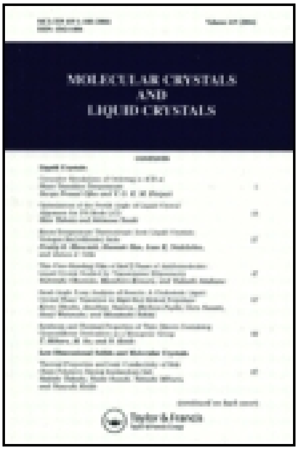

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Thermotropic Liquid Crystals Derived from Amphiphilic Mesogens

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Thermotropic Liquid Crystals Derived from Amphiphilic Mesogens

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It is well-established that the presence in amphiphilic molecules of two distinct and incompatible segments leads, in general, to the formation of molecular organizates certain of which exhibit thermotropic liquid crystalline phases. In the present review the decisive role of amphiphilicity in inducing the formation of thermotropic smectic and columnar mesophases is discussed. Following a brief discussion of the main classes of ionic and nonionic amphiphiles that exhibit thermotropic liquid crystalline character, the emphasis is being placed to amphiphiles bearing multiple hydroxy groups and primarily to those with molecularly recognizable moieties able to form a system of hydrogen bonds. The discussion of this topic, primarily seen from the organic chemistry scope, is hoped to trigger further interest towards the synthesis of novel and unconventional amphiphiles with liquid crystalline properties.

Keywords: amphiphilic mesogens, thermotropic, liquid crystals, amphiphilicity

INTRODUCTION

A decade ago liquid crystals derived from amphiphilic mesogens were almost ignored, at least to the community of researchers, that were involved in structure-property relationships of rigid-rod liquid crystals and their applications in display industry.[1] Liquid crystals derived from amphiphilic mesogens could not however be disregarded by scientists involved with molecular organizates such as micelles, liposomes, vesicles, surfactant membranes[2] which are formed by the dissolution or dispersion of amphiphilic mesogens, usually in water. In this connection it should be noted that the majority of amphiphilic compounds can form both thermotropic and lyotropic liquid crystals as well as the various other molecular organizates mentioned above. These compounds are characterized as amphotropic.[24] In the present account however the discussion will cover amphiphiles that form thermotropic liquid crystals and we will not enter in the vast field of organized molecular assemblies of primarily smectic character.

Smectic liquid crystals of alkali metal carboxylates were known at least from 1910 and the first report was that of Vorlander.[3] Following the early work of Vold *et al.*[4] on the various phases of anhydrous soaps systematic studies on the same materials were performed by Skoulios and Luzzati[5] and in the early seventies by Ubbelohde *et al.*[6] In the eighties several laboratories all over the world investigated several classes of ionic amphiphiles establishing the relevance of amphiphilicity to liquid crystallinity. In the last few years research activity has been directed towards the investigation of non-ionic amphiphiles, such as the alkyl functionalized carbohydrates[7] as well as in the preparation of pairs of amphiphiles each bearing, complementary to the other, hydrogen bonding moieties. In certain cases interaction of complementary amphiphiles induces the formation of liquid crystalline phases.[8] Currently the subject of ionic amphiphiles exhibiting thermotropic mesomorphism has reached to maturity while systematic work is now being performed with amphiphiles bearing groups that form a multiple hydrogen bonding system. In this review the discussion will follow a more or less chronological order summarizing past work and emphasizing current developments.

Amphiphilicity derives from the green work "αμφιφιλος" (αμφι = both, φιλος = friend) meaning that amphiphilic molecules, consisting of two physicochemically distinct and segregated segments, are related with two types of media. For instance, concerning solubility the lipophilic moiety dissolves in lipophilic solvents while the hydrophilic to water and other polar solvents. It has however to be noted that amphiphilic molecules cannot only be judged on the basis of their differentiation in solubility but they can equally well be assessed by considering other properties such as the incompatibility of the two segments due to their differing polarizabilities.[9] By these considerations, it was possible to extend the spectrum of compounds showing amphiphilicity to molecular structures beyond the typical surfactants.

The topic on amphiphilic liquid crystals has been reviewed in this Journal, in 1985 by Busico *et al.*[10] highlighting on the mesomorphic structure of ionic amphiphiles. Skoulios and Guillon[9] in their review have extended amphiphilic character to include other types of compounds and used amphiphilicity to rationalize the formation of smectic and columnar liquid crystals. With these in mind and in order to avoid overlapping with these reviews, the emphasis in the present paper is placed in showing the diversity of molecular structures exhibiting liquid crystallinine phases derived from amphiphilic mesogens and primarily to discuss the new developments in the field i.e. of amphiphiles bearing recognizable hydrogen bonding moieties. A classification of the amphiphilic compounds with liquid crystalline properties can be the following:

a) Liquid crystals derived from ionic amphiphilic and bolaamphiphilic compounds;
b) Liquid crystals from metal complexes functionalized with long aliphatic chains; and
c) Liquid crystals derived from amphiphiles bearing groups able to form hydrogen bonding system(s)

Certain molecules belonging to the above classes of compounds can be functionalized with polymerizable groups. The polymers obtained from these monomers will also be investigated as to the extent that their liquid crystalline behavior is differentiated from that of their monomeric counterparts.

1. LIQUID CRYSTALS FROM IONIC AMPHIPHILIC AND BOLAAMPHIPHILIC COMPOUNDS

1.1. Alkali Metal Carboxylates

As already discussed the liquid crystalline character of alkali metal carboxylates was known as early as 1910 but only in the sixties these soap molecules were

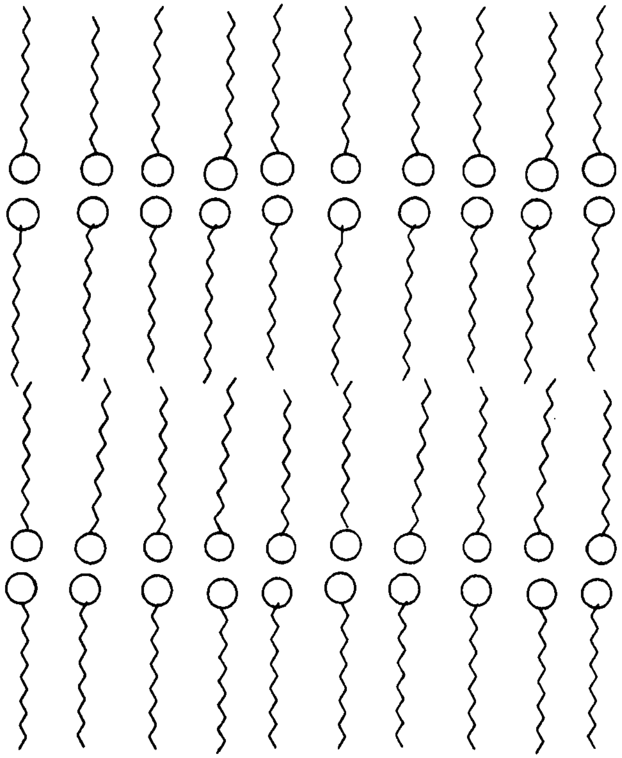
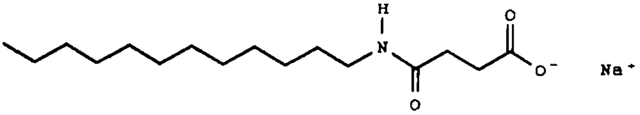


FIGURE 1 Douple polar layer model of ionic amphiphilic molecules.

systematically investigated by Skoulios and Luzzati[5] who proposed the well known model[5b] shown in Figure 1, in which the double polar layer is separated by the paraffinic layer. The salts exhibit multiple melting behavior and their x-ray diffraction patterns are typical of smectic A phases giving long spacings in the ratio $1:\frac{1}{2}:\frac{1}{3}:\frac{1}{4}$ characteristic of a lamellar structure.[5a,10] It is of interest to note however that short chain carboxylates also show smectic A structure as determined by optical and x-ray studies.[6a,6b,11] The arrangement of polar ionic groups in the smectic layers and the differences observed between short and long chain compounds were reinvestigated by Busico *et al.*[10] who proposed an electrostatic model to rationalize these experimental results and which is described in detail in Reference 10.

Concerning the textures of alkali metal carboxylates two smectic phases were established i.e. Smectic I, which is viscous and birefringent with regular layer stacking and Smectic II, fluid and optically isotropic, due to the small dimensions of the liquid crystalline domains. The latter exhibit also fluctuations in the interlayer distances as shown by x-ray diffraction patterns.[10] This behavior is not only characteristic of amphiphilic carboxylates but it is also shared by other amphiphiles such as bis(*n*-alkylammonium) tetrahalogenozinkates[12] and primary *n*-alkylammonium halides[13] as it will be further discussed in the following paragraphs. Thus comparing melting and clearing point transition temperatures as well as the thermodynamic parameters for *n*-alkylammonium chlorides and various alkali metal carboxylates the existing similarities in their mesomorphic behavior become evident. The liquid crystalline phases of these amphiphiles are qualitatively independent of their end group.[13] It is therefore established that amphiphilic character is of crucial importance for the exhibition of liquid crystalline behavior by these compounds.

