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Invited article
Supramolecular hydrogen-bonded liquid crystals†

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The role of hydrogen-bonding interactions in the formation and/or stabilization of liquid crystalline phases has been recognized in recent years and significant work has been conducted. Following the first and well-established examples of liquid crystal formation through the dimerization of aromatic carboxylic acids, several classes of compounds have been prepared by the interaction of complementary molecules, the liquid crystalline behaviour of which is crucially dependent on the structure of the resulting supramolecular systems. In this review the main classes of liquid crystals prepared through hydrogen-bonding interactions are presented, with the aim of establishing, in the first place, the diversity of organic compounds that can be used as building elements in the process of liquid crystal formation. Rigid-rod anisotropic or amphiphilic-type molecules, appropriately functionalized with recognizable moieties, interact in the melt or in solution and lead to the formation of supramolecular complexes that may exhibit thermotropic liquid crystalline character. Depending on the nature, number and position of the groups able to form hydrogen bonds, a diversity of supramolecular structures, both dimeric and polymeric, have been obtained, affording in turn various liquid crystalline phases. The structure and stability of these hydrogen-bonded supramolecular complexes and their relation to the observed liquid crystalline phases are the main topics of this review.

1. Introduction

The preparation and characterization of supramolecular liquid crystals, obtained through hydrogen-bonding interaction of complementary molecules, has been extensively studied in the last 10 years. The field started to be systematically investigated in the early 1990s and the first general review [1] appeared in 1995, including some of the early reports on the subject [2–14]. The subject was also reviewed in the new *Handbook of Liquid Crystals* [15] in 1998. Other shorter reviews [16–21] have been published in recent years, while those dealing with liquid crystalline amphiphilic carbohydrates will be referred to in the appropriate chapter. The subject of supramolecular liquid crystals is expanding while it is simultaneously gaining in maturity; therefore a new review was considered to be necessary. For the formation of liquid crystalline materials through hydrogen-bonding interactions, complementarity of the interacting components coupled with the directionability of hydrogen bonds are the main (but not the sole) factors contributing to the exhibition of liquid crystallinity. The appropriate shape and stability of the hydrogen-bonded complexes are also required.

The first hydrogen-bonded complexes exhibiting liquid crystalline behaviour resulted from the dimerization of aromatic carboxylic acids [22, 23]. Lengthening of the rigid-rod segment occurs, inducing in this way liquid crystalline behaviour. *Trans*-*p*-methoxy- and *trans*-*p*-ethoxy-cinnamic acids [22, 2] and their higher homologues [9], as well as the *p*-*n*-alkoxybenzoic acids, exhibited liquid crystalline phases as reported by Gray and Jones [8, 22] more than 45 years ago.

A single hydrogen bond between carboxyl and pyridyl moieties was found to be extremely fruitful for the formation of liquid crystals. The first example of such a type of liquid crystal was reported by Kato and Fréchet [24] in 1989. In the same year, at the beginning of the current period of systematic and intensive work on supramolecular hydrogen-bonded liquid crystals, Lehn *et al.* [25] reported that the interaction of long chain alkylated 2,6-diaminopyridines and uracil derivatives afforded metastable columnar hexagonal phases. In this case three hydrogen bonds were utilized for the formation of the liquid crystalline complexes. Another molecular feature that proved extremely useful for the formation

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†Dedicated on the occasion of his 66th birthday to Dr A. Skoulios.

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of liquid crystals was the presence of several hydroxy groups in amphiphilic carbohydrates and in certain other multi-hydroxy molecules. Due to the presence of such hydroxy groups, a hydrogen-bonded network is formed, the presence of which induces the formation of supramolecular structures that exhibit liquid crystalline behaviour.

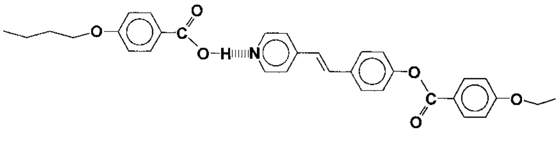
Employing recognizable moieties for the functionalization of rigid-rod or amphiphilic molecules, a diversity of supramolecular structures was obtained that exhibited liquid crystalline properties. Thus, heterodimeric supramolecular structures were obtained by the interaction of complementary components each bearing one or two recognizable groups. In a similar way, molecules with multiple hydrogen-bonding moieties led to the formation of liquid crystalline networks. Furthermore, polymers bearing recognizable groups can be used as templates for the formation of liquid crystals through hydrogen bonding interactions with mesogenic molecules, while main-chain liquid crystalline polymers could be formed through the interaction of low molecular mass molecules bearing two functional groups with the ability to form hydrogen bonds. Finally by combined hydrogen bonding and ionic interactions liquid crystals were produced through a two-level process. Therefore, several liquid crystalline materials can be obtained by the interplay of the nature, the number and the location of the recognizable groups in various substrates.

In this review, the discussion of supramolecular hydrogen-bonded thermotropic liquid crystals will be based on a categorization of the interacting components according to their structural features. In addition, the structure of the resulting supramolecular complexes and their relation to the liquid crystals obtained will be the main theme of this review. It should be noted that the phase diagrams of interacting components, although included in most recent publications, will not be included in this work, not because of their lack of significance, but in order to keep this review within a certain length. It is intended rather to highlight the description of the main phases that are observed, while suggesting to the readers that they resort to original publications for details.

2. Liquid crystals derived from complementary components through a single hydrogen-bonding interaction

Complementary components employed for the formation of liquid crystals may be mesomorphic or non-mesomorphic; in both cases, however, novel liquid crystals can be obtained. As already mentioned, a single hydrogen bond between components has been proved to be very fruitful in generating novel liquid crystals primarily using components bearing pyridyl and carboxyl moieties. Hydrogen bonding leads to an elongation of the rigid-rod segment of the individual components as schematically shown in figure 1. In this manner the formation of liquid crystals is induced.

Benzoic acid and stilbazole derivatives were the most frequently employed components for the formation of liquid crystalline materials through such hydrogen-bonding interaction. Thus, in a first experiment [24], the interaction of the nematic 4-butoxybenzoic acid (147–160°C) with the nematic *trans*-4-(4-ethoxybenzoyloxy)-4′-stilbazole (165–213°C) afforded complex **1** which exhibited a smectic phase in the temperature range 136–160°C. This phase was not shown by either of the interacting components, and the complex also exhibited a nematic phase in the region 160–238°C. The mesophase stabilization of the 1 : 1 complex **1** was attributed to the formation of a new and elongated mesogen, obtained through a single intermolecular hydrogen bond which allowed the complex to behave as a single liquid crystalline compound. Complex formation was supported by FTIR measurements according to which the initial dimeric acid was replaced by the heterodimeric complex.



1

The primarily adopted experimental method for the preparation of this complex, as well as of analogous liquid crystalline complexes, was by a slow evaporation of pyridine from an equimolar mixture of the interacting components [24]. In this way the hydrogen bonds of the 4-butoxybenzoic acid dimer were broken. Another mode of complex formation is by the simultaneous melting and mixing of the components; this method has also been followed in several experiments.

In a more recent publication by Kato *et al.* [26], liquid crystals were obtained by the interaction 4-alkoxy- or 4-alkyl-benzoic acids ($n = 6$–$8, 10$) with 4-octyl- or 4-undecenyl-pyridine affording complexes **2** and **3**. For a series of such supramolecular complexes, nematic and smectic liquid crystals were obtained in the vicinity of room temperature. A mixture resulting from these nematogenic complexes, due to its broad nematic range, has indeed been employed for electro-optic experiments. In addition, for a 1 : 1 complex resulting from substituted

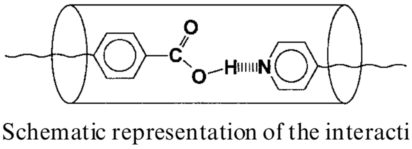
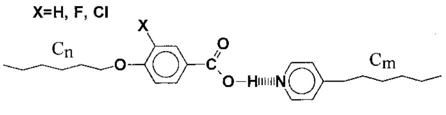


Figure 1. Schematic representation of the interaction between pyridyl and carboxyl moieties.

4-hexyloxybenzoic acids and 8-octylpyridine, the effect of lateral substitution was investigated by employing 3-chloro and 3-fluoro derivatives. Isotropization temperatures were depressed, while smectic phases were induced for the complexes.



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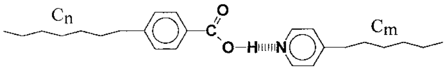
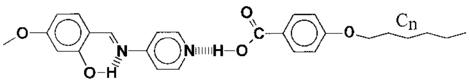


3

In an analogous manner, complexes were prepared [27, 28] by separately interacting non-mesomorphic *N*-(*p*-methoxy-*o*-hydroxybenzylidene)-*p*-aminopyridine and *N*-(*p*-methoxy-*o*-hydroxybenzylidene)-*m*-aminopyridine with a series of *p*-alkoxybenzoic acids. Complexes **4** and **5** ($n = 1$–10, 12, 14, 16) were obtained in which the anil moiety is protected from hydrolysis by the presence of the *ortho*-hydroxy group. Detailed studies were performed for the complexes **4**, including the phase diagrams of the interacting components, but the main results can be summarized as follows: (a) the formation of 1 : 1 hydrogen-bonded complexes exhibiting smectic C and/or nematic phases; (b) the stabilization of the alkoxybenzoic acid mesophases over a wide range of compositions (up to slightly above 50% of the anil derivative); (c) the complete miscibility of the acids with the complexes in the mesomorphic state. Specifically, the complexes functionalized with methoxy to heptyloxy substituents exhibited only nematic phases, those bearing octyloxy to dodecyloxy moieties both smectic and nematic phases, while smectic phases only were exhibited by the derivatives bearing tetradecyloxy to hexadecyloxy substituents. As far as the complexes **5** are concerned, preliminary studies have shown that only long alkoxy chains induce the formation of nematic and smectic phases.



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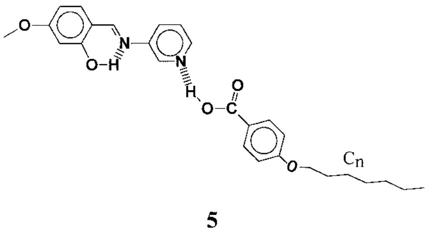
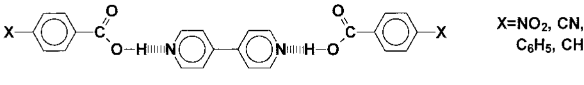


5

The use of a bifunctional acceptor offers the possibility of formation of 1 : 2 symmetric complexes [29]. Thus 4,4′-bipyridine when interacted with a series of substituted benzoic acids afforded complexes of type **6**. Carboxylic acids when interacted with 4-cyano- or 4-nitro-4′-stilbazole afforded complexes of the general formulae **7** and **8**. Although none of the derivatives bears alkyl chains, most of the complexes exhibit nematic mesomorphism with very high clearing temperatures. The nature of the terminal substituents has a crucial effect upon mesomorphism and they were investigated in this study in this context.



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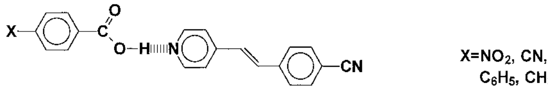

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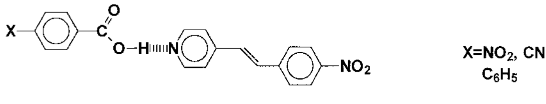
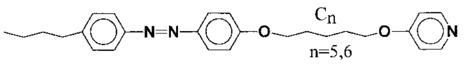


8

Employing the dimeric acceptors 1-(4-pyridyloxy)-5-[4-(4-butylphenylazo)phenoxy]pentane and 1-(4-pyridyloxy)-6-[4-butylphenylazo)phenoxy]hexane, **9**, liquid crystalline complexes were prepared [30] by hydrogen-bonding interaction with 4-octyloxybenzoic acid, **10**. Both systems were miscible over the whole range and exhibited smectic A phases. The clearing temperature of the complex containing the higher homologous acceptor **9** was considerably higher than that of the analogous complex with the shorter chain. Also the entropy change associated with the clearing transition showed an analogous behaviour. It is therefore concluded that for the system containing the higher homologous component, hydrogen-bonding complexation with the acid not only enhances liquid crystalline behaviour, but also increases the degree of molecular ordering.



