 and $m = 3$ start degrading at 150°C, at temperatures independent of the length of the alkyl chain as determined by thermogravimetric analysis. Quaternaries with $n = 16$ and $m = 3$ or 6 degrade at about 150°C while the quaternary with $n = 16$ and $m = 2$ is more stable, degrading above 180°C (Fig. 1).

As far as carboxylated quaternaries are concerned, compound with $n = 16$ and $m = 1$ begins to degrade at about 110°C while compound with $n = 16$ and $m = 5$ is more thermally stable, degrading significantly only above 200°C (Fig. 2).

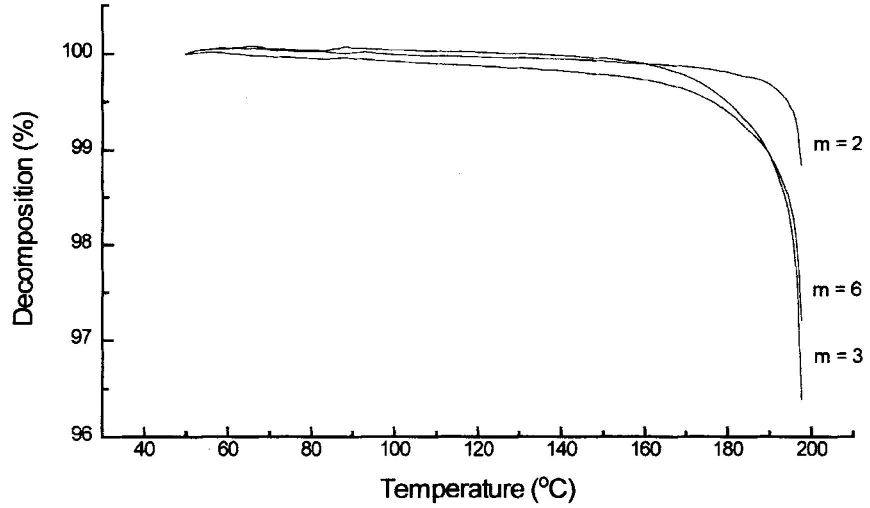


FIGURE 1 Thermal degradation of compounds 16-*m*-OH. Numbers in the plot represent the number of methylene groups in the spacer group.

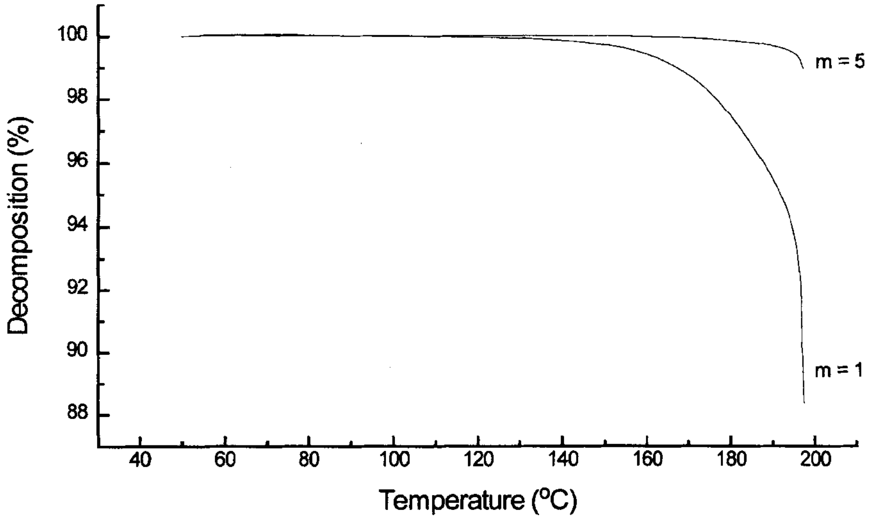


FIGURE 2 Thermal degradation of compounds 16-*m*-COOH. Numbers in the plot represent the number of methylene groups in the spacer group.