Structural modification of typical amphiphilic carboxylates has conveniently been obtained by interacting maleic or succinic anhydride with long-chain primary or secondary amines. The sodium salts of *N*-dodecylsuccinamic and *N*-dodecylmaleamic acids, 1 and 2 respectively, exhibit multiple melting behavior and their mesomorphic character[14a] was shown by DSC and optical microscopy. The presence of the double bond in the proximity of the carboxylate group modifies drastically the thermal stability of mesomorphic phases, the succinamic acid derivative being thermally stable while maleamic acid derivative thermally unstable.



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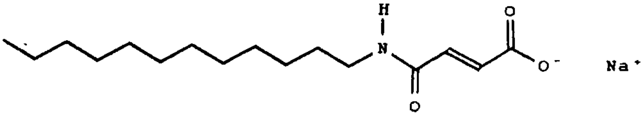

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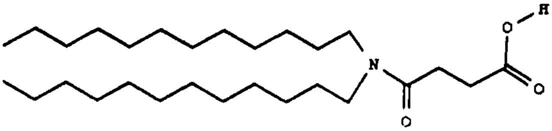
For compounds 3 and 4 the mesomorphic-like behavior was attributed[14b] to the dimeric structures (Scheme I) that were formed through hydrogen bonding of the free carboxylic groups, in analogy with appropriately functionalized aromatic acids which, as it is well-established, form liquid crystalline phases.[1]



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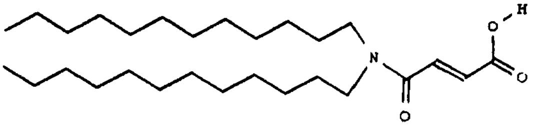

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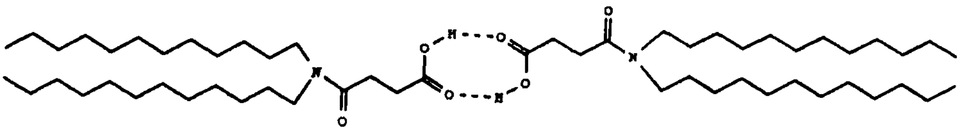
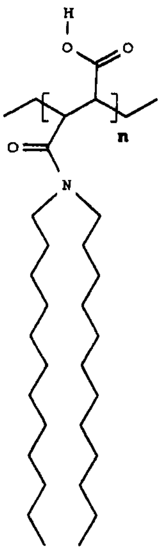


SCHEME I

Polymeric counterparts of polymaleamic acid derivatives have also been prepared[15] by the reaction of polymaleic anhydride ($\bar{D}P = 70$) with long-chain aliphatic primary and secondary amines or alcohols affording, for instance, the polymeric acids 5, 6 and 7.



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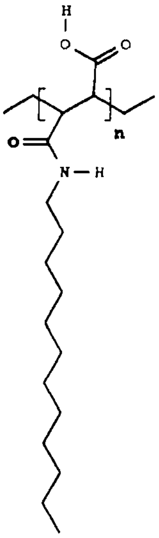

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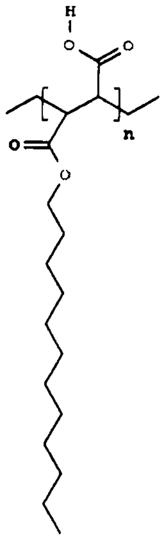

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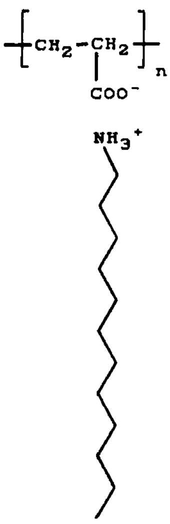
In a similar fashion copolymers have been prepared[15b] by interacting polymaleic anhydride with mixtures of amines and alcohols in various molar ratios. The appearance of liquid crystalline phases, was attributed to the formation of hydrogen bonded superstructures of analogous structures to their monomeric counterparts as evidenced by FT-IR studies[15c] and x-ray diffraction patterns.[15d] The exhibition of liquid crystalline behavior is in this case dependent on the balance of lipophilic-hydrophilic segments coupled with the hydrogen bonding ability of the amide group. Ester group does not favor the formation of a stable lamellar structure and therefore smectic phases do not appear. It was found for instance that amide bearing polymers with $n = 18$ (interaction of polymaleic anhydride with octadecyl amine) or $n = 12, 12$ (interaction with didodecyl amine) exhibit liquid crystalline behavior due to the appropriate balance of the structural parameters.

1.2. *n*-Alkylammonium and Bis(*n*-alkylammonium) Salts

Neutralization of long-chain alkyl amines with halogen acids leads to the formation of *n*-alkylammonium halides exhibiting liquid crystalline character.[16] Subsequently, interaction of long chain *n*-alkylammonium halides with the halide of a divalent metal leads to the formation of salts of the general formula $(RNH_3)_2MX_4$ that they also exhibit liquid crystalline phases.[17] Modification of the liquid crystalline character is in general obtained by modifying the length of the aliphatic chains and/or replacing existing counter ions. Except of the simple halide counterions polymeric counter ions, such as polyacrylate or polymaleate[18] have been employed. In this case the carboxylic polymer neutralizes the long-chain amine acting simultaneously as a template modifying the organizational properties of the protonated amines (polymeric salts 8 and 9).



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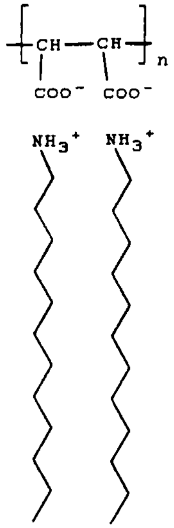

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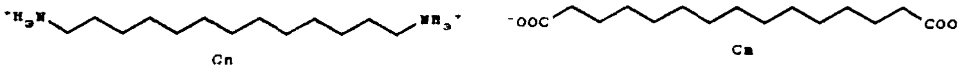
The *n*-alkylammonium chlorides form in the solid phase a bilayer structure, of low electrostatic energy, in which segregation of ionic and lipophilic segments has been obtained. The smectic phase of long-chain primary *n*-alkylammonium chlorides, is associated with a bidimensional fusion of the ionic sheets through an intermediate appearance of a plastic phase, in which almost complete conformational disorder of the alkyl chains occurs.[16b] This behavior is in agreement with DSC studies where only a slight dependence on alkyl chain length is observed for the entropies of fusion and which are comparable with the entropies of fusion of AB salts without conformationally flexible bonds.[16b]

Gault *et al.*[16d] characterized this intermediate "plastic phase" as liquid crystalline since this phase is uniaxial by convergent light observations and also the material melts on exercising pressure on the cover slide. It is also of interest to note that the layer structure persists to the isotropic phase.

From the broad class of *n*-alkylammonium tetrahalogenometallates,[17] bis(*n*-alkylammonium)bromo zincates[12] with $n = 10-16$ show two sharp solid-solid phase transitions and melt to smectic phases as established by DSC, polarizing microscopy and x-ray diffraction up to at least 277°C. The x-ray patterns of these mesophases are typical smectic liquid crystalline phases. Fusion of the salts is practically a bidimensional melting of the inorganic regions as shown by the absence of high angle reflection maxima in the x-rays diffraction patterns.[12]

In connection with the discussion of the smectic liquid crystalline character of long-chain alkylammonium salts the interesting class of alkyl(diammonium) dicarboxylate amphiphilic salts, 10, prepared by simply mixing equimolar quantities of the corresponding diacid and diamine justifies some rather detailed discussion. Several materials have been synthesised but only those containing a long and a relatively short alkyl chain exhibit smectic S_A phases. Interchange of the diammonium and dicarboxylate alkyl segments does not necessarily produce another liquid crystalline salt, and therefore mesomorphic behavior cannot be solely dependent on the ratio of alkyl chain lengths.



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Due to the thermal instability of the salts high temperature x-ray diffraction measurements were not possible. For the salts with one or two long alkyl chain the diffraction patterns suggest a nontypical lamellar structure. The model that it was proposed, shown in Figure 2, maintains the segregation of ionic and lipophilic moieties but it also allows disorder within the layers which are formed by the aggregation. The variable layer spacings even when only one chain length is modified are therefore justified. In Figure 2 is shown how the model applies to a salt with a short and a long alkyl chain. For the mesomorphic phase to appear some of the order of the crystalline phase is preserved. In this phase the rigid ionic layers containing a short alkyl chain alternate with hydrocarbon regions formed by aligned alkyl chains possessing some flexibility. It seems that an appropriate balance of the chain length of the two alkyl sections is necessary for the exhibition of the smectic phase. Specifically one of the alkyl groups must be short enough to link in a way ionic end groups, while the other must be a long alkyl chain.