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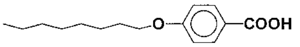
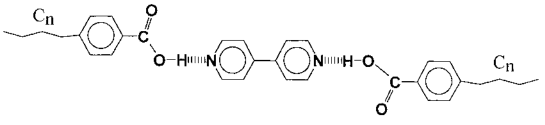


10

Liquid crystalline complexes were also formed by interacting 4-alkoxybenzoic acids (*n* = 1–8, 10) or 4-alkylbenzoic acids (*n* = 4, 5, 8) with the bifunctional acceptors 4,4′-bipyridine [31] or *trans*-1,2-bis(4-pyridyl)ethylene. For instance, complexes **11** and **12** were obtained by allowing 4,4′-bipyridine or *trans*-1,2-bis(4-pyridyl)ethylene to interact through hydrogen bonding with 4-alkoxybenzoic acids in a 1 : 2 molar ratio. The materials exhibited nematic phases; both nematic and smectic (SmA, SmC) or only smectic mesophases, the type depending on the length of the aliphatic chain. Short aliphatic chains favour nematic character, while long chains favour smectic mesophases. Analogous phase behaviour was observed for the complexes obtained by the interaction of 4-alkylbenzoic acids with the same acceptors.



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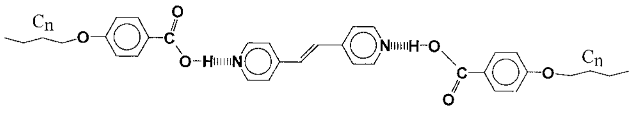
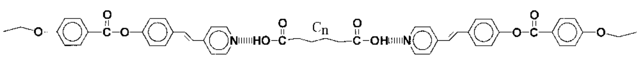


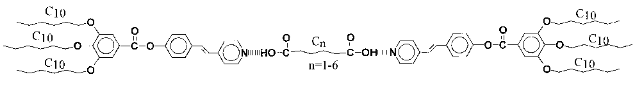
12

The complexes **13** were formed [32] by hydrogen-bonding interaction between a bifunctional non-mesogenic dicarboxylic acid (*n* = 5–9) with the mesogenic *trans*-4-(4-ethoxybenzoyloxy)-4′-stilbazole. Twin-type liquid crystalline complexes were formed which exhibited both smectic and nematic phases. An odd–even effect was observed for these complexes as has also been reported for twin (dimeric) liquid crystals formed through covalent bonding [33] between mesogens and a flexible spacer.



13

Phasmidic liquid crystalline complexes [34] were prepared by the interaction of appropriate stilbazole derivatives with several monocarboxylic and dicarboxylic acids. The series of complexes prepared, **14–16**, differ in rigidity and shape. For complexes **14**, when the length of dicarboxylic acid was greater than *n* = 4, columnar phases were obtained. Enhancing the rigidity of the mesogenic group as in the complexes **15**, liquid crystallinity is favoured. Finally, for complexes **16** appropriate choice of the components leads to the formation of room temperature liquid crystals.



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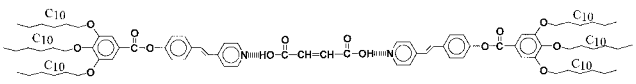

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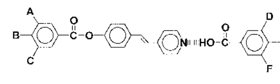
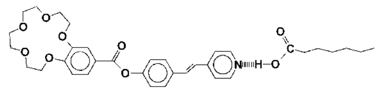


A, B, C = $C_{10}H_{21}O$; D, E, F = $C_{10}H_{21}O$
A, B, C = $C_{10}H_{21}O$; D, F = H; E = $C_{10}H_{21}O$
A, C = H; B = $C_{10}H_{21}O$; D, E, F = $C_{10}H_{21}O$

16

Mesomorphic phases were also induced [35] by the interaction of 4′-carboxybenzo-15-crown-5-stilbazolyl ester with a variety of mono- or di-carboxylic acids. Typical complexes **17** and **18** were obtained by the interaction of the stilbazolyl derivative with monocarboxylic acids and dicarboxylic acids in 1 : 1 and 2 : 1 molar ratios respectively. The stilbazolyl acceptor is a monotropic mesogen forming a nematic phase upon cooling and although the interacting alkanoic and alkandioic acids do not display mesomorphic behaviour, they do stabilize the nematic phase of the complex and/or induce a smectic A phase. For the hydrogen-bonded complexes of the above mentioned acceptor with alkoxybenzoic acids, **19**, the stability range of the induced smectic A phase decreases with increasing number of alkoxy chains.



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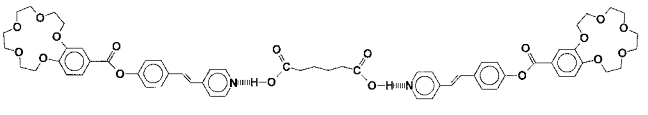

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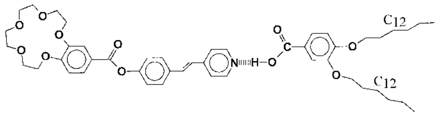
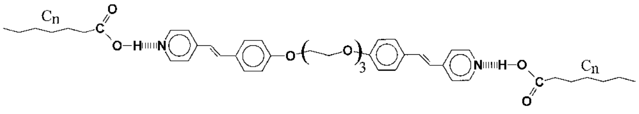


19

In an analogous fashion, by interacting two stilbazole moieties linked by a triethylene glycol spacer with various fatty and aromatic acids, liquid crystalline compounds **20** and **21** were obtained [36], respectively.

Thus, monotropic smectic B phases were observed for the complexes with nonanoic up to tetradecanoic acids. Enantiotropic nematic and in some cases monotropic smectic A phases were obtained with 4-methyl, 4-methoxy and 4-halogeno benzoic acids as donors. The stability of the induced mesophases was decreased with 3- and 2-substituted benzoic acid derivatives, while with aliphatic dicarboxylic acid donors liquid crystalline phases were not observed.



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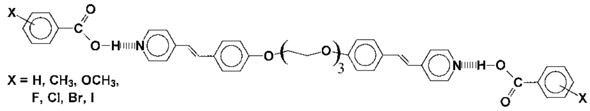
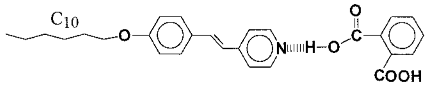


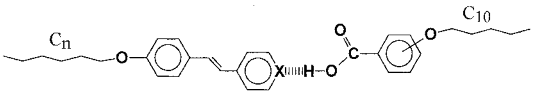
21

The interaction of the bifunctional phthalic acid with *trans*-4-alkoxy-4′-stilbazole derivatives ($n = 7, 8, 10$) would normally lead to the formation of 2:1 bent complexes, as was originally reported by Kato and Fréchet and their collaborators [37]. However recent results [38] from the same laboratories have led to a reinterpretation of the phase behaviour of the same complexes. According to these results a 1:1 complex, **22**, was formed as established by the phase diagram of the components. The fact that a 2:1 complex is not formed is attributed to the p*K*a of the second carboxyl proton, which changes following hydrogen-bond formation with the first carboxylic group (cf. the p$K\text{a}_1$ and p$K\text{a}_2$ values of pure phthalic acid which are 2.89 and 5.51, respectively). This makes the formation of the second hydrogen bond unfavourable.



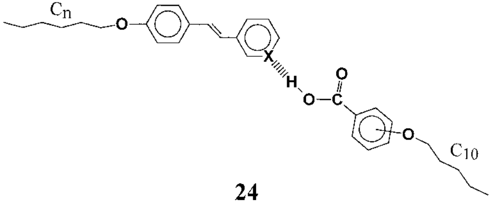
22

Angular mesogenic hydrogen-bonded complexes, **23–25**, were obtained [39] through interaction in a 1:1 molar ratio of *trans*-4-alkoxy-3′(or 4′)-stilbazoles with 3(or 4)-decyloxybenzoic acids; the analogous *N*-oxides were similarly studied. By controlling the relative bending positions of the hydrogen-bonded complexes, a diversity of supramolecular structures of different linearity were obtained. In this manner, tuning of the molecular shape becomes possible, as well as modification of the molecular packing and the liquid crystalline properties. The results can be summarized as follows: lower mesomorphic transition temperatures are favoured in the angular structures; in addition, angular structures may show new or even broader range liquid crystalline phases in comparison with their linear isomeric structures. A new approach to the design of liquid crystalline assemblies is therefore proposed by these first results.



23

X = N, N→O
$n = 8, 12, 16$



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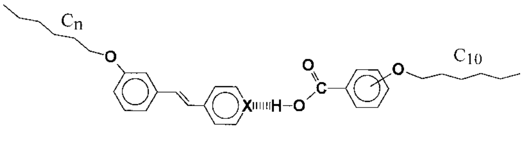
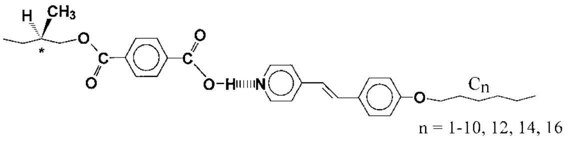


25

Ferroelectric liquid crystals, **26**, were prepared [40] by hydrogen-bonding interaction of chiral mono-2-methylbutyl terephthalate with 4-alkoxy-4′-stilbazoles affording a smectic B phase ($n = 1–10, 12, 14, 16$). Depending upon chain length, blue phases, chiral nematic (N*) and chiral smectic C (SmC*) phases were obtained for these complexes. Furthermore, by interacting 4-(*S*)-2-chloro-3-methylbutyroyloxy-4′-stilbazole with 4-alkoxybenzoic acids, complexes of the general formula **27** were obtained [41] and exhibited chiral smectic C phases, smectic A phases and chiral nematic phases. This behaviour is dependent, as expected, on the length of the alkoxy-chain. With $n \geqslant 7$, only chiral smectic phases were observed. On similar grounds the interaction of 4-alkoxybenzoic acids with chiral *S*-(+)-*trans*-4-(2-methylbutoxy)-4′-stilbazole and *S*-(−)-*trans*-4-(2-methoxypropyloxy)-4′-stilbazole led to the formation [42] of complexes **28** and **29**, exhibiting a diversity of liquid crystalline phases, i.e. chiral smectic C, smectic A and chiral nematic. The occurrence of these phases was dependent on the length of the alkoxy chain of the benzoic acids and the chiral centre of the stilbazoles.

Furthermore, a supramolecular chiral liquid crystalline complex, **30**, was obtained [43] by the interaction of 4,4′-bipyridyl with 4-((*S*)-(−)-2-methylbutoxy)benzoic acid, neither of which was mesomorphic. According to the phase diagram, mixtures containing from 0.1 to 0.5 mol fraction of 4,4′-bipyridyl exhibited chiral nematic, blue and smectic A phases. As predicted, the induced mesomorphic behaviour was attributed to the formation of an elongated hydrogen-bonded complex.



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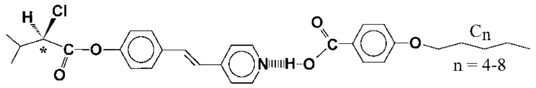

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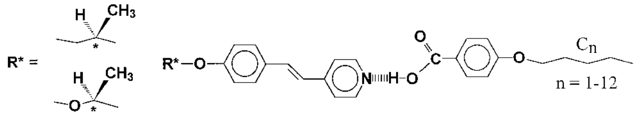

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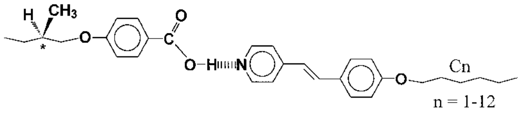

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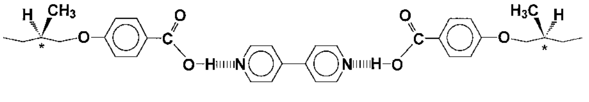
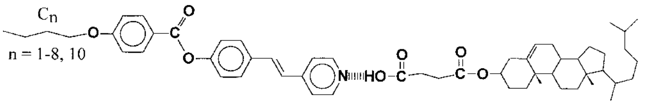


30

Cholesterol-based liquid crystals were also prepared [44] by hydrogen bonding interaction of 3-cholesteryloxycarbonylpropanoic acid with 4-(4-alkoxybenzoyloxy)-4′-stilbazoles and *N*-(4-pyridylmethylidene)anilines affording complexes **31** and **32**, respectively. In addition to unidentified smectic phases, smectic A, smectic C and nematic phases were observed. For comparison purposes, new covalently bonded cholesteryl esters, the *N*-[4-(3-cholesteryloxycarbonylpropionyloxy)-benzylidene]-4-alkoxyanilines, **33**, were investigated for which it was found that the phase transition temperatures were higher than those for the analogous of hydrogen-bonded complexes.