3.2.2. Thermotropic Polymorphism

The thermotropic polymorphism of the hydroxy and carboxy compounds was also investigated by differential scanning calorimetry at temperatures ranging from 30°C to 200°C, and in some cases exceeding the temperature of their thermal stability. Sharp peaks indicative of first order phase transitions were observed. In the temperature range from 30°C to 70°C there is a multiplicity of peaks indicative of a crystalline polymorphism not observed with the nitrile functionalized quaternaries [17]. This polymorphism is attributed to the presence of multiple hydrogen bonding of the hydroxy group (broad peak centered at 3300 cm^{-1}) or the carboxy group (broad peak in the area of 3000 cm^{-1}), the breakage of which at specified temperatures corresponds to these crystalline-crystalline phase transitions.

The polymorphic character and the mesomorphism of most of these compounds was also established by polarizing optical microscopy. Thus hydroxy derivatives with $n = 12, 14, 16, 18$ and $m = 3$ are enantiotropic liquid crystals. On the other hand quaternaries with $n = 12, 14, 16$ and $m = 6$ are monotropic liquid crystals while the compound with $n = 18$ and $m = 6$ is enantiotropic. Hydroxy derivatives with $m = 2$ were crystalline materials, not exhibiting liquid crystalline textures at high temperatures. Carboxylated quaternaries with $n = 12, 14, 16, 18$ and $m = 1$ and compounds with $n = 16, 18$ and $m = 5$ exhibit smectic A phases. The phase transitions of compounds *n*-*m*-OH and *n*-*m*-COOH are shown in Tables V and VI.

TABLE V Thermotropic polymorphism of compounds *n*-*m*-OH. (K, S, and I are for crystal, smectic liquid crystal, and isotropic melt; temperatures are given in °C)

	$n = 12$	$n = 14$	$n = 16$	$n = 18$
$m = 2$	$K_{1}50K_{2}74K_{3}81K_{4}$	$K_{2}72K_{3}88K_{4}$	$K_{1}46K_{2}84K_{3}93_{4}K_{4}$	$K_{1}48K_{2}84K_{3}97K_{4}$
$m = 3$	$K_{1}42K_{2}66S150I$	$K_{1}58K_{2}76S$	$K_{1}64K_{2}79S$	$K_{1}74K_{2}89S$
$m = 6$	$K_{1}60K_{2}(39S)71I$	$K_{1}60K_{2}(40S)85I$	$K_{1}58K_{2}(59S)89I$	$K_{1}70K_{2}95S153I$

TABLE VI Thermotropic polymorphism of compounds *n*-*m*-COOH. (K, S, and I are for crystal, smectic liquid crystal, and isotropic melt; temperatures are given in °C)

	$n = 12$	$n = 14$	$n = 16$	$n = 18$
$m = 1$	$K_{1}132K_{2}147S$	$K_{1}134K_{2}146S$	$K_{1}135K_{2}143S$	K89S
$m = 5$	$K_{1}66K_{2}102I$	$K_{1}69K_{2}109I$	$K_{1}70K_{2}114S153I$	$K_{1}75K_{2}115S$

3.3. Structural Behavior

3.3.1. Crystal Structure

The X-ray patterns of the crystalline phases of the hydroxylated and carboxylated derivatives contained occasionally up to five, 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. In the ambient temperature, the hydroxy compounds exhibited a multiplicity of crystalline forms which for the compounds with $m=3$, 6 transform to one crystalline form at temperatures ranging between 42–74°C. The carboxy compounds exhibited two crystalline forms, one at ambient temperature, which is transformed to another crystalline modification, at higher temperatures both having almost equal lamellar periods. The lamellar periods for both homologous series depend on the number of the carbon atoms of the alkyl chains. Thus these results suggest that, even if not strictly identical, the molecular arrangements of the investigated compounds are related to one another.