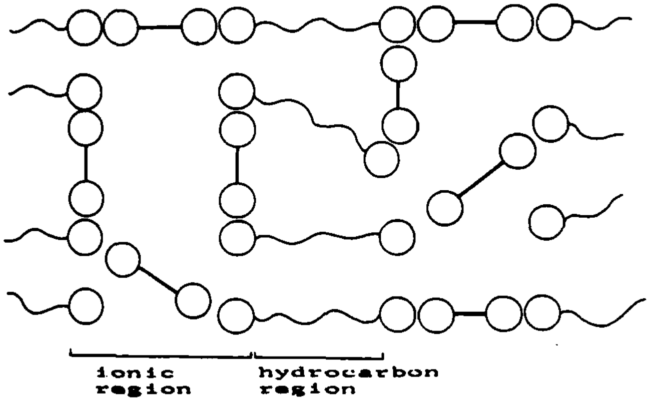
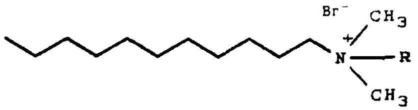


FIGURE 2 Structural model of alkyl(diammonium) dicarboxylates.



R=CH_2CH_3

R=$CH_2CH_2CH_3$

R=$CH_2CH_2CH_2CN$

R=CH_2CH_2OH

R=$CH_2CH_2CH_2OH$

R=CH_2COOCH_3

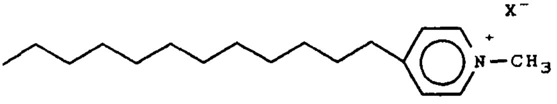
R=$CH_2COOCH_2CH_2OH$

SCHEME II

1.3. Amphiphilic Quaternary Ammonium Salts

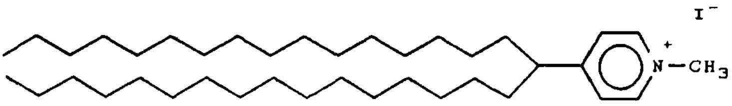
The extremely polar quaternary ammonium and/or pyridinium group coupled with a long aliphatic chain or chains form typical amphiphilic compounds and therefore susceptible to the formation of thermotropic liquid crystals. Aliphatic quaternary ammonium salts[20] were conveniently prepared by the quaternization of tertiary aliphatic amines and structural modifications are easily obtained either by changing the length of the amphiphilic chain or more conveniently by modifying the polar group as shown in Scheme II. This is performed by the reaction of the tertiary amine moiety with an appropriately functionalized primary bromide.

Pyridinium amphiphiles[21] were prepared by the quaternization or protonation of pyridine derivatives. Some representative compounds of this class of amphiphiles, 11–14, are shown below.



11A: X = I
11B: X = ClO₄

11



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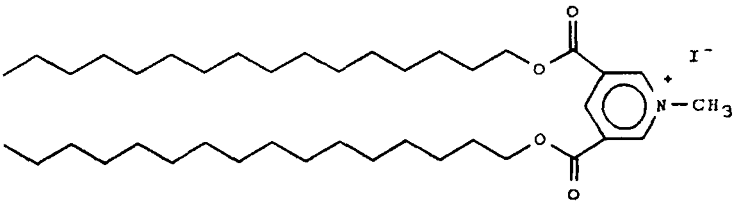

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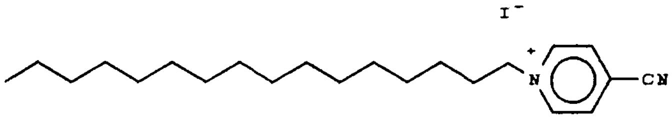

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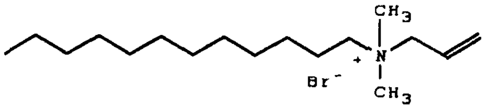
Investigation of *n*-Alkyltrimethylammonium halides[20a] with optical, DSC and x-ray diffraction methods, has shown that the layer structure in the solid state is transformed by a first, solid-solid transition, to a material characterized as "mesophase" or mesomorphic-like.[20a] The salts in this phase are not typical mesomorphic since although the aliphatic chains have been melted the ionic layers are practically unaffected being similar to that in the solid phase. At the clearing transition the quaternaries change to a transparent liquid and subsequently decomposition occurs. As expected the transition enthalpy and entropy changes increase almost linearly with the number of carbon atoms of the long aliphatic chains.[20a]

The mesomorphic-like phases of functionalized at the polar head quaternary ammonium salts,[20b–20d] shown in Scheme II, at least as judged by optical microscopy and DSC studies, are relatively more thermally stable compared to the previously discussed trimethylammonium quaternaries. In addition their mesomorphic-like phases are crucially dependent on the functional group at the polar head. Specifically, the introduction of methylene group(s) at the functional R group results[20d] in a decrease of the clearing point transition. In addition it has been found that substitution of the alkyl groups with groups bearing a hydroxy moiety enhance the thermodynamic stability of smectic-like phases. This latter group also stabilizes the mesophase more effectively as compared to the non-hydroxylic, cyano bearing groups.[20d]

Smectic phases observed for pyridinium salts[21] are crucially affected by the nature of the head group. Thus protonated pyridinium salts and salts with counterion a chloride ion do not show liquid crystalline phases. An explanation that was provided is that the melting point of the protonated derivatives is high as compared to methylated compounds. On the other hand the chloride anion could be unfavorable for liquid crystalline character formation because of its smaller ionic radius as compared to iodide, which could lead to less shielding of the positive charges of the pyridinium rings and therefore to an increased electrostatic repulsion of the head groups. Within this context i.e. of the effect of the polar head and the packing conditions in the lamellar structure, the diversity of smectic phases observed for certain pyridinium amphiphiles is rationalized. Thus smectic-A phases are observed for 11A and 11B amphiphiles and C and H phases are exhibited by 12 and 13 amphiphiles respectively. For 14 a smectic-B phase is shown.

The convenient introduction of allyl, vinyl, acrylate and methacrylate groups at the head or at the end of the lipophilic groups of aliphatic quaternary ammonium salts leads to the formation of monomers, 15–19, which, as expected, and in analogy with other aliphatic quaternary ammonium salts exhibit mesomorphic behavior. The monomers were polymerized under conventional polymerization conditions, usually with the monomers in their micellar state. The polymers although not fully characterized as far as their mesomorphic character is concerned, they definitely show anisotropic behavior which is strongly dependent on the nature and position of the monomers polymerizable group. Thus the polymer resulting from the allyl monomer exhibits a broader mesomorphic range as compared to its monomeric counterpart.[22a] The polymers derived from monomers with the acrylate[22b] or methacrylate[22c] group at the end of the lipophilic chain exhibit broad mesomorphic ranges whereas the vinyl group[22b] or methacrylate group[22c] attached in the vicinity of the quaternary nitrogen do not induce the formation of liquid crystalline polymers. Apparently the presence of extremely polar quaternary centers in the vicinity of the main chain creates severe packing problems in the formation of the lamellar structures of the polymers.



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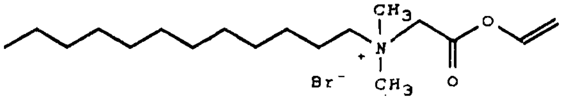

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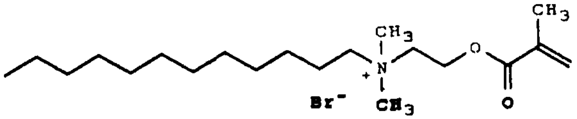

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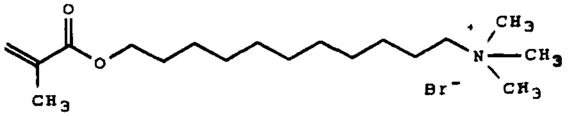

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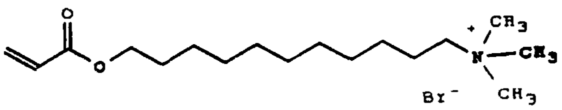

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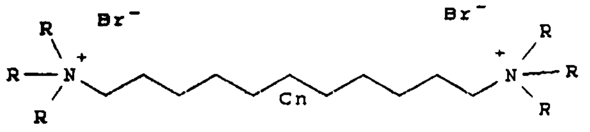
1.4. Ionic Bolaamphiphilic Compounds

The bilayer structure, characteristic of simple amphiphilic compounds can alternatively be formed by compounds bearing two polar heads and a long lipophilic chain, i.e. bipolar amphiphiles or bolaamphiphiles.[23] These compounds which are usually employed for the formation of monolayer membranes or for spanning bilayer membranes[24] conform, in general, with the structural features of molecules that form thermotropic liquid crystalline phases. Modification of the polar heads or of the lipophilic chain length affects the mesomorphic phase and it may even lead to its destruction.

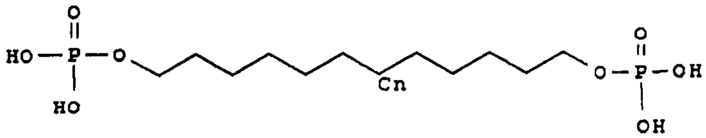
For the diquaternary ammonium amphiphiles, 20, the aliphatic chain was either C_{12} or C_{20}. It has been found[25] that the appearance of thermally stable mesomorphic phases is favored by a combination of a long alkyl chain (C_{20}) with triethylammonium group as polar heads. On the contrary, bulky diallylethylammonium polar head group has a rather destructive effect on the existence of the mesophase. For phosphate bipolar amphiphiles, 21, a C_{16} chain as compared to C_{12} favors the formation of liquid crystalline phases.