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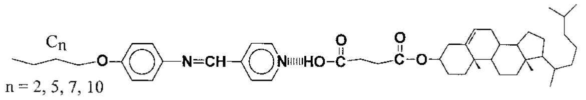

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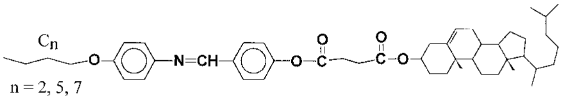
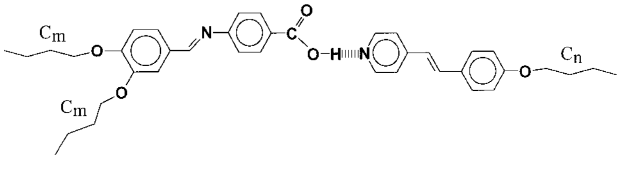


33

Two homologous series of tricatenars, the hydrogen-bonded complexes **34** ($m = 5, 11$, $n = 3, 6, 8, 10, 12, 14$) and **35** ($n = 2, 6, 16$, $m = 3, 6, 10, 15$) were prepared [45] by interacting alkoxy- and dialkoxy-stilbazole derivatives with dialkoxy- and alkoxy-benzylideneaminobenzoic acids. These asymmetric tricatenar mesogens exhibit enantiotropic nematic and smectic C phases. It is interesting to note that three of the interacting components were not mesomorphic, while the alkoxystilbazole in complexes **34** gave rise to smectic B and crystal E phases. It was therefore possible, from non-mesomorphic components, to form complexes which have the mesomorphic characteristics of a simple tricatenar mesogen, namely nematic and smectic phases.



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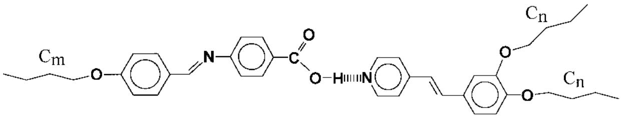

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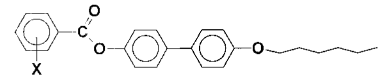
Following a rather extensive qualitative discussion of the ability of carboxyl and pyridyl groups to form hydrogen-bonded liquid crystalline complexes, a quantification of this behaviour was attempted. It is known that the induction of liquid crystalline character is associated with the strength of hydrogen bonding between the interacting components. For probing and quantifying [46] this behaviour certain benzoates, **36**, were compared as far as their mesomorphic character is concerned with the corresponding hydrogen-bonded complexes, **37**. The clearing temperature criterion was employed for the assessment of the stability of the resulting liquid crystalline phases; it was found that the hydrogen-bonded complexes under investigation exhibit maximum liquid crystalline stability when weakly electron withdrawing substituents are employed.



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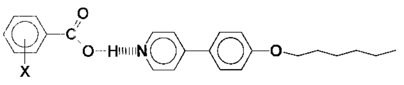
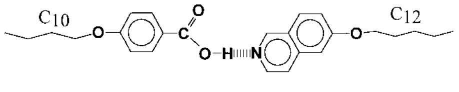
X = H, p-$C_8H_{18}NH$, p-$C_8H_{18}O$, p-$ClCH_2$, m-F, m-NO_2



37

After this extensive application of the pyridyl-carboxyl system as a means for formation of hydrogen-bonded liquid crystals, a limited number of reports have recently appeared in the literature employing other complexation systems. Thus, in one publication [47], pyridine derivatives were replaced by 6-dodecyloxyisoquinoline and interacted with one of two monocarboxylic acids affording hydrogen-bonded heterodimers **38** and **39**, exhibiting smectic A phases. The same isoquinoline derivative interacting with 2,5-thiophendicarboxylic acid led to the formation of a kinked trimer, **40**, which exhibited a nematic phase. The isoquinoline-based structures use lone pair electrons from fused heterocyclic rings, thereby reducing the phase transition temperatures and enhancing the solubility of the components for the formation novel supramolecular complexes.



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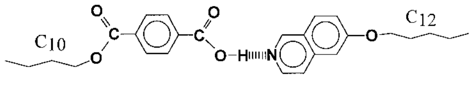

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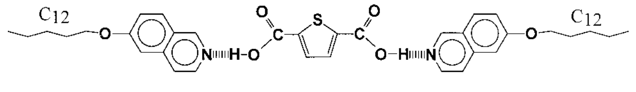

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Carboxylic acid donors were also replaced by phenols, which are weaker acids. Thus 4,4′-bipyridine was interacted with long alkyl or alkoxy chain derivatives in a 2:1 molar ratio affording complexes **41** and **42**, which exhibited [48] liquid crystalline character. Specifically for complexes **41**, smectic phases were obtained for the members having an alkoxy chain longer than C_9, while for complexes **42**, the members with an alkyl chain shorter than C_7 did not show liquid crystalline behaviour. In a relatively recent study [49], 4-alkoxy-4′-stilbazole ($n = 1$–13) was reacted with nitrophenols affording three hydrogen-bonded complexes, **43**, **44** and **45** all of which exhibited nematic and smectic A phases. For the smectic A phase, an interdigitated bilayer structure was proposed, and for the nematic phase an antipararallel dimer as shown in figure 2 for the 3-nitrophenyl complex. Electronic spectroscopy of the 2,4-dinitrophenol-decyloxystilbazole complex has shown that an ionic hydrogen-bonded state, corresponding to proton transfer, contributed significantly to the molecular population in the

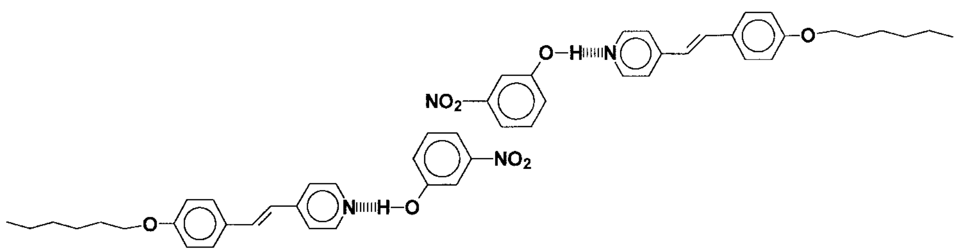
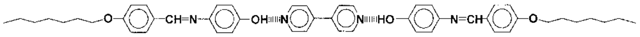


Figure 2. Antiparallel structure adopted by the nematic hydrogen-bonded complexes [49]. Reproduced from *J. Mat. Chem.*, 1997, **7**, 883 by permission of the Royal Society of Chemistry.

mesophase, providing additional stabilization for this state.



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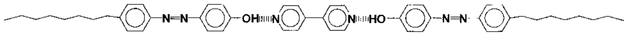

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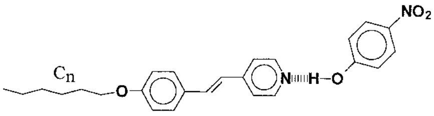

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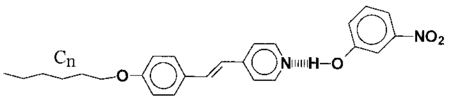

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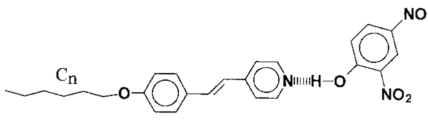

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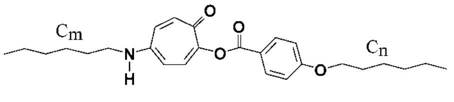
Another example of the preparation of liquid crystals [50] employing other than the well-established pyridyl-carboxyl system is the formation of a hydrogen-bonded system, inducing the formation of a smectic C phase, using troponoid-based compounds **46** ($m = 6, 8, 11, 12, 14, 18$; $n = 1, 4, 12$) and **47** ($m = 12, 14, 18$; $n = 8, 10, 12, 18$). Considering intermolecular hydrogen bonding, two architectures may be envisaged for these two compounds in the liquid crystalline phase, i.e. the folded and extended models as shown in figure 3. Between these two structures, the extended model readily justifies the appearance of the smectic C phase, since the molecules are tilted with respect to the layer plane. It has to be noted that only molecules with long chains exhibit the smectic C phase while those with short chains are not mesomorphic, since hydrogen bonding raises the melting point above the anticipated mesophase–isotropic transition.



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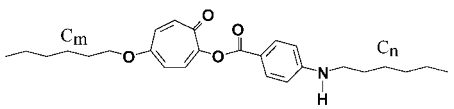
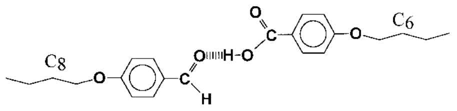


47

Closing this chapter, mention should be made of the attempts [51] to employ ketones and aldehydes as proton acceptors. These molecules were interacted with different carboxylic acid donors leading to the formation of hydrogen-bonded complexes such as **48** and **49**, exhibiting smectic A and nematic phases.



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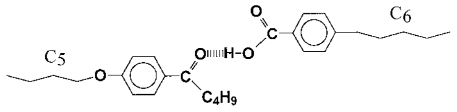

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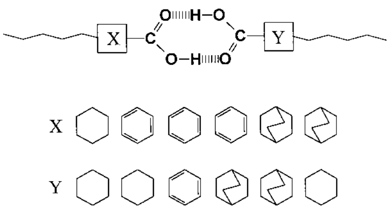
3. Liquid crystals derived from complementary components through multiple hydrogen-bonding interactions

Within the domain of liquid crystals prepared from multiple hydrogen bonding interactions, liquid crystals derived from the dimerization of carboxylic acids [22], although studied long ago [8, 22], are still investigated. Thus, recently Kang and Samulski studied [52] binary mixtures of *p*-substituted ‘short-tailed’ benzoic acid derivatives which by themselves do not exhibit a liquid crystalline phase. For instance, liquid crystalline character for *p*-alkylbenzoic acids was observed for the derivatives with four-carbon alkyl chains or longer. It was found that the mesophase stability increased in equimolar mixtures of acids having incommensurate length, i.e. the larger the difference between the tail substituents of the mixed organic acids, the broader is the nematic phase range observed. On similar grounds, this work was extended [53] to mixtures of acids having the same tail length, but different chemical constitutions, and to mixtures of different acids derived from aromatic and aliphatic moieties. In the latter case the authors considered three classes of organic acids: *p*-substituted phenyl-, 4-substituted cyclohexane- and bicyclo[2.2.2]-octane-carboxylic acids, **50**. From these studies it was established that the stability of the nematic mesophase, as evidenced by the broad mesomorphic ranges of binary mixtures, is enhanced in mixtures of disparate species, i.e. in mixtures of acids differing in tail length and acid type.