In Figure 3 are shown the lamellar *d* periods of hydroxy compounds with $m=3$, 6 as a function of n for K_2 crystalline form while in Figure 4 the *d*

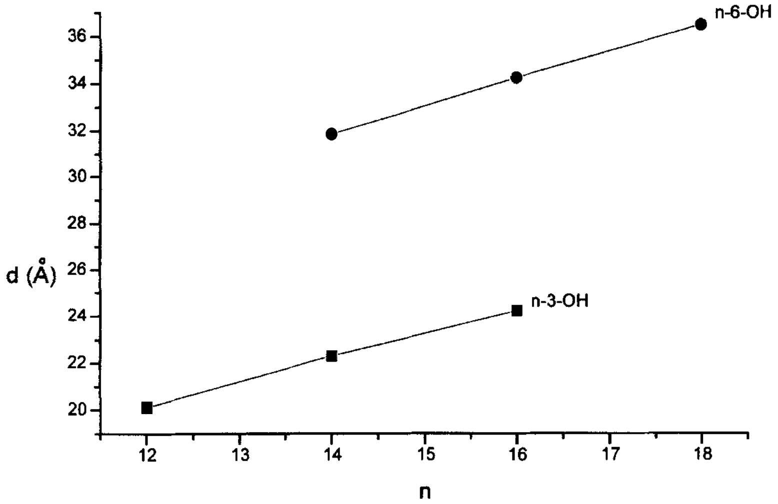


FIGURE 3 Lamellar period of the crystal phases of compounds *n*-*m*-OH at temperatures higher than room temperature (42–74°C) as a function of the number *n* of the carbon atoms in the alkyl chains.

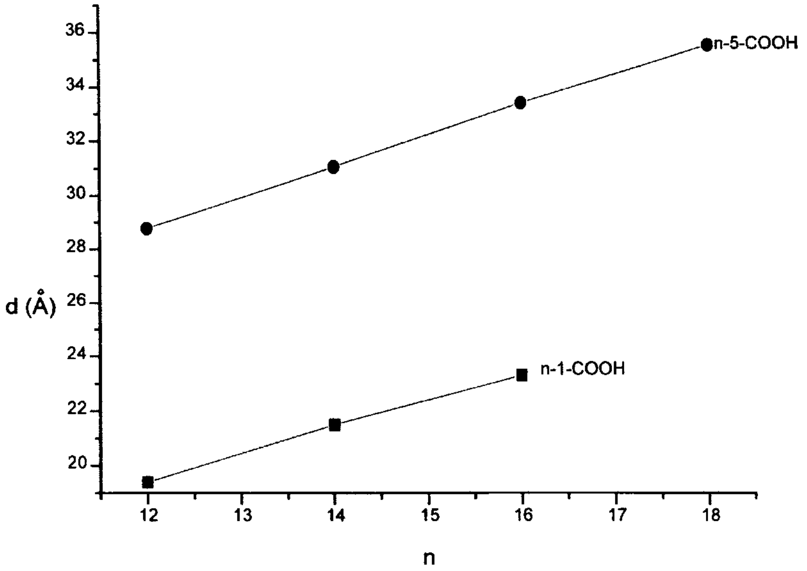


FIGURE 4 Lamellar period of the crystal phases of compounds *n*-*m*-COOH at room temperature as a function of the number *n* of the carbon atoms in the alkyl chains.

spacings of carboxy compounds for $m = 1, 5$ at ambient temperatures. In both cases the spacings increase linearly with the length *n* of the long alkyl chains. The corresponding straight lines are almost parallel to one another and shift upwards when *m* increases. The Y-intercepts and slopes are given in Table VII.

TABLE VII Variation of the lamellar period ($d = d_0 + \delta_n$) for the hydroxy quaternaries at 42–74°C and at room temperature for the carboxy derivatives with the number *n* of carbon atoms in the alkyl chains and the number *m* of methylene groups in the spacers. Tilt angles θ_1 and θ_2 of the alkyl chains (supposed to be arranged in single and double layers respectively) with respect to the layer normal

m-OH	$d_0/Å$	$\delta/Å$	θ_1/deg	θ_2/deg
3	7.80	1.03	36	66
6	15.64	1.16	24	63
m-COOH	$d_0/Å$	$\delta/Å$	θ_1/deg	θ_2/deg
1	7.67	0.98	39	67
5	15.29	1.13	27	64