$n = 12, 20$

$R = CH_3, C_2H_5, CH_2CH{=}CH_2$

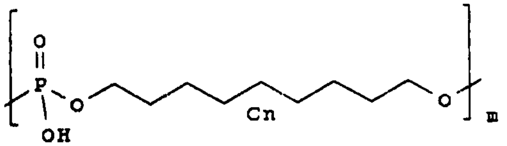
20



$n = 12, 16$

21

Polymeric analogues of bipolar amphiphiles[26] have also been prepared by reacting phosphorous oxychloride with long chain diols and under conditions that favor the formation of straight chain polyphosphates. These polymeric or rather oligophosphates, 22, of $\overline{DP} = 8-12$, show on cooling from their isotropic melts, metastable liquid crystalline phases. Further work is planned for the characterization of these polymers.

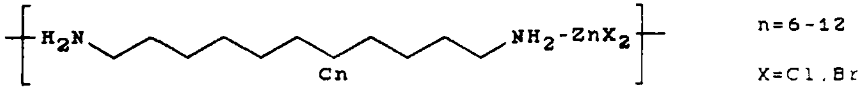


$m = 8-11$

$n = 12, 16$

22

The presence of polar and lipophilic groups along the polymeric chains seems that it induces, under certain conditions, the formation of mesophases. Thus polymers[27] of the formula 23 (abbreviation C_mX, with X = Cl, Br and $m = 6, 7, \ldots 12$) were formed by interacting, at room temperature, equimolar amounts of ZnX_2 and α,α diamines. In the solid phase, at room temperature, the polymeric chains run, in parallel, in such a manner that layers of ZnX_2 are formed. This segregation is more or less preserved in the melt phase only for the compound $C_{12}Cl$ which exhibits smectic phases as shown by optical and x-rays studies. The appearance of a liquid crystalline phase by this compound is a highly cooperative phenomenon between the disordered polymethylenic chains, the organized polar ends and of the halogen attached on Zn.



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2. LIQUID CRYSTALS DERIVED FROM METAL COMPLEXES FUNCTIONALIZED WITH LONG ALIPHATIC CHAINS

Liquid crystalline phases were also exhibited by compounds prepared by complexing metal ions with ligands bearing long aliphatic chains. In this case, the metal ion with the complexing functional groups constitute the polar head or core and as it is always the case the aliphatic chains constitute the lipophilic segment. Examples of materials forming mesomorphic phases are the complexes formed from Copper(II) when it was reacted with long-chain carboxylates or amines,[28,29] Lead(II)[30] and Rhodium(II)[31] ions in their reaction with long-chain carboxylates.

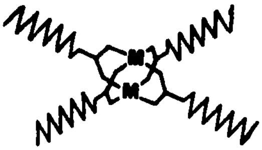
Specifically, copper (II) dodecanoate gives a discotic mesophase[29a] characterized by a hexagonal columnar lattice with a repeat distance of about 20 Å. Each column is made of units with a period of about 4.7 Å as shown in Scheme III.

Lead carboxylates[30] and specifically dodecanoate were extensively studied, including in addition to the classical characterization methods for liquid crystals, ^{207}Pb NMR and Raman spectroscopy.[30a] For dodecanoate and shorter chain compounds smectic phases were exhibited[30] while for tetradecanoate and above a smectic phase was not observed, the crystals melting directly to the isotropic melt.

Rhodium (II) carboxylates[31] are isostructural to copper (II) and form a columnar mesophase. In this case the intercolumnar distance is 16.7 Å for rhodium (II) caprylate and around 20 Å for rhodium (II) dodecanoate and varies slightly with temperature. The broad band at wide angles corresponds to a distance of 4.65 Å for rhodium caprylate and a distance of 4.60 Å for rhodium dodecanoate. These distances compare well with 4.7 Å determined for the mesophase of copper dodecanoate.

3. LIQUID CRYSTALLINE PHASES RESULTING FROM AMPHIPHILES BEARING GROUPS ABLE TO FORM MULTIPLE HYDROGEN BONDING SYSTEM(S)

The accumulation of groups at the end or at the ends of the hydrophobic chain with the property to form a multiple hydrogen bonding system may lead, in principle, to the formation of thermotropic liquid crystals in analogy with ionic am-



SCHEME III

phiphiles. As it is the case with other amphiphiles, the segregation of the polar hydroxy groups from the lipophilic segments is the driving force for the formation of lamellar structures. An important class of compounds forming thermotropic liquid crystals as well as molecular organizates in solution are the carbohydrate amphiphiles, certain polyhydroxy compounds and also some long alkyl-chain derivatives of iminodiacetic acid. A novel class of amphiphilic liquid crystals is now under development which are prepared by molecular recognition, through hydrogen bonding, of amphiphiles bearing complementary moieties. To these liquid crystals emphasis will be placed in the last paragraphs of this article.

3.1. Amphiphilic Carbohydrates

The observation by E. Fischer[32] of a "double melting point" of certain long-chain *n*-alkyl pyranosides in 1911 was the first indication for the exhibition of thermotropic liquid crystalline character by this type of compounds. The subject of carbohydrate liquid crystals has however been ignored for several years except of a paper by Noller *et al.*[33] that appeared in 1938. It was only in the eighties that Jeffrey renewed the interest on these compounds and reviewed[7] the topic in 1986. At the present time work is continuing in many laboratories[34] and diversified classes of amphiphilic carbohydrates have been prepared and characterized. In fact taking into consideration the possibilities offered by the use of various carbohydrate moieties and the nature and number of aliphatic chains that can be used, a vast number of liquid crystals may be prepared. There is no intention to cover in detail the subject of amphiphilic carbohydrates but simply to set forth a model justifying the formation of liquid crystalline phases. Some typical carbohydrate liquid crystalline compounds are shown below:

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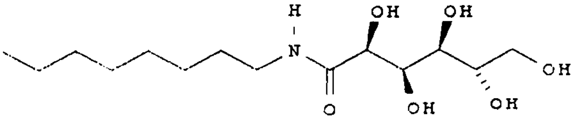

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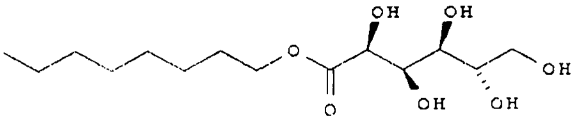

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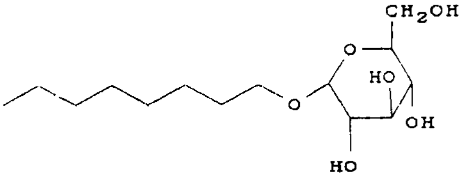

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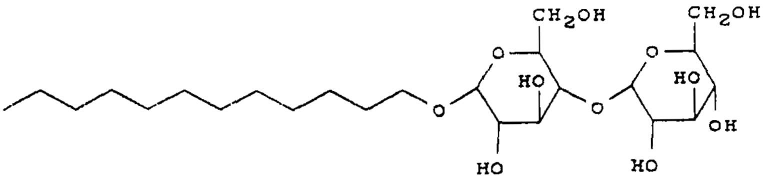

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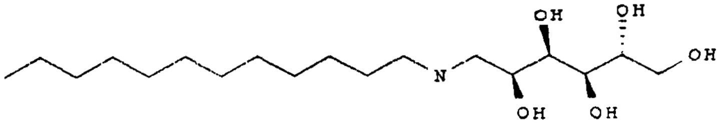

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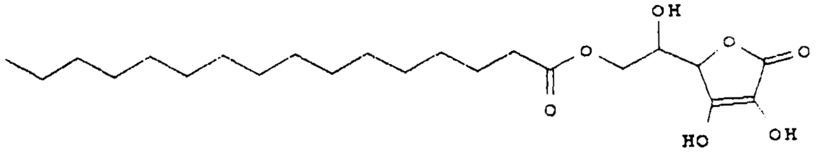

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The majority of amphiphilic compounds studied so far form smectic A_d mesophases with partially overlapping carbohydrate moieties and with the alkyl chains pointing outwards. Such a hypothetical model for the layer structure of alkylated carbohydrates is shown in Figure 3. The hydrogen bonding within the layers is

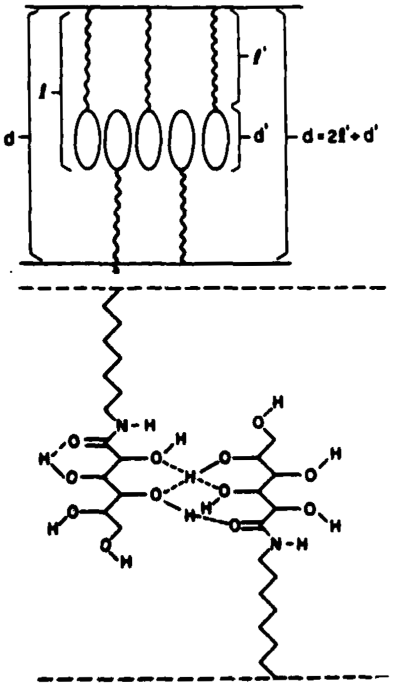
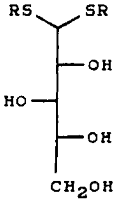


FIGURE 3 Hypothetical model of the layer structure of alkylated carbohydrates (A). Hydrogen bonding within the layers formed by *n*-octyl gluconamide (B).

shown for *n*-octyl gluconamide. It has to be noted that this model is only one of the many possible structures that can be drawn justifying the smectic phase. The molecules are in a dynamic state, the chains being relatively fluid and the hydrogen bonding system breaking and reforming again.