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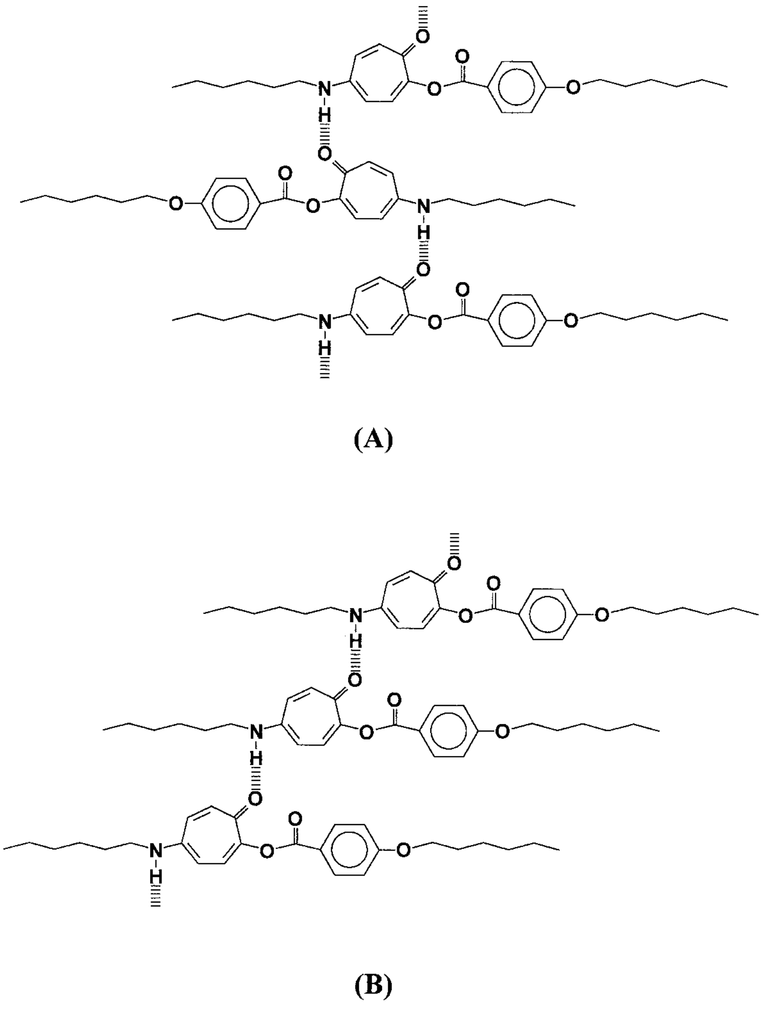
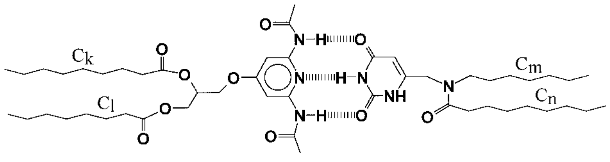


Figure 3. Folded (A) and extended (B) molecular packing for compound **46**. Reproduced by kind permission of authors and publisher [50].

Complementary alkylated heterocyclic compounds attracted interest for the formation of supramolecular hydrogen-bonded liquid crystals. Lehn and his co-workers [25] reported the functionalization of 2,6-diaminopyridine and uracil with long aliphatic chains with the prospect of forming liquid crystals through a system of three hydrogen bonds. Upon interaction of these components, both crystalline and/or liquid crystalline materials were obtained. The heterocyclic moieties together with the hydrogen-bonded system constitute the 'rigid polar segment' which is segregated from the long lipophilic alkyl chains forming the supramolecular complex **51**. All the interacting components showed solid state polymorphism, but none of them exhibited a mesomorphic phase. In addition all 1 : 1 mixtures showed crystalline polymorphism, while five complexes with long aliphatic chains, exhibited a metastable mesomorphic phase. X-ray diffraction (XRD) studies of the mixtures established the formation of columnar hexagonal mesophases. The columns consisted of a stack of disks, each containing two units of complex, arranged side by side as shown in figure 4.

Mesophases were also obtained when two uracil-based components combine with the complementary bifunctional tartaric acid derivative forming the supramolecular complex **52**, having a columnar structure of rectangular section [54].



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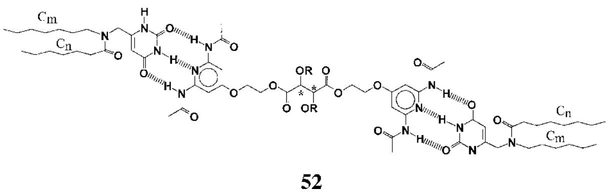

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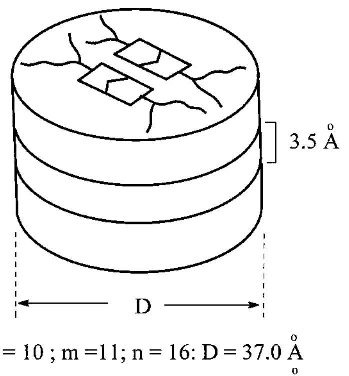
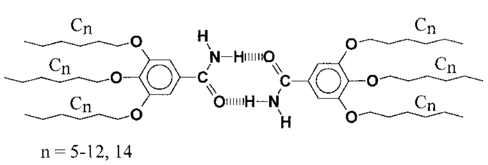


Figure 4. Schematic representation of the columnar mesophase formed from complex **51** [25*b*]. The letters *k*, *l*, *m* and *n* refer to the alkyl chain lengths with the carbon numbers in structure **51**. Reprinted with permission from Lehn, J.-M., *Macromol. Chem. Macromol. Symp.*, 1993, **69,** 1.

The liquid crystalline character of 3,4,5-trialkoxybenzamides can be interpreted by assuming the formation of a supramolecular structure. Specifically, Lattermann and Beginn [55] deduced a columnar or stack-like structure based upon the dimeric structure **53**. It was also proposed that since the amide groups were tilted with respect to the planes of the aromatic rings, not only intradimeric but also interdimeric hydrogen bonding took place, stabilizing the columnar structure. The existence of interdimeric hydrogen-bonding interaction was supported by infrared spectroscopy. In addition, bromination in the aromatic 2-position or the synthesis of 2,3,4-trialkoxybenzamides results in the loss of mesomorphism; apparently steric hindrance does not favour interdimeric hydrogen bonding.



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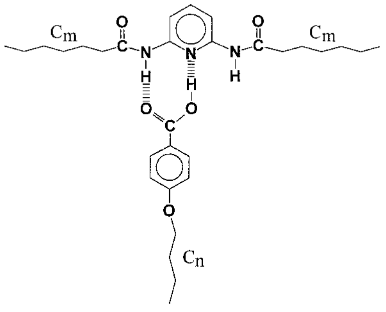
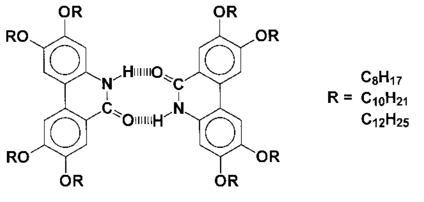
Doubly hydrogen-bonded complexes of the general formula **54** having an unconventional shape were obtained [56] upon interaction of 2,6-diacylaminopyridines with 4-alkoxybenzoic acids. A mosaic texture with oblong sheets and a homeotropic texture were exhibited by the complex with $m = 4$ and $n = 12$. Some H-type shapes were observed in the mosaic texture, possibly characterizing a smectic B phase [57]. All the complexes **54** show monotropic behaviour and similar textures. In this connection, the unique shape of the molecule should be noted, not at all typical of the shape of complexes which exhibit liquid crystalline phases.



54

Dimerization through the hydrogen-bonding interaction of tetrakis(*n*-alkoxy)-6(5H)-phenanthridinones led to the formation of disk-like dimers **55**, which exhibited columnar hexagonal liquid crystalline phases [58, 59] with an intercolumnar spacing of 31 ± 1 Å and an intracolumnar disk-stacking distance of 3.6 Å. Infrared studies revealed that hydrogen-bonded aggregates existed well above the clearing points.



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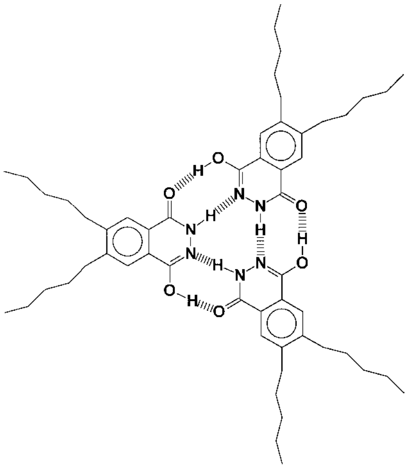
In an analogous manner, long alkyl chain 6,7-bis-(alkyloxy)-2,3-dihydrophthalazine-1,4-diones [60] self-assemble into lactim-lactam trimeric cyclic structures, **56**. Polarizing optical microscopy (POM) showed the existence of a columnar mesophase of hexagonal symmetry. However, for $n = 14$, a fingerprint texture that developed up to 200° indicated an additional columnar mesophase of rectangular symmetry as established by XRD studies. The hexagonal symmetry was unambiguously demonstrated for $n = 10$ and $n = 14$; the structure was formed by stacking of the aromatic cores of the molecules in columns surrounded by the disordered aliphatic chains and packed laterally in a hexagonal fashion. For $n = 8$ two reflections, characterizing a two-dimensional hexagonal lattice, i.e. $\sqrt{3}$, $\sqrt{4}$, were hardly visible, apparently because the diameter of the aromatic cores is, in this particular case, close to the thickness of the aliphatic crowns. The rectangular symmetry was also established by the presence of five sharp reflections in the small angle region.



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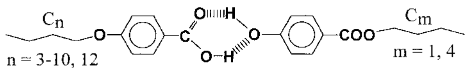
The formation of hydrogen-bonded complexes **57** resulted from the interaction of *p*-*n*-alkoxybenzoic acids (*n* = 3, 10, 12) with the non-mesogenic butyl *p*-hydroxybenzoate [61] and methyl *p*-hydroxybenzoate [62]. The interest in these complexes lies in the dual function of carboxylic acid and phenolic moieties, i.e. they act both as proton donor and acceptor, forming two hydrogen bonds. All complexes exhibited, among other phases, a highly ordered induced crystal G phase.



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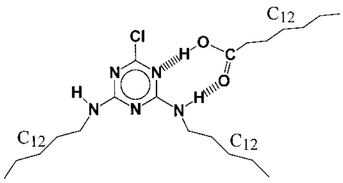
In preliminary experiments [63], the mesomorphic character of some long chain 2,4,6-trichloro-1,3,5-triazine derivatives was being investigated. These molecules, containing in the ring the typical, N=C−NH moiety which is recognizable by carboxyl groups [64], interacted in the melt with long chain carboxylic acids. For instance, lauric acid interacted with one disubstituted triazine derivative affording complex **58**. As judged, at least from DSC and POM studies, the complex showed a mesomorphic texture, which was not however completely identified. Following on this study, self-assembly of a sheet-shaped 2,4,6-triarylamino-1,3,5-triazine bearing decyloxy groups at the periphery with two-fold alkoxy substituted non-mesomorphic benzoic acids afforded [65] a hydrogen-bonded complex. The liquid crystalline properties were summarized as follows: the hexagonal columnar mesophase of the initial triazine derivative was modified through molecular recognition by the benzoic acid derivatives. The two-dimensional lattice parameters of the binary mixtures prepared from the triazine and the two-fold alkoxy substituted benzoic acids were controlled by the positions and the length of the alkyl chains of the acid components. However a 1 : 1 molar ratio complex, **59**, was formed, apparently for steric reasons, by the mono-alkoxy benzoic acid with a decylchain.



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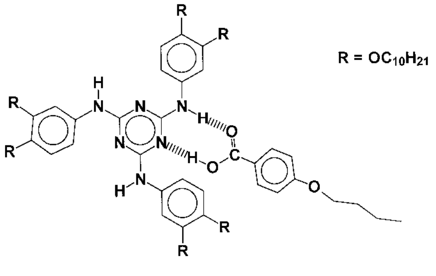

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4. Liquid crystals induced by the formation of a hydrogen-bonded network originating from multi-hydroxylated amphiphiles

Amphiphilic carbohydrates, as well as other multihydroxylated compounds, due to the presence of a plethora of hydroxy groups, form hydrogen-bonded networks, which in turn induce the formation of liquid crystalline phases. Amphiphilic carbohydrates are additionally categorized on the basis of the observed mesomorphic phases.