To obtain some information on the molecular arrangement of the long alkyl chains in the crystalline phase, it is useful to calculate their tilt angle and molecular area. Their tilt angle may be estimated by comparing the slope of the $d_m(n)$ straight lines with the known elongation per methylene group of linear paraffin chains in a fully extended all-trans conformation ($2.54/2 = 1.27 \pm 0.03$ A [22, 23]). It can therefore be ascertained that, if arranged in single layers, the alkyl chains would have to be tilted by an angle varying from 24–39 degrees [$\theta_1 \cong \cos(\text{slope}/1.27)$], while if arranged in double layers, they would have to be tilted away from the layer normal by an angle $\theta_2 \cong \cos(\text{slope}/2.54)$ of about 65 degrees (Tab. VII), which is comparable to the angle of the nitrile quaternaries [17].

As far as the molecular area S is concerned, it may be determined from the slope $2V_{CH_2}/S$ of the d_m straight lines using the known value of the volume of each methylene group in the crystalline state ($V_{CH_2} = 25 \pm 1$ A^2 at room temperature) as estimated [24] from the crystal structure of the B form of stearic acid. Actually the volume of two molecules: $2V = 2V_m + n \times 2V_{CH_2}$ (where V_m is the volume of one molecule deprived of all the methylene groups of the non-functionalized alkyl chain, including that of the methyl endgroup) 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 becomes:

$$d = 2V/S = 2V_m/S + (2V_{CH_2}/S)n$$

The value of S generally found is in the range from 43 to 51 A^2. As for the Y-intercepts of the $d_m(n)$ straight lines, Table VII, they represent the thickness of the hydroxy- or carboxyalkyldimethylammonium sub-layers.

Smectic Structure

Smectic mesophases were observed for almost all of the investigated compounds except of 2-*n*-OH and 5-*n*-COOH derivatives with $n = 12$ and 14. The X-ray patterns of the smectic phases were analogous with those reported for the nitrile quaternary ammonium salts [17] indicating smectic A structures. They contain one sharp reflection in the small-angle region, related to smectic period, and a diffuse band in the wide angle region at 4.5 A, indicative of the disordered conformation of the molecules within the layers.

The smectic structure is similar in many respects to that of the crystalline phases, particularly as far as the location of the chains and ionic groups in separate sublayers are concerned. The smectic structure has two characteristic features, namely the liquid-like conformation of the molecules and the disordered packing of the ionic groups. The first feature shows up through the diffuse band in the wide-angle region of the X-ray diffraction patterns; while the second one leads to some overlap of the electron density distribution of the bromide anions along the layer normal, producing an apparent thickening of the scattering layers and therefore causing a significant attenuation of the Bragg harmonics.

The smectic periods decrease slightly as a function of increasing temperature, as shown in Figure 5 for compounds *n*-3-OH and in Figure 6 for the quaternaries 18-*m*-OH and 18-5-COOH, in accordance with what is usually observed in smectic A liquid crystals. More interestingly it is also shown (Tab. VIII) that the spacings increase appreciably with the number *n* of carbon atoms of the alkyl chains. This is quite normal as it simply reflects the fact that the alkyl-chain sublayers increase in volume and so become thicker. On the other hand the smectic periods of the *n*-6-OH compounds are smaller than the respective periods of the *n*-3-OH compounds which is rather unexpected. This is however consistent with the decrease of the smectic periods with increasing *m* as it was also observed for the nitrile quaternaries [17]. The same behavior is also observed for the compound 18-*m*-COOH. In this case there is a decrease of the spacing as one proceeds from $m = 1$ to $m = 5$. This behavior may be attributed to the slight increase of