Recently carbohydrate liquid crystals have been identified of columnar hexagonal mesophase.[34g] Specifically double-tailed dithioacetals, although different in stereochemistry, they form only one type of hydrogen-bonded disk-shaped structure. The mesomorphic structure is formed by about five molecules placed in columns with the hydrogen bonded system surrounded by thioalkyl groups. A schematical representation of the aldose dithioacetals, of amphiphiles 30–33 is shown in Figure 4. The terminal hydroxyl group is essential for the formation of the columnar hexagonal mesophase since the 5-deoxy carbohydrate dithioacetals were shown that they were not mesomorphic.



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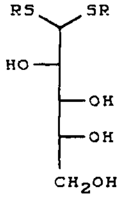

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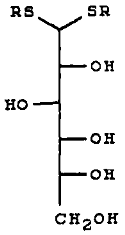

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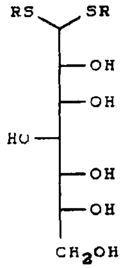

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$R = C_8H_{17}$ for 30, 31, 33

$R = C_7H_{15}, C_8H_{17}, C_9H_{19}$ for 32

3.2. Multihydroxy Amphiphilic and Bolaamphiphilic Compounds

The property of hydroxy groups to form hydrogen bonds and their location at the ends of lipophilic chains is, at it is always the case, the crucial factor, for the formation of this novel type of liquid crystals. Diols or polyols with one-polar

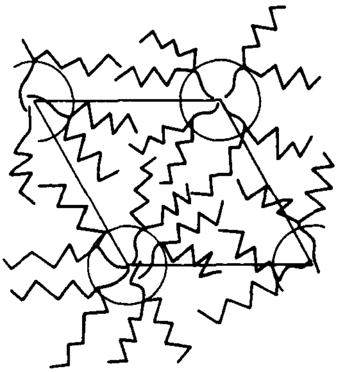
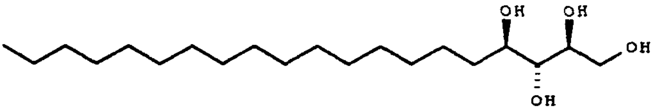


FIGURE 4 Schematic representation of the molecular assembly of dithiacetals in their columnar hexagonal mesophase.

head[35] as well as bolaamphiphilic polyols[36] exhibit thermotropic liquid crystalline behavior. The structures of such polyhydroxy amphiphiles, 34–37, with one polar head are shown below:



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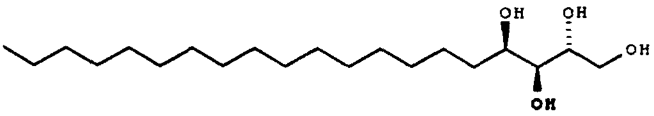

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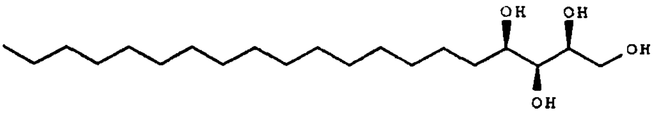

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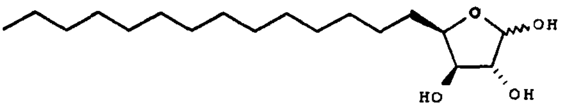

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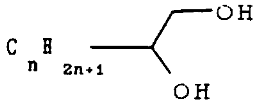
Compounds of the formula 38 with $n = 5$ exhibit monotropic mesophases[37] which are stabilized by addition of water. These compounds are structurally related to carbohydrate liquid crystals and can be regarded as the simplest members of this large class of amphiphilic mesogens.



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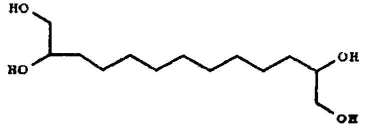
It has been found[36] that stabilization was obtained by the coupling of two amphiphilic diols via their hydrophobic molecular moieties affording bolaamphiphilic compounds, 39–44. Of these compounds the unsymmetrical tetrol, 40, has the greatest mesophase diversity. On cooling the isotropic melt, a fan-like texture, typical of lamella α-phases which can be oriented very easily homoetropically by shearing is obtained. The hydroxy groups, like those of amphiphilic diols should be coupled via a dynamic network of cooperative hydrogen bridges which are separated by the conformationally molten polymethylene chains forming a L_α phase. On further cooling to 75°C the texture changes and viscosity increases due probably to transition to a more highly ordered mesophase with rigid parallel polymethylene chains, i.e. a L_β phase. At 43°C another transformation occurs which cannot be studied in detail due to onsetting crystallization. The liquid crystalline phases of polyols can be modified by the addition of water. Specifically the mesophases of compounds with long aliphatic chains are stabilized while those with shorter polymethylene chains are destabilized.



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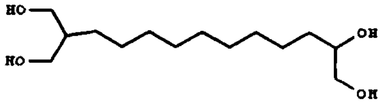

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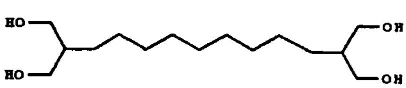

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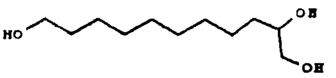

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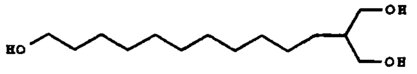

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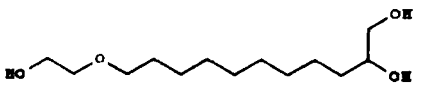

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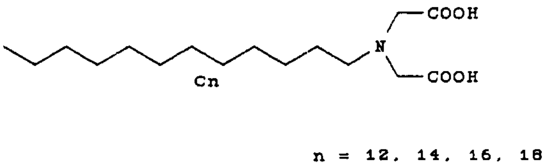
3.3. Amphiphilic Iminodiacetic Acid Derivatives

It is well-established[1] that aromatic acids form liquid crystalline phases due to a dimer formation induced by hydrogen bonding of the individual acids. In this case the exhibition of liquid crystalline phases is induced by the rigid-rod character of the dimeric supramolecular structure. Recently we have discovered[38] that long aliphatic chain derivatives of iminodiacetic acids, 45, exhibit smectic liquid crystalline character in analogy with ionic amphiphilic compounds.



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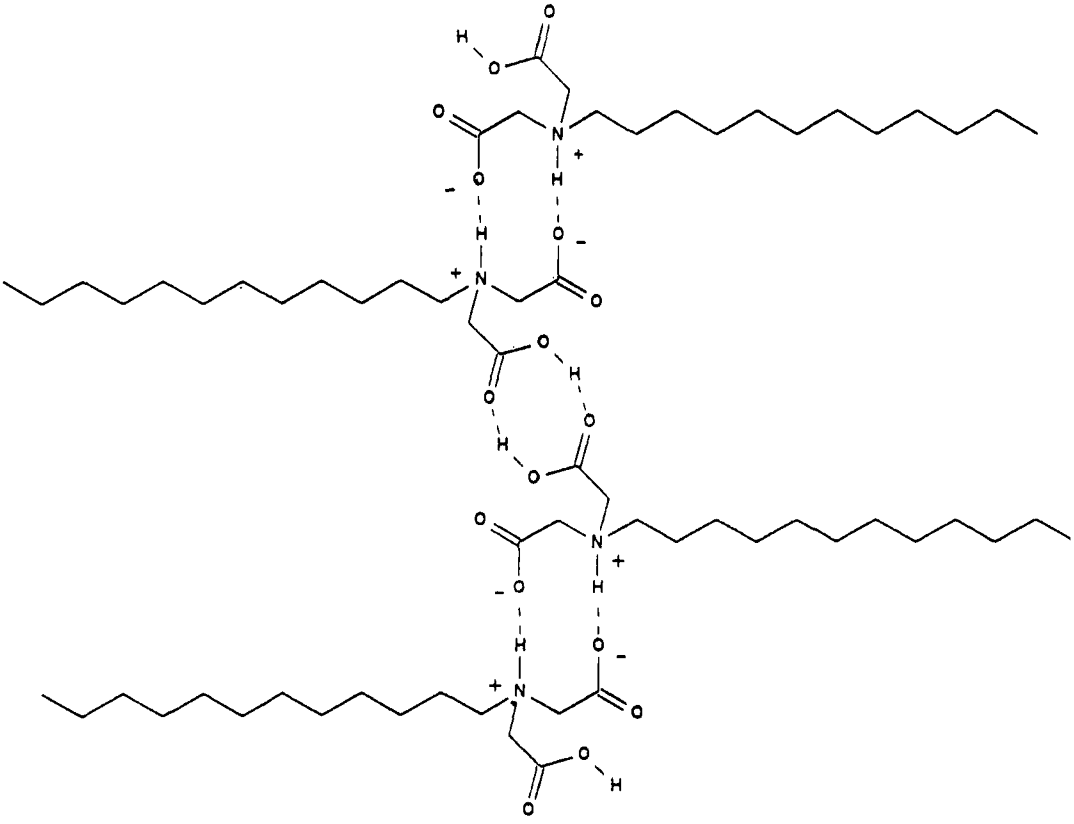
Taking into consideration the zweiterionic character[39] of the acid as well as the presence of proton donors and acceptors that create the possibility of a multiple hydrogen bonding system between the two iminodiacetic acid derivatives and the nonmiscibility of the alkyl chains we can envisage a structure, shown in Scheme IV, for the alkyl derivatives of iminodiacetic acid. It should be noted, that in the crystalline phase the hydroxy group does not act as an acceptor since carbonyl and carboxylate are better acceptors than hydroxy groups.[39] Considering the Bragg d spacings[38b] which are shorter than the dimensions determined by molecular modeling we have to assume that either there is an overlapping of the aliphatic chains or that the molecules are tilted within the layers.