4.1. *Liquid crystalline behaviour of amphiphilic carbohydrates*

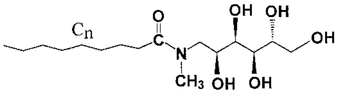
Carbohydrate liquid crystals are formed by the alkylation of carbohydrate moieties with one or more long aliphatic chains. The structural diversity of the carbohydrate moieties, coupled with the number of long alkyl chains that can be introduced, leads to the existence of a great variety of amphiphilic carbohydrates. Fischer [3] and Salway [4], almost 90 years ago, first reported the synthesis of β-hexadecyl-D-glucoside and ceryl-β-D-d-glucopyranosides, respectively and observed the occurrence of an 'anomalous' melting behaviour. This character could not be explained at that time and no mention of liquid crystallinity was made. The subject of carbohydrate liquid crystals was then ignored for several years and only a paper which appeared in 1938 [6] interpreted the 'double melting' of the amphiphilic glucoside prepared by Fischer as due to the exhibition of a liquid crystalline phase. In addition there were some reports [10–12] in the late 1950s on alkyl carbohydrates, including amphiphilic derivatives. Research on liquid crystalline carbohydrates was however intensified in the eighties, and it is now possible to correlate the observed liquid crystalline phases with the structural features of the amphiphilic carbohydrates. The subject has been reviewed by a number of groups [66–69].

It is not therefore intended in this review to give an exhaustive coverage of the mesomorphic properties of the amphiphilic carbohydrates synthesized so far. Emphasis will be given to the supramolecular models, which are responsible for the exhibition of a variety of liquid crystalline phases. From the literature survey that follows, it can safely be concluded that single-tailed carbohydrate amphiphiles form smectic phases, while carbohydrates with more than one lipophilic chain lead, in most of the cases, to columnar mesophases. Recently cubic phases have also been reported for specific amphiphilic carbohydrates.

4.1.1. *Smectic liquid crystalline phases originating from amphiphilic carbohydrates*

Smectic A liquid crystalline phases were found for *n*-alkyl-1-*O*-β-glucopyranosides [70] for which a bilayer structure was postulated. The carbohydrate moieties overlap with each other and are held together in the middle of the bilayer, through extensive hydrogen bonding interactions, while the aliphatic chains are located at the exterior of the lamellar supramolecular structure. Shortly following this work, Markus and Finn [71] performed miscibility experiments on *n*-decyl-β-glucopyranoside and showed that its smectic phase was thermodynamically identical to the lyotropic lamellar phase exhibited by a 20% solution of sodium bis-2-ethylhexyl-sulphosuccinate (Aerosol OT). In an analogous manner it was found [72] that the liquid crystalline phases of *n*-alkylgluconamides were miscible with those of the *n*-alkyl-1-*O*-β-D-glucopyranosides and formed phases classified as smectic A, and tentatively at that time as smectic A_d, in which, in the latter case, an interdigitated bilayer structure was formed. The *d*-spacing should then be close to twice the length of the aliphatic chain plus the length of the carbohydrate moiety. However in this same period Baeyens-Volant *et al.* [73] proposed a monolayer smectic phase based on the determination of the length of the *d*-spacing.

Monoalkyl monosaccharide derivatives exhibit in general smectic phases. Thus amphiphilic derivatives of 1-*O*-alkyl-2,5-anhydrohexitols [74] exhibited smectic phases; some of the members were liquid crystals even at room temperature. Also, for a series of acyclic carbohydrates, viz. 1-deoxy-1-(*N*-methylalkanamido)-D-glucitols, **60** (*n* = 4–10), as well as their closely related derivatives, the *N*-[2-(alkanamido)ethyl]-D-gluconamides, **61** (*n* = 4–8) and *N*-[2-(*N*-methylalkanamido)ethyl]-D-glucanamides, **62** (*n* = 4–8), the phases were shown [75] to be smectic A_d phases due to the interdigitated bilayer ordering of the supramolecular structures. Smectic A* phases were observed for 1-*O*-alkyl-D-glucitols [76] originating from alkyl-D-glucopyranosides, and for carbohydrates incorporating calamitic mesogens [77]. For the latter compounds, the introduction of the calamitic mesogenic units greatly increases the potential to form a number of carbohydrate liquid crystalline phases and allows greater control of the thermal properties.



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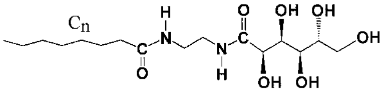

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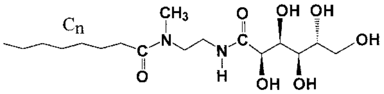
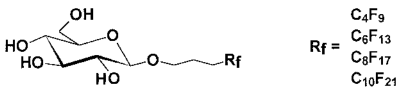


62

Analogous to the above, we have the behaviour of the recently prepared and characterized perfluoroalkyl carbohydrates, **63–65**. These compounds, afforded [78] only smectic A* phases, like all single-tailed alkylated carbohydrates. The observed phases were however favoured compared with the non-fluorinated analogues because of the increased intramolecular contrast within the molecules and because of the greater stiffness of perfluoroalkyl chains. Consequently, these compoŋds can show liquid crystalline properties when their hydrophobic molecular segment is as short as a perflurobutyl chain.



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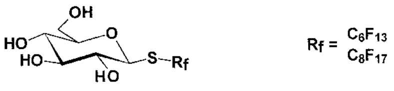

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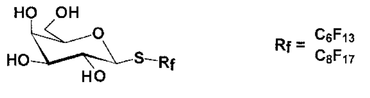
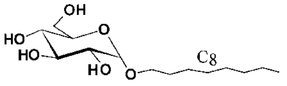


65

In addition, several α- and β-alkyl glucosides were prepared [79] and the liquid crystalline properties of the mono-, di-, and tri-saccharides were compared. In all cases smectic A phases were obtained. The investigation of several monoalkyl glycosides, **66–72** was continued by Seddon *et al.* [80] and it was established that small structural modifications can lead to extensive changes in phase behaviour. The compounds exhibited thermotropic smectic A* liquid crystalline character in addition to exhibiting lyotropic phase behaviour. It seems however that there is an exception to the rule. Thus, three homologous monoalkyl fructopyranosides (octyl, decyl and dodecyl), **73**, displayed a rather viscous monotropic phase [81] the nature of which has still to be clarified by XRD. The as yet unidentified texture is sensitive since it crystallizes on fast cooling.



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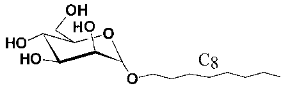

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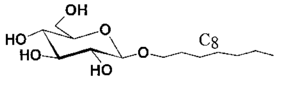

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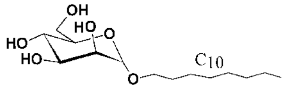

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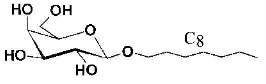

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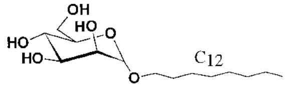

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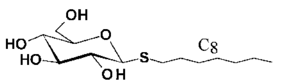

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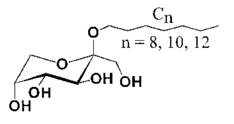
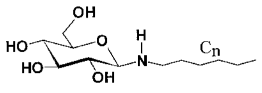


73

In an early comparative work [68], the liquid crystalline behaviour of six homologous series of D-glucose and 2-deoxy-D-glucose derivatives with an amino-linked alkyl chain was studied. All these classes of amphiphilic carbohydrate, **74–79** ($n = 7–16$), exhibited smectic A_d phases. In all cases the d-spacing corresponded to $l < d < 2l$ where l is the length of the fully extended molecule and d is the observed layer thickness.



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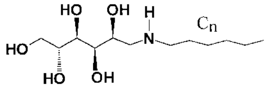

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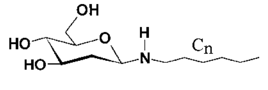

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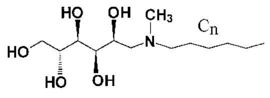

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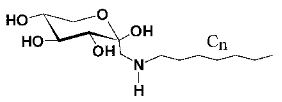

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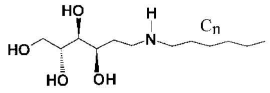
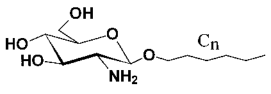


79

Liquid crystalline amphiphilic carbohydrates [82] based on glucosamine and 6-amino-6-deoxyhexopyranoses have been prepared. In previously reported examples of amino carbohydrates [68], a secondary amino group was placed in the bridge between the hydrophilic and hydrophobic segments, while in the case of the glucosamines, a primary amino group is located in the hydrophilic section of the carbohydrates. In addition to simple alkyl glucosamines, **80** ($n = 8, 10, 12, 14, 18$), and the hydrochloride **81** ($n = 12$), which exhibited smectic phases, the hydroxy derivative **82** ($n = 16$) also showed smectic behaviour. The amides of 6-amino-6-deoxygalactose, **83** ($R = SO_2\ C_{16}H_{33}$, $CO\ C_{17}H_{35}$), had only one alkyl group connected at the amino group and they formed smectic A phases. The clearing temperatures are higher than those of the alkyl glucosides and the sulphonamide has a higher clearing temperature than the carbonamide because of differing polarities. A particularly interesting feature of amino carbohydrates is their ability to form intra- and inter-molecular salts with organic acids, resulting in the formation of a diversity of liquid crystalline materials. Thus depending on the acid used, smectic, columnar or cubic phases can be prepared. The liquid crystalline properties of amino carbohydrates are summarized as follows: the N-alkylglucosamines show SmA phases with lower clearing temperatures than those of alkyl glucosides; high clearing points are induced when the amino group is located at a bridge position between the hydrophilic and the hydrophobic segments.



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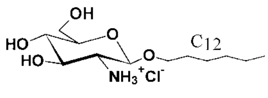

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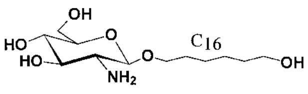

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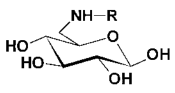
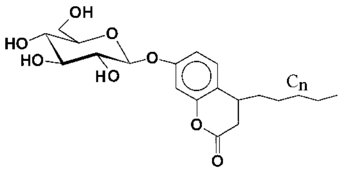


83

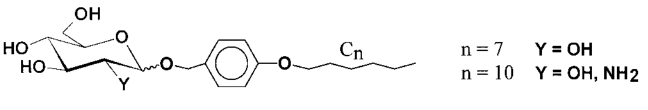
The work on amphiphilic carbohydrates was extended [83] to the preparation and characterization of carbohydrate liquid crystals incorporating large non-amphiphic moieties. Thus, a coumarin moiety has been incorporated and compounds of the formula **84** ($n = 7, 9, 13$) have been prepared. The rigid and relatively flat coumarin unit is flanked by the hydrophilic carbohydrate head group and a lipophilic tail *R*. Although the structures of these carbohydrates are not typical of those that are most suitable to give mesomorphic character, two of them also show liquid crystalline properties. Thus, although the heptyl derivative is not liquid crystalline, the nonyl and tridecyl derivatives exhibit smectic A liquid crystalline phases.



84

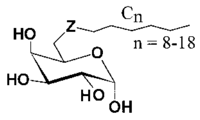
A diversity of *N*-acyl-β-D-glycopyranosylamines incorporating aliphatic and aromatic groups was synthesized [84] in a one-step reaction employing the appropriate acid chloride and D-glycosamines. The presence of the amide linkage leads to high transition temperatures, rendering the compounds insoluble in water. This is probably due to a high degree of intermolecular hydrogen bonding which also involves the amide linkage. The high melting point rationalizes the fact that from the great diversity of synthesized compounds only *N*-(4-alkoxybenzoyl)-β-D-glucopyranosylamine and *N*-(*trans*-4-pentylcyclohexylacetyl)-β-D-glucopyranosylamine exhibit observable smectic A* thermotropic liquid crystalline phases.