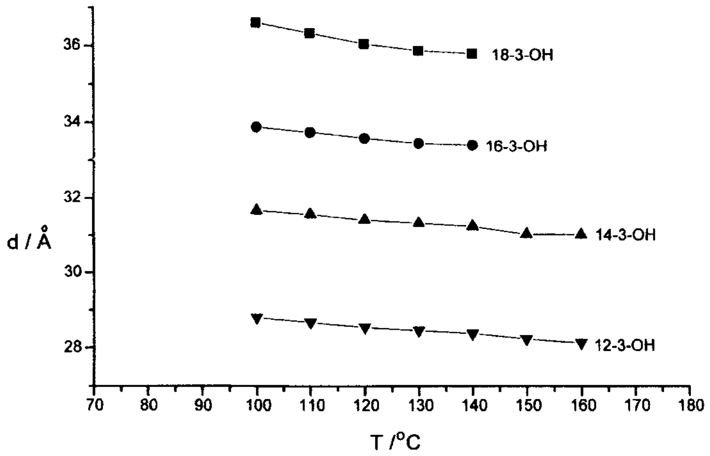


FIGURE 5 Lamellar period of the smectic A phase of compounds *n*-3-OH as a function of temperature.

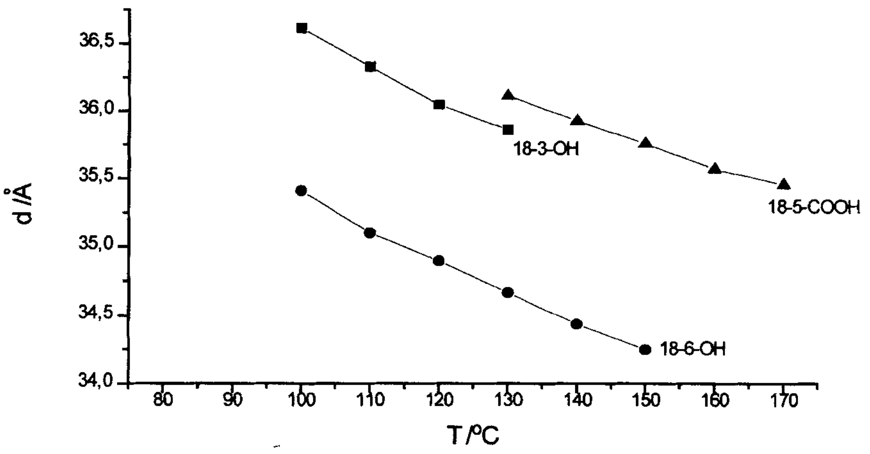


FIGURE 6 Lamellar period of the smectic A phase of compounds 18-*m*-OH and 18-*m*-COOH as a function of temperature.

TABLE VIII Smetic periods (in Å) of compounds *n*-*m*-OH and *n*-*m*-COOH measured at 100°C (other temperatures 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 spacers

	$m = 3$ $X = OH$	$m = 6$ $X = OH$	$m = 1$ $X = COOH$	$m = 5$ $X = COOH$
$n = 12$	28.80	27.98 (39°C)	27.70 (150°C)	–
$n = 14$	31.66	29.95 (40°C)	30.31 (150°C)	–
$n = 16$	33.89	33.72 (59°C)	33.09 (150°C)	34.16 (120°C)
$n = 18$	36.61	35.41	38.68 (150°C)	36.12 (130°C)

the molecular area with the length of the aliphatic chains, in contrast to its considerable increase with the length of the functionalized spacers. On spreading out laterally the smectic layers inevitably become thinner.

4. CONCLUDING REMARKS

Crystalline and smectic mesophases of amphiphilic quaternary ammonium salts originate from the segregation of hydrophilic from the liphophilic segments of these molecules. The hydrogen bonding forming groups attached at the polar head affect the crystalline and liquid crystalline character of these compounds through the so-called secondary interactions. This secondary effect is further appreciated if one compares the smectic character exhibited by these compounds with the ordered smectic T previously reported [25] for *N*, *N*-dialkyl-*N*, *N*,-dimethylammonium bromides. In the latter case single layers of tetragonally arranged ammonium and bromide ions, separated by sublayers of disordered alkyl chains, were formed. Thus the presence of the hydrogen bonding forming groups at the end of the spacer lead to the pairing of the molecules. The supramolecular arrangement of the molecules is therefore modified and consequently the nature of the smectic phases.

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