SCHEME IV

3.4. Amphiphiles with Molecular Recognizable Moieties

As already established and previously discussed the formation of dimeric structures through hydrogen bonding is an effective strategy for inducing the formation of liquid crystalline phases. The effectiveness of hydrogen bonding may however be enhanced by employing compounds with complementary functionalities. A very well-known case of such interaction is that of nucleobases in nucleic acids.

The first reported example of compounds that could, in principle, form liquid crystals resulted from the functionalization of 2,6-diaminopyridine and uracil with long aliphatic chains.[40] These compounds with complementary moieties, as far as the formation of hydrogen bonding is concerned, formed crystalline or liquid crystalline materials. Three hydrogen bonds were formed between the interacting heterocyclic bases. These bases together with the hydrogen bonding system constitute the "polar segment" which is segregated from their lipophilic moiety. The supramolecular structure of the complex is shown in Figure 5. In general, the complexes can be prepared either by the interaction of the complementary bases in organic solvents, usually chloroform or by melt crystallization or even by solid mixing. In the present case the heterocyclic bases were interacted in chloroform.

Lehn *et al.*[40] prepared several compounds by modifying alkyl chain length while maintaining the same basic core. Pure compounds show solid polymorphism but none of them exhibits mesomorphic phase. All the 1:1 mixtures that had been investigated show crystalline polymorphism and five of them with long aliphatic chains exhibited a metastable mesomorphic phase. To the moment there is no direct evidence for the formation of the complex in the mesomorphic phase. The fact however that an analogous triply hydrogen bonded system has been established

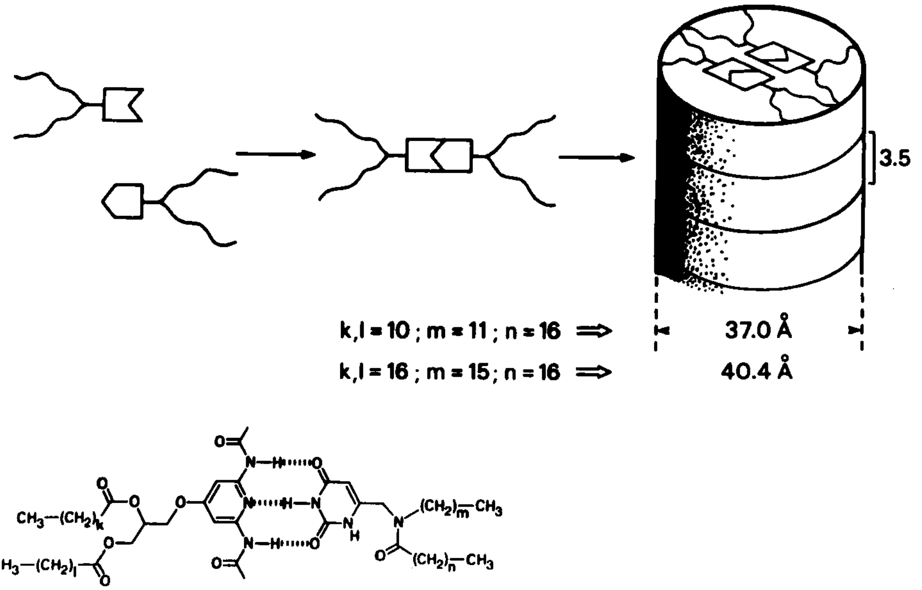


FIGURE 5 Formation of a hydrogen bonded system and its columnar mesomorphic structure (The figure was kindly provided by Prof. J. M. Lehn).

both in the solid state and in solution[40] is a convincing evidence that the same structure may be maintained in the melt and which is responsible for the formation of the liquid crystalline phase. X-ray diffraction data of the mixtures with chain lengths as specified in Figure 5 agree with the exhibition of mesophases of the columnar hexagonal type. The columns have 37 and 40.4 Å diameter respectively and they are formed by a stack of disks, each of which contains two supermolecules side by side, with a contact distance of 3.5 Å between the successive plates as shown in Figure 5. With the use of these complementary amphiphiles and their intermolecular interaction it became possible to amplify the molecular information of the recognition phenomenon and to express it macroscopically by the exhibition of the liquid crystalline phases.

A molecule possessing two at least groups and which are respectively complementary with two other groups placed on another molecule can lead, in principle, to the formation of polymeric structures resulting from this interaction. Such a bifunctional system is shown schematically in Figure 6.

Compounds with two complementary groups have already been prepared[41] and their complexes have been characterized as far as their liquid crystallinity is concerned. Specifically uracil (U) and 2,6-diacylamino pyridine (P) have been introduced in tartraric acid (T) and the compounds allowed to interact forming triply-hydrogen bonded complementary pairs as shown in Scheme V. Due to the presence of the chiral centers in tartraric acid it is also possible to study their effect on the properties of the material formed.

The components LP_2, LU_2, DP_2, MP_2 and MU_2 are prepared from L(+), D(−) and meso (M) tartraric acid which can associate through heterocyclic moieties.[41] In fact, 1:1 mixtures of the complementary pairs (LP_2 + LU_2) and (MP_2 + MU_2) gave compounds different from their components both in the bulk and in solution as established by NMR and circular dichroism spectra of (LP_2 + LU_2).

The thermal transitions of pure compounds and of 1:1 mixtures have been studied by DSC and polarizing microscopy. The pure compounds show solid polymorphic behavior whereas 1:1 mixtures exhibit liquid crystalline behavior from below room temperature to above 200°C. Optical textures are different for LL and MM mixtures as it was shown for the mixtures (LU_2 + LP_2) and (MU_2 + MP_2).[41]

The x-ray patterns of LL, DL and MM mixtures indicate that they show hexagonal columnar liquid crystalline phases. The diameter of the columns is about the same for the three systems i.e. about 37 Å. For LL mixture a period of 3.45 Å along

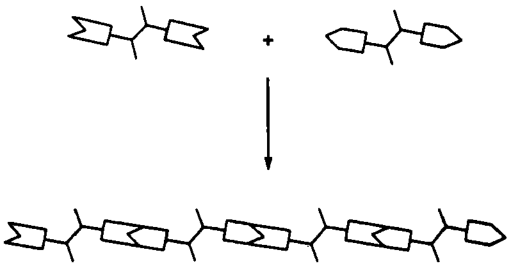
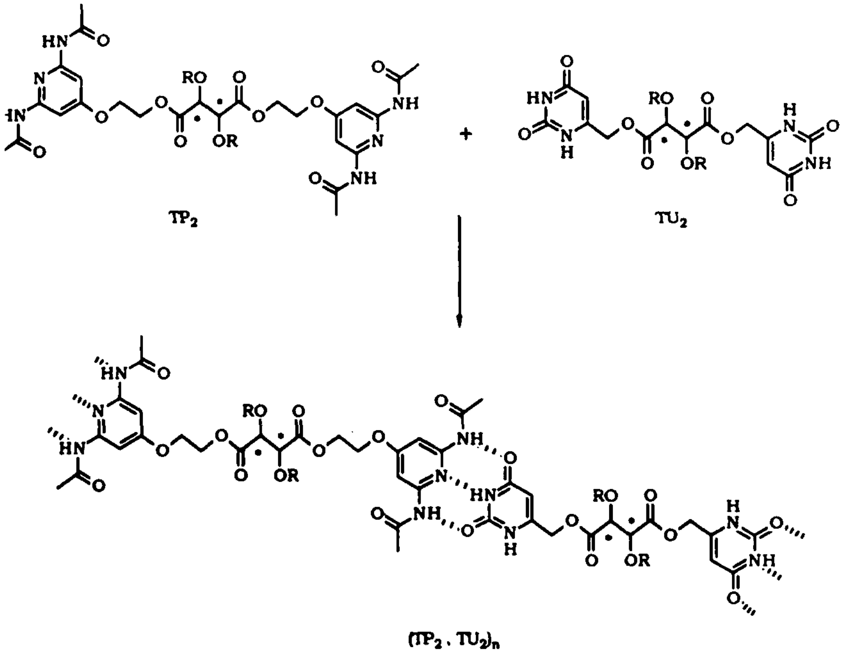


FIGURE 6 Schematic interaction of compounds bearing two recognizable groups.