Various 4-substituted-benzyl 1-*O*-α-and-β-D-glucopyranosides, 4-substituted-benzyl 2-deoxy-2-trifluoroacetamido-α-and-β-D-glucopyranosides and 4-substituted-benzyl 2-acetamido-2-deoxy-α-and-β-D-glucopyranosides were synthesized [85] as shown below by the general structure **85**. They were prepared by one-step alkylation of commercially available carbohydrates. Due to the structural diversity of these amphiphilic carbohydrates, the effect of hydrogen bonding, molecular shape, dipole moments and chain lengths on their mesomorphism can be assessed. For those of the carbohydrates that exhibit thermotropic liquid crystalline character, the simultaneous presence of both homeotropic and focal-conic textures indicates that the mesophase type is calamitic smectic A*.



85

Recent work by Goodby *et al.* [86] concerned three homologous series of 6-*Z*-*n*-alkyl-α-D-galactopyranoses, **86**, where the linking group *Z* represents a carboxy group, a sulphur or oxygen atom, or a propylthio group. The length of the aliphatic chain was also varied systematically. Enantiotropic smectic A* phases were observed for each of the homologous series, as expected for single chain amphiphiles. The order of efficiency of the linking group *Z* in favouring the formation of liquid crystalline phases, for the same homologues, is $S \approx OCO > O > OC_3H_6S$, correlating well therefore with the polarizability of *Z*.



86

Concluding the above discussion, it should be stressed that the smectic A_d phase is now well established for single-tailed amphiphilic carbohydrates. However the structure of the originally proposed [67, 87] Model I for the arrangement of the molecules within the layers has been questioned, see figure 5. In that model, the carbohydrate moieties constituting the lamellar core are held together in a dynamic hydrogen-bonded network and the aliphatic chains are located in the exterior of the supramolecular structure. The new Model II, figure 5, was proposed by Jeffrey [88] and was further supported by van Doren and Wingert [87]. Contrary to Model I, the interdigitated alkyl chains constitute the core of the smectic bilayer and the hydrogen-bonding carbohydrate moieties are located at the exterior surfaces. This latter model is identical, with the exception of the absence of

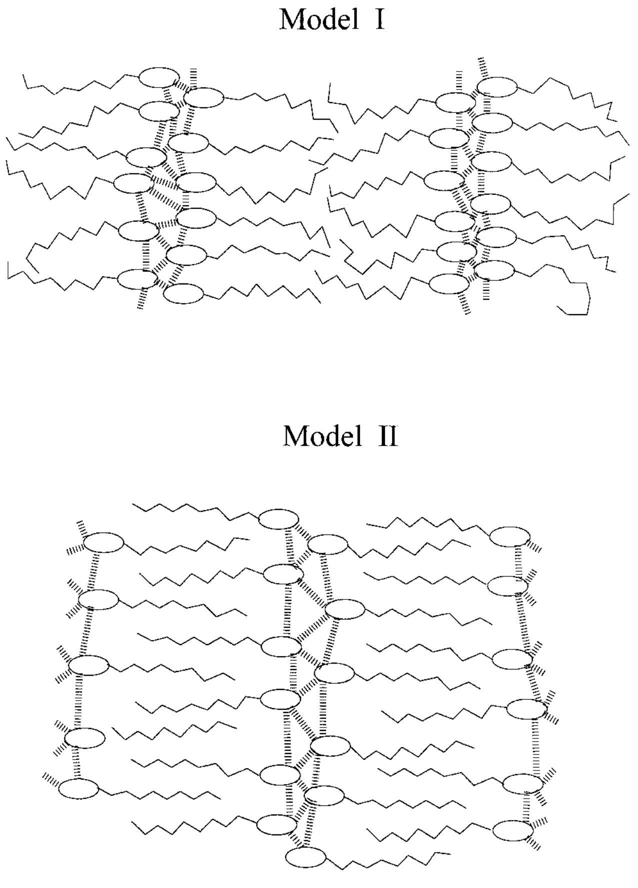
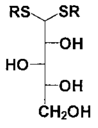


Figure 5. Supramolecular Models I and II for single-tailed carbohydrates. Reproduced by kind permission of the authors and publisher [67].

water, to the lamellar lyotropic phase (L_α) and is consistent with the available experimental data. It also explains [67, 68] the thermal behaviour and the influence of minor structural changes in the carbohydrate moiety. This is in line with the view that the hydrogen bonds between the carbohydrate moieties are more sensitive to increase in thermal energy than are the van der Waals forces between interdigitating alkyl chains [67].

4.1.2. *Discotic columnar mesophases from amphiphilic carbohydrates*

Double-tailed dithioacetals were investigated [89–91] almost simultaneously by three research groups; initially a smectic A_d [89] and a smectic B [90] phase were identified. A little later, based on XRD data, a hexagonal columnar structure [92] was assigned to the phases of these Y-shaped molecules since three sharp peaks were observed. Specifically, double-tailed dithioacetals, **87–90** ($n = 8$ for **87**, **88**, **90** and $n = 7, 8, 9$ for **89**), although differing in stereochemistry, form only one type of hydrogen-bonded disk-shaped structure through multimer formation. The supramolecular structure which may rationalize these findings is shown in figure 6, as modified by Jeffrey and Wingert [67]. The terminal hydroxyl group is essential for the formation of the columnar hexagonal mesophase since the 6-deoxy carbohydrate dithioacetals were shown not to be mesomorphic [92].



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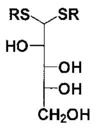

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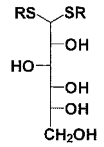

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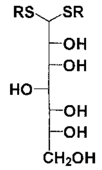


90

In a similar manner, 6,6-dialkyl-D-galactopyranoses formed columnar supramolecular structures due to the formation of multimers held together by hydrogen bonding. The miscibility of one member of the series, 6,6-di-*C*-*n*-octyl-α/β-D-galactopyrasone, with *S*,*S*-di-octyl-D-arabino-dithioacetal which exhibits a hexagonal columnar mesophase, verifies [93] the formation of columnar phases in this case. Furthermore, a series of cellobiose octa-alkanoates [94] with alkyl chain lengths in the range $n = 7$–14 were investigated in detail. All the compounds form enantiotropic discotic columnar phases; in this case the columns are formed by a regular stacking of the cellobiose moieties in a two-dimensional lattice. The types of phase formed depend on the member of the homologous series and on the temperature. Thus

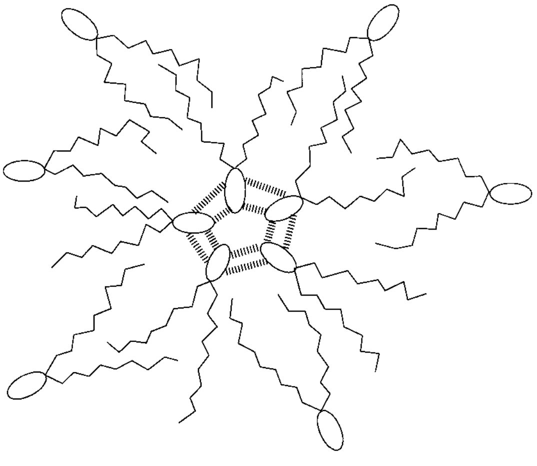
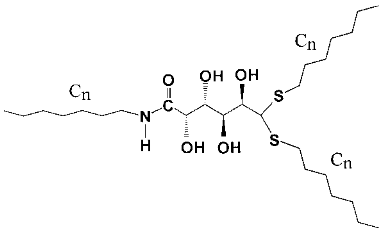


Figure 6. Supramolecular structure of double-tailed amphiphilic carbohydrates exhibiting a hexagonal columnar mesophase. Reproduced by kind permission of the authors and publisher [67].

homologues with $n = 9$–14 form hexagonal ordered columnar ($\mathrm{Col_{ho}}$) phases whereas the member with $n = 7$ forms a rectangular ordered columnar ($\mathrm{Col_{ro}}$) phase. The carbohydrate with $n = 8$ forms a $\mathrm{Col_{ho}}$ phase at high temperature and a $\mathrm{Col_{ro}}$ phase at low temperatures.

Several new amphiphilic dithioacetal carbohydrates [95], **91** ($n = 8, 12$) and **92** ($n = 12$, $m = 15$) have been prepared and characterized in addition to those previously discussed and intensively investigated. These carbohydrates exhibit enantiotropic hexagonal columnar disordered phases as found by POM and XRD. It should be noted that thiocetals behave like the corresponding acetals, showing the same liquid crystalline phases and the same dependence on the chain length, but the clearing points are about 30°C higher [96]. Carbohydrate **91** forms monotropic phases, the first of which has been identified as a hexagonal columnar disordered phase $\mathrm{Col_{hd}}$, at high temperature, while the second phase is a rectangular columnar disordered phase $\mathrm{Col_{rd}}$, at low temperature. The columnar phases observed for these trisubstituted acyclic compounds are surprising as they contrast structurally with the previously mentioned disubstituted derivatives which also form hexagonal columnar phases; in this case, however, multimers cannot be formed. It was suggested rather that the columns are now built from single molecules arranged one above the other without preferred orientation and the construction is supported by strong hydrogen-bonding interactions and by the segregation of the hydrophilic from the lipophilic moieties.



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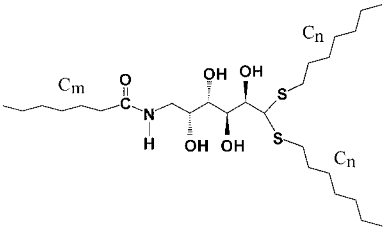
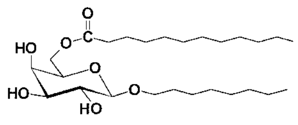


92

The synthesis of alkyl-6-*O*-acyl-glycopyranosides **93–96** by a chemoenzymatic procedure led to the development of a new supramolecular model [97] for the observed liquid crystalline properties. The β-glycosides **93** and **94** form columnar discotic mesophases with clearing points above 80°C, while the α-glycosides **95** and **96**, which presumably also form discotic phases, show clearing points below 20°C. Definite textures were not however assigned for the latter two compounds. Figure 7 shows the proposed model, according to which the driving force for the formation of these mesophases resides in the tendency of the hydrophobic and hydrophilic segments or moieties to segregate from each other. In this way the surface between these segments constitutes a cylindrical jacket. Along this bent plane the amphiphilic molecules have a two-dimensional freedom of movement and rotate about the longitudinal axis. Carbohydrates **93** and **94** carry equatorial aglycons and therefore the alkyl groups enclose a smaller angle compared with carbohydrates **95** and **96** that bear an axial aglycon. It is concluded that **93** and **94** are favourably packed within the mesophase and have a higher freedom of movement and consequently a higher entropy. An acute triangle rotates more than an obtuse one. Taking into consideration these results, as well as those previously mentioned, the postulated model of multimers for the formation of columnar phases, as applied to dialkyl mercaptans, cannot be considered to have general applicability.



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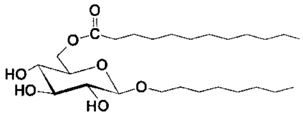

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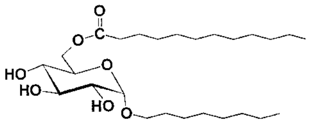

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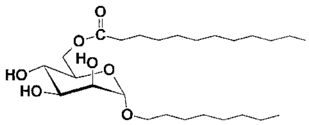
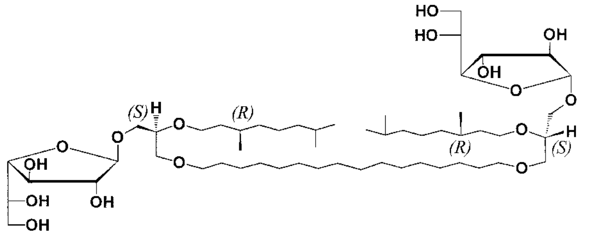


96

It seems that the structural features and complexity of amphiphilic carbohydrates dictate their specific supramolecular structure when melted. However this should not be generalized, as a recent paper by Goodby *et al.* [98] implies. Three glycosylated pseudo-tetraethers, **97–99**, have been prepared which were designed to mimic archael glycolipids. On cooling all of these compounds, they exhibited textures associated with the appearance of disordered columnar hexagonal phases. Two supramolecular structures can be envisaged to justify these properties: (a) first, with the aliphatic chains on the exterior of a 'new' pearl-like structure with carbohydrate moieties in the interior; (b) second, a structure where the aliphatic chains are in the interior and the carbohydrate moieties on the outside. It was established that the aliphatic chains are located in the external surfaces of the columns forming the supramolecular structure shown in figure 8.



