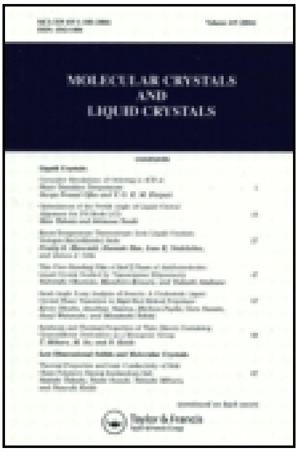

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Smectic Mesophases from Quaternary Amphiphilic Ammonium Salts Functionalized with Interacting Endgroups

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Smectic Mesophases from Quaternary Amphiphilic Ammonium Salts Functionalized with Interacting Endgroups**

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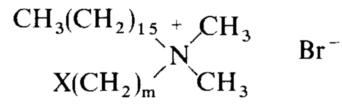
The functionalization of amphiphilic quaternary ammonium salts with properly chosen interacting endgroups constitutes an easy way to produce novel liquid crystalline materials with diversified physical properties.[1] Additional cyano endgroups introduce dipole-dipole interactions susceptible to strongly affect the liquid crystalline behaviour. Thus, the dialkyldimethylammonium bromides were found to produce smectic mesophases in which, because of the strong coulombic interactions between the ionic species, the lateral packing of the molecules within the layers is ordered and tetragonal in symmetry.[2] Introduction of a cyano endgroup attached to one of the alkyl chains, namely a propyl chain, was found to immediately transform the ordered smectic into a disordered smectic *A* structure.[3] This is due to the fact that the cyano group induces supramolecular dimerization through its dipolar interactions. We thought it of interest to extend this study by taking quaternary alkyl(hexadecyldimethylammonium) bromides carrying a variety of endgroups *X*. This paper describes some preliminary, but encouraging, results along this line.



$$\begin{array}{ccc} CH_3(CH_2)_{15} & {}^{+} & CH_3 \\ & N & \\ X(CH_2)_m & & CH_3 \end{array} \quad Br^-$$

$X = CN, COOH, OH$

The compounds considered in the present work (whose chemical formula is abbreviated to m–X) are listed in the Table below. Their thermotropic liquid crystalline polymorphism was investigated using the traditional experimental techniques,

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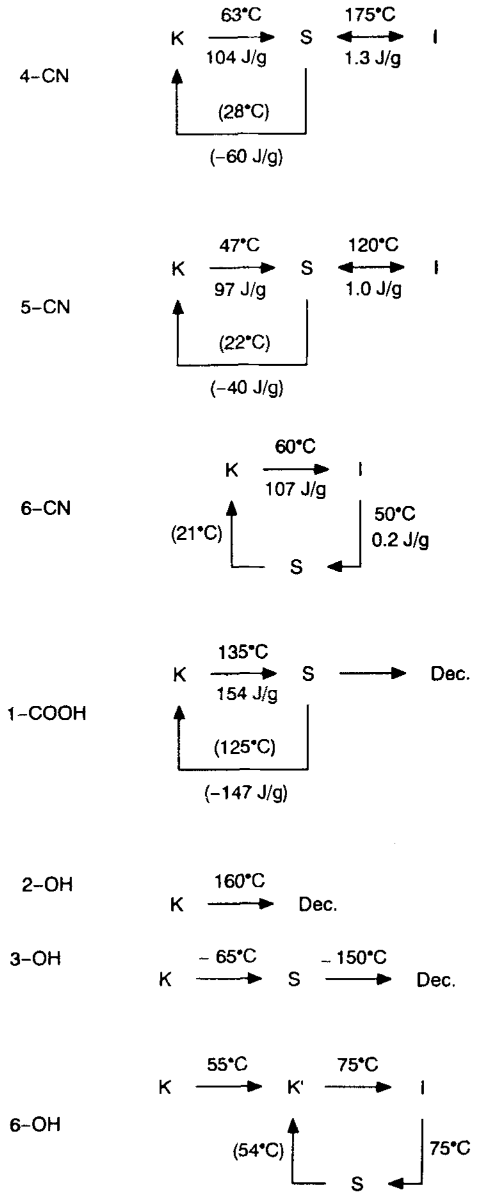
that is, differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction.