SCHEME V

the column axis is indicated. This distance corresponds to the stacking distance between the flat heterocyclic moieties. Taking into consideration the density of the material, the obtained results are consistent with a model in which the columns have a triple helix superstructure composed of three strands resulting from the poly-association of the two components TP_2 and TU_2. The structure is shown schematically in Figure 7, A. In this figure a single helical strand and the full triple helix are shown in the bottom and the top of the column respectively. The aliphatic chains stick out of the cylinder almost perpendicular to its axis.

For the MM mixture, the main period is $c = 3.55$ Å with a twofold superstructure. The data are in agreement with a model built by three polymeric strands in an arrangement as shown in Figure 7, B. The LD mixture exhibits a mesophase with columns of almost the same characteristics. These results show clearly the effect of chirality of tartaric acid on the superstructures that are formed.

Triggered by the interaction of complementary nucleobases in nucleic acids and the formation of the double helix, adenine and thymine nucleobases were functionalized with long aliphatic chains transforming these bases to amphiphilic-type compounds.[42] Since it has been found that in non-biological systems recognition is significantly enhanced with solvents that do not form hydrogen bonds,[43] the interaction of amphiphilic nucleobases was performed in chloroform or in the melt. It is of interest to note that in aqueous media vertical stacking has been found to predominate.[44]

To this end we have initiated an investigation on the possibility to obtain liquid crystalline phases from the alkylated derivatives of adenine and thymine, i.e. from

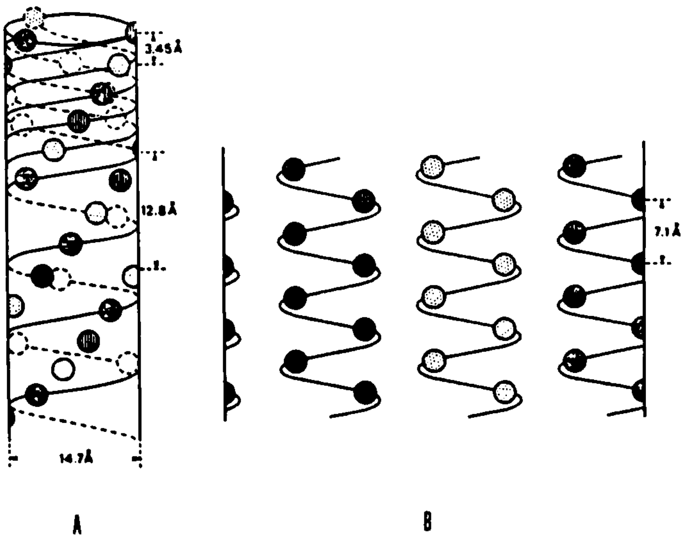
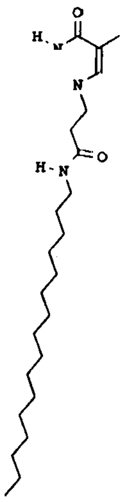


FIGURE 7 Columnar superstructure for $(LP_2, LU_2)_n$ as determined by x-ray diffraction data.

46, 47, 48 and 49, as well as by their complementary complexes. Adenine with its amino group, having available two hydrogens for hydrogen bonding and with more than one hydrogen bonding acceptor may in principle recognize two molecules of thymine. This is the reason that complexes with



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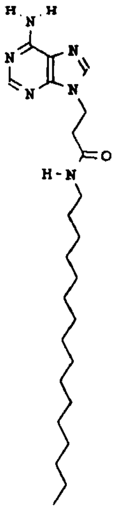

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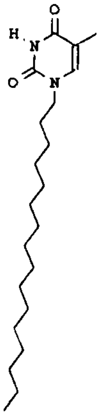

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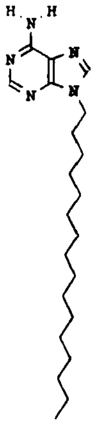

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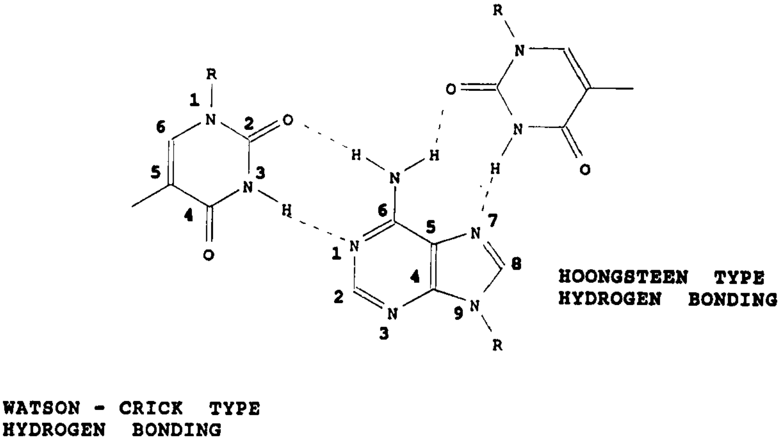
molar ratio 1:1 and 1:2 adenine-thymine could be prepared[42] through the Watson-Crick and Hoogsteen mode of hydrogen bonding interaction as shown in Scheme VI.



SCHEME VI

It should also be noted that aliphatic chains were introduced at 1 and 9 positions of thymine and adenine respectively i.e. at sites remote from the functionalities involved in the recognition process. This strategy must be followed in all cases that molecular recognition is seeked. The amide bearing substituents of 48, 49 may affect the organizational characteristics of the nucleobase amphiphiles due to the possibility of hydrogen bonding interactions because of the presence of amide groups.

The detailed optical and DSC studies as well as x-ray diffraction investigation concerning these novel nucleobases can be summarized in the following: Pure adenine and thymine derivatives and their binary mixtures are organized in the solid state, at low temperature, forming lamellar structures as it is generally the rule with amphiphilic compounds. This ordering is maintained to the isotropization of the material as shown with x-ray diffraction studies. The optical textures that were observed which indicated the formation of metastable mesomorphic phases seem to contradict the x-ray results. Thus the mesomorphic phases observed may be interpreted as monotropic, occurring on cooling from the isotropic melt which were not stable enough to be detected by x-ray diffraction. We may attribute the absence of stable mesomorphic phases to the structure and shape of the molecules and of their complexes, which cannot properly be accommodated to a supramolecular structure affording liquid crystalline phases. The work is continuing with other amphiphilic recognizable compounds in order to assess the role of amphiphilicity and molecular recognition in the formation of novel liquid crystals.

CONCLUDING REMARKS

In concluding this review, we should stress once more the structural features of amphiphilic molecules which are responsible for the exhibition of thermotropic mesomorphism by reference to an extreme example of a molecule showing liquid crystalline phases. This is the case of a half-fluorinated hydrocarbon i.e. of (perfluorodecyl) decane ($F(CF_2)_{10}(CH_2)_{10}H$)[45] which it was established that it is liquid crystalline. The segregation, due to the immiscibility of the perfluorinated moiety in the hydrocarbon portion was the driving force for the formation of a lamellar structure leading macroscopically to a smectic liquid crystalline phase. As it is always the case segregation of the molecular portions governs the appearance of mesomorphic phases.