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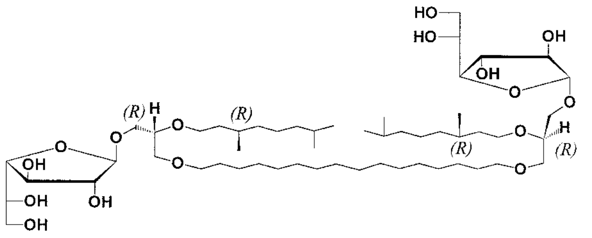

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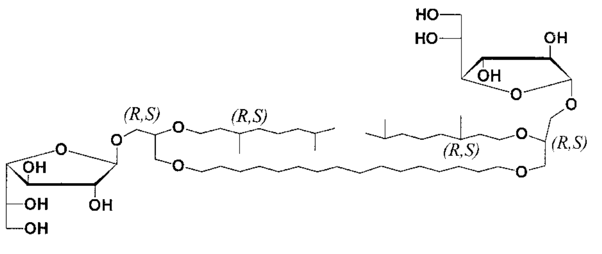


99

4.1.3. *Lamellar, columnar and cubic mesophases originating from amphiphilic carbohydrates*

Inositol (1,2,3,4,5,6-hexahydroxycyclohexane) monoethers, diethers, triethers, tetraethers and pentaethers have allowed detailed studies to be made on the relationship between the type of substitution in the cyclohexane ring and the liquid crystalline character. The type of mesomorphism exhibited was dependent on the number and stereochemical arrangement of the hydroxyl groups, the length of alkoxy chains and also on their ring positions. The main results on the liquid crystalline behaviour of inositol ethers can be summarized [99] as follows: (1) axial groups weaken the mesophase since the molecular symmetry does not favour the formation of mesophases; (b) the transformation from hexagonal columnar to smectic phase, shown for compounds **100** and **101**, is due to the stereochemical effect of two vicinal hydroxy groups.

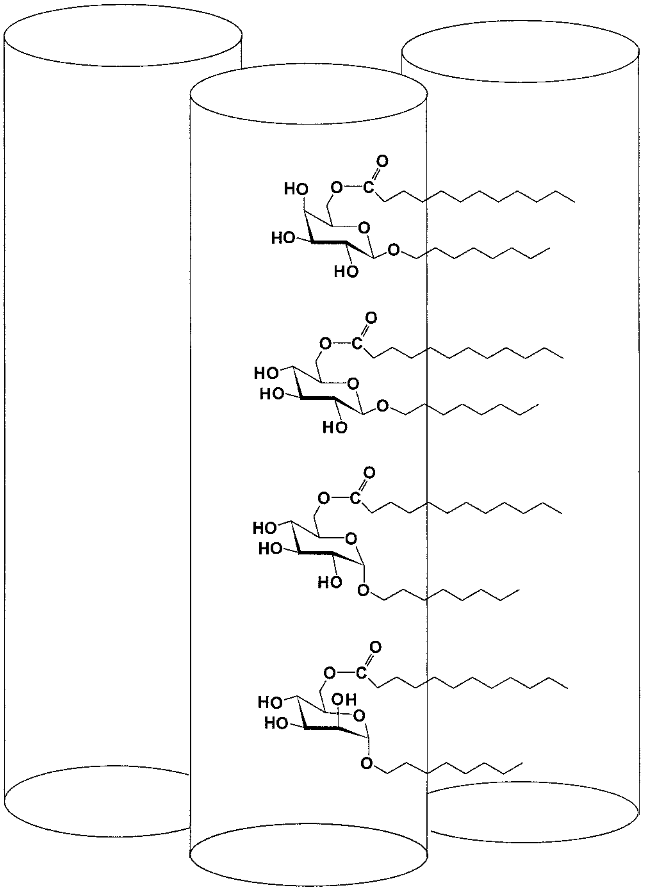
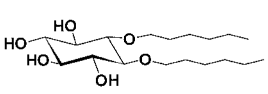


Figure 7. Supramolecular model for the formation of discotic mesophases for certain alkyl-6-*O*-acylglycopyranosides. Reproduced by kind permission of the authors and publishers [97].



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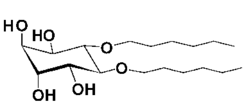

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Novel amphiphilic glucamine derivatives have been synthesized [100, 101], viz. *N*-benzoyl-1-deoxy-1-methylamino-D-glucitols and *N*-benzoylamino-1-deoxy-D-glucitols, **102**, in which one, two or three alkyl chains ($n = 3$, 6 and 12) have been introduced via an aromatic linking unit to the carbohydrate moiety. In this way the number of hydroxy groups remains the same, independent of the increasing number of chains. Depending on the number and the length of the alkyl chains, lamellar, bicontinuous cubic, hexagonal columnar or inverted micellar cubic mesophases were detected by analogy with

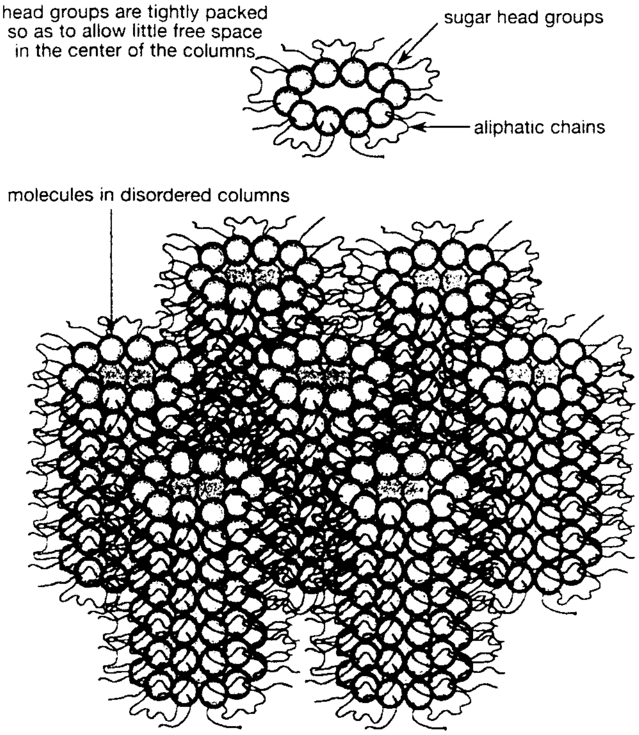
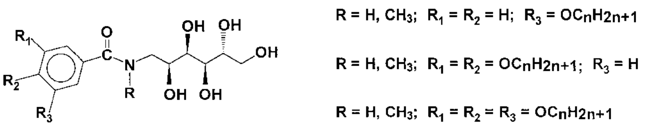


Figure 8. The columnar structure formed by amphiphiles **97–99** [98]. Reprinted with permission from Velty, R. A., Benvegnu, T., Plusquellec, D., Mackenzie, G., Haley, J. A., and Goodby, J. W., *Angew. Chem. Int. Ed. Engl.*, 1998, **37**, 2511.

lyotropic systems. Thus, single chain derivatives form lamellar α phases (L_α), and carbohydrates with two dodecyloxy chains display a spherulitic texture which is typical for a hexagonal columnar mesophase, while with two hexyloxy chains they exhibit a lamellar L_α phase. The triply hexyloxy substituted derivatives form hexagonal columnar phases while the triply substituted dodecyloxy derivatives form inverse discontinuous cubic mesophases (I_{II}-phases). In the contact region between the lamellar phases of single chain amphiphiles and the micellar cubic mesophases of the triply substituted carbohydrates, hexagonal columnar phases can be induced. A hexagonal columnar phase can also be induced in the contact region between a bicontinuous and a micellar cubic mesophase. Analogous investigations originating from the same laboratory extended the previous work on both amphiphilic glucitol derivatives and amphiphilic diols, triols and tetraols proposing [102] a model for the transition between the different mesophases. In a strongly similar way to lyotropic systems, the type of thermotropic mesomorphism depends on the surface area of the hydrophilic parts at the hydrophilic–lipophilic interface and the size of the lipophilic groups, which determine the mean interfacial curvature. Lamellar (SmA), columnar (H_{II}) and two types of cubic mesophases (V_{II} and I_{II}) were obtained.



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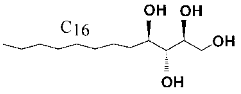
4.2. *Multihydroxy amphiphilic and bola-ampiphilic compounds*

The liquid crystalline character exhibited by multihydroxy amphiphiles, in the same way as for amphiphilic carbohydrates, can be attributed to the ability of their hydroxy groups to form a dynamic network of cooperative hydrogen bonds coupled with the lipophilic chains. Diols or polyols with one polar head [103], as well as bola-amphiphilic polyols [104] exhibit thermotropic liquid crystalline behaviour. The chemical structures of such polyhydroxy amphiphiles, **103–106**, with one polar head are shown below. Compounds of the general formula **107** ($n = 8$–14) exhibit metastable smectic A and B phases when $n < 11$, while the higher homologues form only a monotropic smectic B phase [105]. Addition of water leads to a remarkable stabilization of the liquid crystalline behaviour. These compounds, which are structurally related to carbohydrate liquid crystals, can be regarded as the simplest members of this large class of amphiphilic mesogens.



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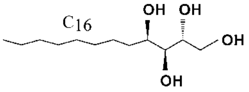

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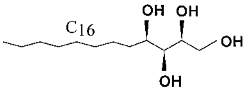

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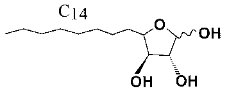

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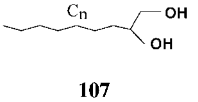

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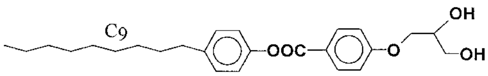
The liquid crystalline phases of the above-mentioned compounds can be modified and stabilized by the introduction of rigid-rod moieties. For instance, the introduction of a 1,2-diol moiety at the end of the *n*-alkoxy group of a non-amphiphilic phenyl benzoate, afforded compound **108**, which showed a smectic phase in place of the nematic phase exhibited by the starting material [106]. In addition, the introduction of the diol moiety to the known 4-alkoxy-4′-cyanobiphenyl liquid crystals, resulted in the compounds of general formula **109** ($n = 1, 2, 4, 6, 8, 9$). These compounds show enhanced mesophase stability, without however inducing the formation of smectic phases. Since these compounds are amphiphilic, their mesogenic properties are affected by the addition of water which stabilizes the mesophase and induces the formation of smectic phases. An explanation for this behaviour is that water interpenetrates the network of hydrogen bonds of the diol head groups, strengthening the interactions between the groups and therefore hindering the parallel movement of single molecules. It is therefore clear that by affecting hydrogen bonds it is possible to control specifically the molecular arrangement of amphiphilic molecules.

Similarly to the previous findings, imidazole and 2-methylimidazole contribute [107] to the formation of a self-assembled smectic phase over a broad range by complexation to the nematogenic diol compound **109** ($n = 4$). Smectic character is not however observed for the complexes based on the monohydroxy mesogen. Imidazoles together with the diol form hetero-intermolecular hydrogen-bonded networks contributing to the stability of the liquid crystalline phase.