The DSC graphs showed well defined peaks (although partially overlapping in some rare instances), indicative of first order transitions. Upon cooling, crystallization takes place as usual with some delay due to nucleation. For compound 1—COOH, and also (but to a smaller extent) for all the hydroxy derivatives, heating above 150°C causes sizeable degradation of the samples. For compounds 6—OH and 6—CN, cooling from the melt induces monotropic liquid crystalline phases. The transition tempera-



TABLE

Functionalized ammonium salts studied in the present work: *d* (in Å) represents the smectic periods measured by X-ray diffraction

m	*X*	*d*
4	—CN	33
5	—CN	34
6	—CN	35
1	—COOH	–
2	—OH	–
3	—OH	34
6	—OH	34

tures and enthalpies measured are reported in the polymorphic schemes given above (*K*, *S*, and *I* stand for crystal, smectic phase, and isotropic melt, respectively).

The focal conic optical textures observed, of which a typical example is displayed in the figure below, show clearly the presence of (disordered) smectic mesophases. But definite proof of the smectic structure of the high temperature phases was given by X-ray diffraction. For all the compounds considered, except for the case of 2—OH, whose crystal decomposes before melting, the powder patterns recorded contain one sharp reflection in the small-angle region, related to the smectic stacking, and one diffuse band in the wide-angle region, at about 4.5 Å, indicative of the disordered arrangement of the molecules within the smectic layers. The values of the *d* smectic

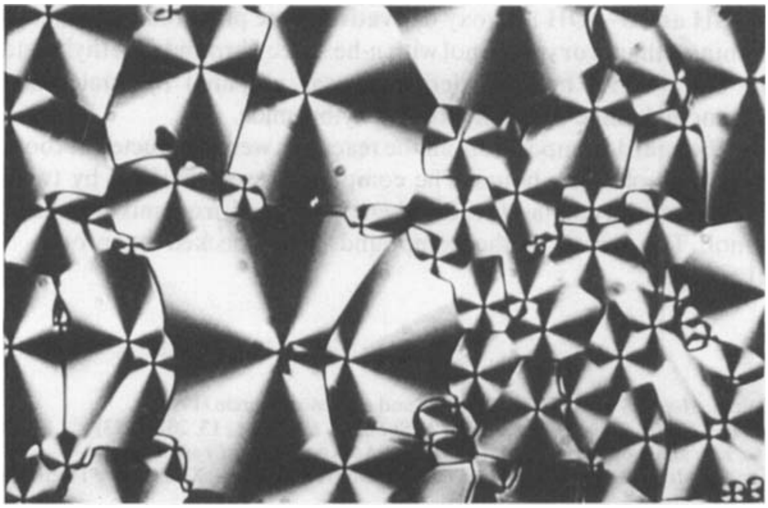


FIGURE Focal conic optical texture of compound 6–CN observed between crossed polars at 50°C upon slow (5°C/min) cooling from the melt.

spacings, measured within the temperature range of stability of each smectic phase, are given in the Table above. They are comparable to the *d* spacing determined previously for the 3—CN compound,[3] suggesting similar molecular areas of the ionic headgroups independently from the nature of the X group and the length of the alkyl spacer.

Further systematic work on the structural behaviour or m–X quaternaries, in which the spacer length m and also the length of the long alkyl chain is modified, is in progress.

EXPERIMENTAL

Instruments

Differential scanning calorimetry was performed using a Perkin-Elmer DSC7 instrument; heating and cooling rates used were of 5°C min^{-1}. Polarizing optical microscopy was carried out with a Leitz Orthoplan microscope, equipped with a Mettler FP82 hot stage. X-ray diffraction data were obtained with Guinier focussing cameras (bent-quartz monochromators, Cu-$K_{\alpha 1}$ radiation), equipped with home-made electrical ovens; patterns recorded photographically and, whenever useful, with an Inel curved position-sensitive detector.

Synthesis

The cyano derivatives were prepared by quaternization,[4] with the appropriate bromoalkylnitrile, of *n*-hexadecyldimethylamine in ethyl acetate used as a solvent.

The carboxylic derivative was prepared by quaternizing, with sodium bromoacetate, *n*-hexadecyldimethylamine in methanol and then by conducting hydrogen bromide gas in the reaction mixture to liberate the carboxylic group.

The 2—OH and 3—OH hydroxy derivatives were prepared by quaternizing N,N-dimethylamino-ethanol or -propanol with *n*-hexadecylbromide in ethyl acetate used as a solvent. The 6—OH hydroxy derivative was prepared by quaternization of *n*-hexadecyldimethylamine with 6-hydroxyhexylbromide.

To avoid thermal decomposition, all the reactions were conducted at room temperature over periods of many hours. The compounds were purified by two successive recrystallizations from ethylacetate or, whenever needed, from mixtures of ethylacetate with ethanol. The purity of the compounds was checked by proton NMR and elemental analysis.

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