References

1. H. Kelker and R. Hatz, Handbook of Liquid Crystals, (Verlag, Chemie, Weinheim, 1980) and references cited therein.
2. a. J. Fendler, Membrane Mimetic Chemistry, Wiley-Interscience, New York, 1982 and references cited therein.
3. D. Vorländer, *Ber. Deutche Chem. Gesell.*, **43**, 3120 (1910).
4. a. M. J. Vold, M. Macomber and R. D. Vold, *J. Am. Chem. Soc.*, **63**, 168 (1941); b. R. D. Vold, *J. Am. Chem. Soc.*, **63**, 2915 (1941).
5. a. A. Skoulios and V. Lussati, *Nature*, **183**, 1310 (1959); b. A. Skoulios and V. Lussatti, *Acta Cryst.*, **14**, 278 (1961); c. B. Gallot and A. Skoulios, *Kolloid Z und Z. Polymere*, **210**, 143 (1966).
6. a. J. J. Duruz and A. R. Ubbelohde, *Proc. R. Soc. London.*, **330**, 1 (1972); b. H. J. Michels and A. R. Ubbelohde, *J. Chemical. Soc.*, Perkin II, 1879 (1972); c. A. R. Ubbelohde, *Nature*, **244**, 487 (1973).
7. G. A. Jeffrey, *Acc. Chem. Res.*, **19**, 168 (1986).
8. J. M. Lehn, *Angew. Chem. Int. Ed. Engl.*, **29**, 1304 (1990).
9. A. Skoulios and D. Guillon, *Mol. Cryst. Liq. Cryst.*, **165**, 317 (1988).
10. V. Busico, A. Ferraro and M. Vacatello, *Mol. Cryst. Liq. Cryst.*, **128**, 243 (1985).
11. J. Bonekamp, B. Hegemann and J. Ionas, *Mol. Cryst. Liq. Cryst.*, **87**, 1 (1982).
12. V. Busico, D. Castaldo and M. Vacatello, *Mol. Cryst. Liq. Cryst.*, **78**, 221 (1981).
13. V. Busico, P. Cernicchiaro, P. Corradini and P. Vacatello, *J. Phys. Chem.*, **87**, 1631 (1983).
14. a. A. Malliaris, C. M. Paleos and P. Dais, *J. Phys. Chem.*, **91**, 1149 (1987); b. C. M. Paleos, G. Margomenou-Leodinopoulou, L. H. Margaritis and Z. Terzis, *Mol. Cryst. Liq. Cryst.*, **129**, 127 (1985).
15. a. D. Tsiourvas, C. M. Paleos and P. Dais, *J. Applied Polym. Sci.*, **38**, 257 (1989); b. D. Tsiourvas, C. M. Paleos and P. Dais, *J. Polym. Sci. Chem. Edit.*, **28**, 1263 (1990); c. C. M. Paleos, D. Tsiourvas, J. Anastassopoulou and T. Theophanides, *Polymer*, **33**, 4047 (1992); d. Own unpublished results.
16. a. V. Busico, P. Corradini and M. Vacatello, *J. Phys. Chemistry*, **86**, 1033 (1982); b. V. Busico, P. Cernicchlaro, P. Corradini and M. Vacatello, *J. Phys. Chem.*, **87**, 1631 (1983); c. V. Busico, P. Corradini, P. Guerra and P. Severino, *Gazzetta Chimica Italiana*, **115**, 17 (1985); d. J. D. Gault, H. A. Gallardo and H. J. Müller, *Mol. Cryst. Liq. Cryst.*, **130**, 163 (1985). e. Y. Matsunaga and K. Nishida, *Bull. Chem. Soc. Jpn.*, **61**, 3435 (1988).
17. a. M. Vacatello and V. Busico, *Mol. Cryst. Liq. Cryst. (Letters)*, **64**, 127 (1981); b. G. H. Needham, R. D. Willet and H. F. Franzen, *J. Phys. Chem.*, **88**, 1984 (1984).
18. C. M. Paleos, D. Tsiourvas and P. Dais, *Liquid Crystals*, **5**, 1737 (1989).
19. R. P. Sellens, P. J. I. Runcimann, A. C. Griffin and E. S. Bryant, *Mol. Cryst. Liq. Cryst.*, **166**, 123 (1989).
20. a. K. Iwamoto, K. Ohnuki, K. Sawada and M. Seno, *Mol. Cryst. Liq. Cryst.*, **73**, 95 (1981); b. A. Malliaris, C. Christias, G. Margomenou-Leonidopoulou, C. M. Paleos, *Mol. Cryst. Liq. Cryst.*, **82**, 161 (1982); c. G. Margomenou-Leonidopoulou, A. Malliaris, C. M. Paleos, *Thermochimica Acta*, **85**, 157 (1985); d. C. M. Paleos, G. Margomenou-Leonidopoulou and A. Malliaris, *Chimica Chronika, New Series*, **14**, 89 (1985); e. C. M. Paleos, G. Margomenou-Leonidopoulou, D. Babilis and C. Christias, *Mol. Cryst. Liq. Cryst.*, **146**, 122 (1987).
21. a. G. A. Knight and B. D. Shaw, *J. Chem. Soc.*, 682 (1938); b. E. J. R. Südholter, J. B. F. N. Engberts and W. H. de Jeu, *J. Phys. Chem.*, **86**, 1908 (1982); c. C. G. Bazuin, D. Guillon, A. Skoulios and R. Zana, *J. Physique*, **47**, 927 (1986).
22. a. C. M. Paleos and P. Dais, in "Recent Advances in Liquid Crystalline Polymers," Ed. L. L. Chapoy, p. 89, Elsevier Applied Science Publishers, London and New York (1983); b. C. M. Paleos, G. Margomenou-Leonidopoulou and A. Malliaris, *Mol. Cryst. Liq. Cryst.*, **161**, 385 (1988);

c. J. Michas, C. M. Paleos and P. Dais, *Liquid Crystals*, **5**, 1737 (1989).

23. J. H. Fuhrhop and D. Fritsch, *Acc. Chem. Res.*, **19**, 130 (1986).
24. H. Ringsdorf and B. Schlarb, *Angew. Chem.*, **27**, 133 (1988).
25. A. Kokkinia, C. M. Paleos and P. Dais, *Mol. Cryst. Liq. Cryst.*, **186**, 251 (1990).
26. C. M. Paleos, A. Kokkinia and P. Dais, in "Liquid-Crystalline Polymers" R. A. Weiss and C. K. Ober, Eds. ACS Symposium Series 435, p. 93 (1990).
27. V. Busico, P. Cernicchiaro, A. Scopa and M. Vacatello, *Colloid and Polymer Sci.*, **261**, 224 (1983).
28. A. M. Giroud-Godquin and P. M. Maitlis, *Angew. Chem. Int. Ed. Engl.*, **30**, 375 (1991).
29. a. A. M. Godquin-Giroud, J. C. Marchon, D. Guillon and A. Skoulios, *J. Phys. Lett.*, **45**, L681 (1984); b. C. M. Paleos, G. Margomenou-Leonidopoulou, J. D. Anastassopoulou and E. Papaconstantinou, *Mol. Cryst. Liq. Cryst.*, **161**, 373 (1983). c. J. C. Marchon, P. Maldivi, A. M. Giroud-Godquin, D. Guillon, A. Skoulios and D. P. Strommen, *Philos. Trans. R. Soc. London A330*, 109 (1990); d. O. Poizat, D. P. Strommen, P. Maldivi, A. M. Giroud-Godquin and J. C. Marchon, *Inorg. Chem.*, **29**, 4853 (1990).
30. a. A. M. Amorim Da Costa, H. D. Burrows, C. F. G. C. Geraldes, J. J. C. Teixeira-Dias, C. G. Bazuin, D. Cuillon, A. Skoulios, E. Blackmore, G. J. T. Tiddy and D. L. Turner, *Liquid Crystals*, **3**, 215 (1986); b. H. Ellis, *Mol. Cryst. Liq. Cryst.*, **139**, 281 (1986).
31. A. M. Giroud-Godquin, J. C. Marchon, D. Guillon and A. Skoulios, *J. Phys. Chem.*, **90**, 5502 (1986).
32. E. Fischer and B. Helferich, *Justus Liebigs Ann. Chem.*, **383**, 68 (1911).
33. C. R. Noller and W. C. Rockwell, *J. Am. Chem. Soc.*, **60**, 2076 (1938).
34. a. J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, **110**, 205 (1984); b. M. A. Marcus and P. L. Finn, *Mol. Cryst. Liq. Cryst., Letters*, **2**, 159 (1985); c. B. Pfannenmüller, W. Welte, E. Chin and J. W. Goodby, *Liquid Crystals*, **1**, 357 (1986); d. D. Baeyens-Volant, R. Fornasier, E. Szalai and C. David, *Mol. Cryst. Liq. Cryst.*, **135**, 93 (1986). e. J. W. Goodby, M. A. Marcus, E. Chin, P. L. Finn and B. Pfannenmüller, **3**, 1569 (1988); f. H. A. Van Doren, R. Van der Geest, C. F. De Ruijter, R. M. Kellogg and H. Wynberg, *Liquid Crystals*, **8**, 109 (1990). g. K. Praefcke, A. M. Levelut, B. Kohne and A. Eckert, *Liquid Crystals*, **6**, 263 (1989).
35. K. Praefcke, B. Kohne, S. Diele, D. Pelzl and A. Kjaer, *Liquid Crystals*, **11**, 1 (1992).
36. F. Hentrich, C. Tschierske and H. Zaschke, *Angew. Chem. Int. Ed. Engl.*, **30**, 440 (1991).
37. C. Tschierske, G. Brezeninski, F. Kuschel and H. Zaschse, *Mol. Cryst. Liq. Cryst. Lett. Sec.*, **6**, 139 (1989).
38. a. C. M. Paleos, J. Michas and A. Malliaris, **186**, 251 (1990); b. C. M. Paleos, J. Michas, A. Skoulios and P. Weber, *Mol. Cryst. Liq. Cryst.* In press .
39. J. Bernstein, M. C. Etter and J. C. MacDonald, *J. Chem. Soc. Perkin Trans.*, **2**, 695 (1990).
40. M. J. Brienne, J. Galard, J. M. Lehn and J. Stibor, *J. Chem. Soc., Chem. Commun.*, 1868 (1989).
41. C. Fouquey, J. M. Lehn and A. M. Levelut, *Advanced Materials*, **2**, 254 (1990).
42. a. J. Michas and C. M. Paleos, *Liquid Crystals*, **11**, 773 (1992); b. J. Michas, C. M. Paleos, A. Skoulios and P. Weber, *Mol. Cryst. Liq. Cryst.* In press.
43. a. L. Katz and S. Penman, *J. Mol. Biol.*, **15**, 220 (1966); b. R. M. Hamlin, Jr., R. C. Lord and A. Rich, *Science*, **148**, 1734 (1965); c. J. Pitha, R. N. Jones and P. Pithova, *Canadian J. Chemistry*, **44**, 1045 (1966); d. Y. Kyogoku, R. C. Lord and A. Rich, *J. Am. Chem. Soc.*, **89**, 496 (1967).
44. J. Rebek, Jr., *Angew. Chem. Int. Eng. Ed.*, **29**, 245 (1990).
45. W. Mahler, D. Guillon and A. Skoulios, *Mol. Cryst. Liq. Cryst., Letters*, **2**, 111 (1985).