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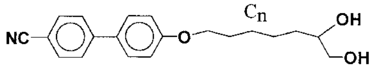

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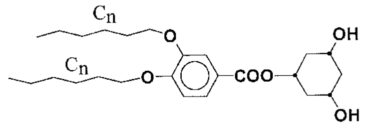
Furthermore, cyclohexan-1,3-diol esters have been synthesized bearing two or three alkyl chains on a phenyl group; these are of general formula **110** ($n = 6, 8$–$10, 12, 14$) and **111** ($n = 4$–14). Detailed characterization studies [108–113] including XRD have shown that the molecules aggregate even in the isotropic phase. In the mesophase they pack in a hexagonal array giving a texture with a structure similar to that of a discotic columnar phase. The mesogen is not a disk-like molecule, but six molecules can assemble via hydrogen bonding, affording a hexagonal structure. In addition to these monomeric diols, a polymeric counterpart was synthesized [113] by employing the known hydrosilylation reaction for polysiloxane preparation. A polymer, **112**, was obtained bearing the 1,3-cyclohexandiol moiety. As is the case with analogous monomeric compounds, hydrogen bonding among the diol moieties is responsible for the formation of a liquid crystalline phase.



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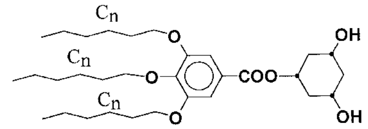

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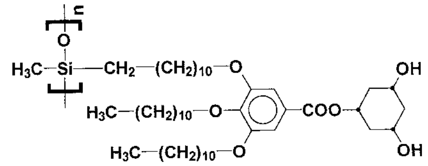

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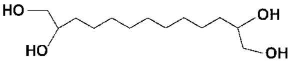
Stabilized liquid crystalline phases were also obtained [104] from polyhydroxy bola-amphiphilic compounds **113–118**. Among these compounds, the unsymmetrical tetraol **114** generates the greatest mesophase diversification. Thus, on cooling from the isotropic melt, a fan-like texture, typical of lamellar α-phases was obtained, and this can be very easily oriented homeotropically by shearing. The hydroxy groups, like those of amphiphilic diols, couple via a dynamic network of cooperative hydrogen bonds that is separated from the conformationally molten polymethylene chains, forming an L_α phase. On cooling to 75°C, the texture changes and the viscosity increases, probably due to a transition to a more highly ordered L_β mesophase with rigid parallel polymethylene chains. At 43°C another transformation occurs which cannot be studied in detail due to the onset of crystallization. The liquid crystalline phases of the polyols can again be modified by the addition of water. Specifically, the mesophases of the compounds bearing long aliphatic chains when saturated with water are stabilized, while those with short polymethylene chains are destabilized.



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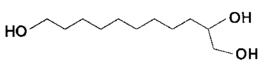

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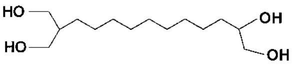

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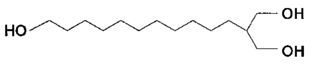

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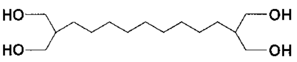

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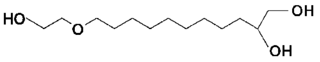
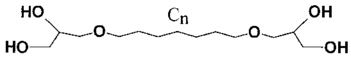


118

Investigations on bola-amphiphilic tetraols continued for the homologous series of 1,2-ψ,ω,n-alkantetraols [114] of general formula **113** (polymethylene chain $n = 4$–18, 20). Those compounds which bear a rather long polymethylene chain exhibit a lamellar symbol α phase and a low temperature mesophase, whereas the derivatives with short chains exhibit only the low temperature mesophase. According to X-ray studies, the low temperature phase is a highly ordered phase in which the alkylene chains are rigid and tilted with respect to the hydrogen-bonding network. On the basis of the experimental d-values and the estimated tilt angle of 28°, a model has been proposed as shown in figure 9. It was assumed that the primary hydroxy groups interact through hydrogen bonding with the secondary hydroxy groups of the corresponding neighbouring molecule. In this way a tilt angle of about 30° could be rationalized. This low temperature mesophase is highly ordered and viscous. Its layer thickness decreases following the transition to the high temperature phase. This transition is accompanied by a high enthalpy change, giving rise to a mesophase in which the alkylene chains are liquid-like as is the case with the L_α phase of lyotropic systems. The melting of the alkylene chains must be accompanied by a reorganization of the hydrogen bonds, a factor which also contributes to the high transition enthalpy. With respect to the high transition enthalpy between the two mesophases and the high viscosity, the low temperature phase may be considered to possess a solid-like character, although the X-ray patterns are very similar to those of the low temperature mesophases of the amphiphilic diols [114]. Furthermore, results in a recent report [115] on a homologous series of single chain diether bola-amphiphiles, **119**, with 10 to 22 methylene groups and bearing dihydroxy head groups, are comparable to those from the previous work [114], the system affording a lamellar L_α phase at high temperatures. At low temperatures a second phase was detected, characteristic of a lamellar L_β phase with monoclinic organization.



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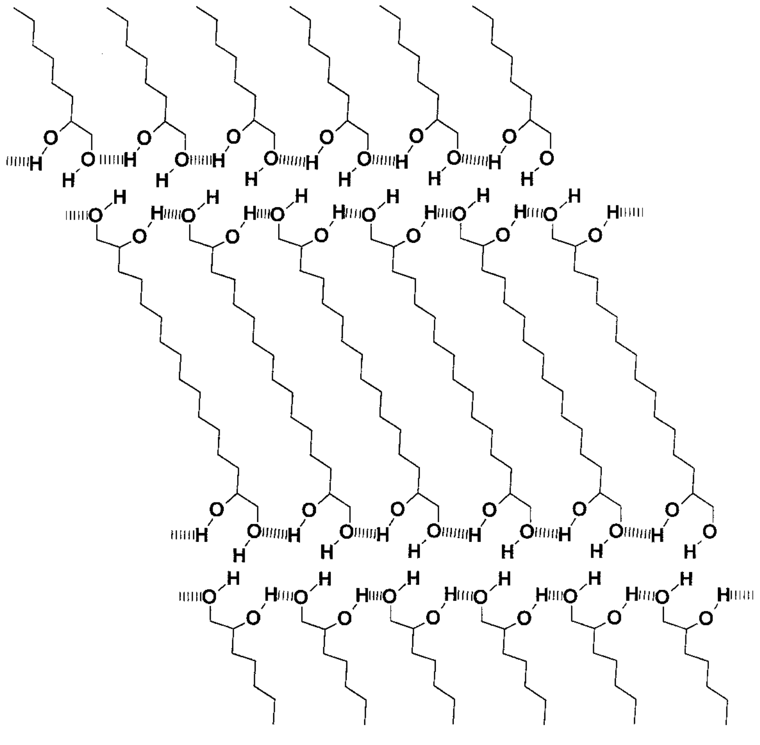
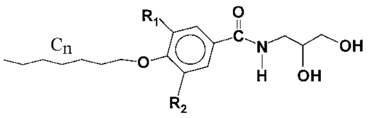


Figure 9. Supramolecular structure of bola-amphiphilic compound **113** showing the hydrogen-bonded network of the low temperature highly ordered mesophase. Reproduced by kind permission of the authors and publishers [114].

Amphiphilic *N*-(2,3-dihydroxypropyl)benzamides [116] can serve as stable model compounds for carbohydrate derivatives. One, two or even three long alkyl chains have been introduced to the phenyl group affording structures **120**. The compound with one dodecyloxy chain ($n = 12$) forms a smectic A_d phase, while a hexagonal columnar phase is exhibited for the double chain compound and a cubic phase for the derivative with three alkoxy groups in the ring. It is thus clear that a diversity of phases can be formed, i.e. from lamellar through columnar to cubic, by changing the number of lipophilic chains on the aromatic moiety.



$R_1 = R_2 = H$

$R_1 = OC_nH_{2n+1}$, $R_2 = H$

$R_1 = R_2 = OC_nH_{2n+1}$

120

5. Hydrogen-bonded networks exhibiting liquid crystalline behaviour formed by the interaction of multi-functional components

A rather early example of the formation of a hydrogen-bonded network exhibiting mesomorphic properties concerned certain diamides of alkyl substituted 1,3-diaminobenzene. They were initially prepared by Matsunaga and Terada [117] and reinvestigated in detail by Malthête *et al.* [118], together with some analogous compounds. The presence of methyl groups at appropriate positions on the benzene ring was crucial for the formation of liquid crystalline phases. In the example shown in figure 10, it may be assumed that a methyl group close to an amide group (4-position) or between two amide groups (2-position) turns at least one amide group out of the plane of the phenyl ring and so should favour self-association and the formation of supramolecular structures leading to mesomorphic phases. In an analogous manner, hydrogen-bonding interactions explain the 'non-conventional nematic phases' exhibited [119] by the homologous series of *N*,*N*′-dialkanoyl-2,5-dimethyl-4-alkanoyloxy-1,3-benzdiamides and their 2-methyl-5-*iso*-propyl and 2-methyl-5-*tert*-butyl analogues, **121**.

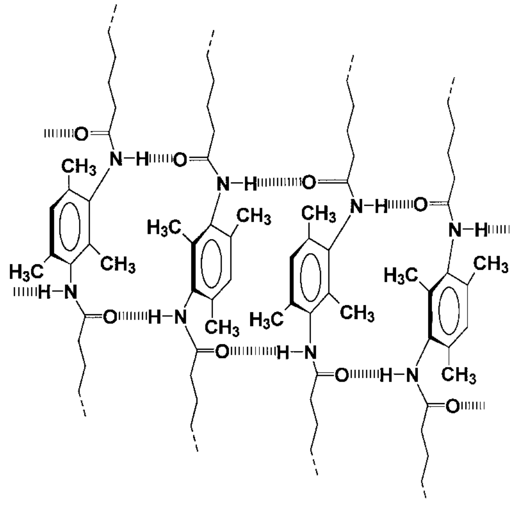
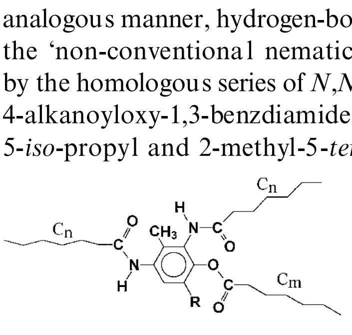


Figure 10. Diagram of the supramolecular structure of a hydrogen-bonded associated diamide [118]. Reprinted with permission from Malthête, J., Levelut, A. M., and Liebert, L., *Adv. Mater.*, 1992, **4**, 37.



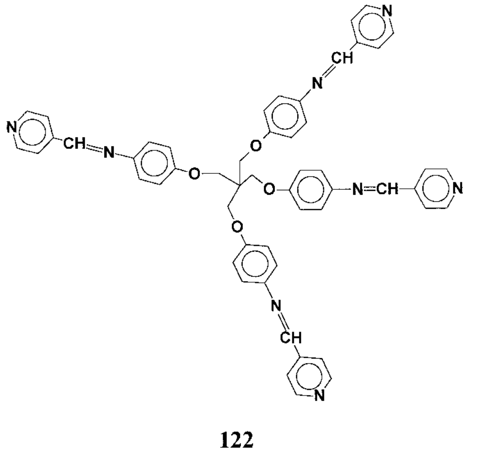
R = CH_3 n = m = 8-11, 13, 15

R = *i* Pr n = 8-11, 13, 15; m = 4-15

R = *t* Bu n = m = 10, 11, 13, 15

121

A hydrogen-bonded liquid crystalline network of the type shown in figure 11 was formed [120] by the interaction of a pentaerythritol-based tetrapyridyl derivative **122** with a flexible dicarboxylic acid **123**. The tetrahedral pyridyl derivative is a semi-flexible unit which can be crosslinked by hydrogen-bonding complexation, in more than one dimension, when mixed with an appropriate dicarboxylic acid, affording a supramolecular network. From molecular modelling it can be shown that the flexibility about the $-CH_2-O-$ linkages of the pentaerythritol core is insufficient for the molecule to adopt a tetrahedral conformation. It exists essentially as a one-dimensional rod with the pyridyl moieties at each of the four ends lying together in pairs. The texture does not closely resemble any well-known liquid crystalline phase although it may be smectic, being similar to certain liquid crystalline polymers. Fibres could be drawn from the mesomorphic melt, a fact that supports a polymeric extended chain structure for the complexes (see also § 7).



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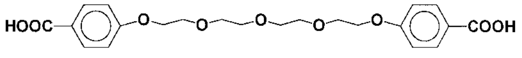

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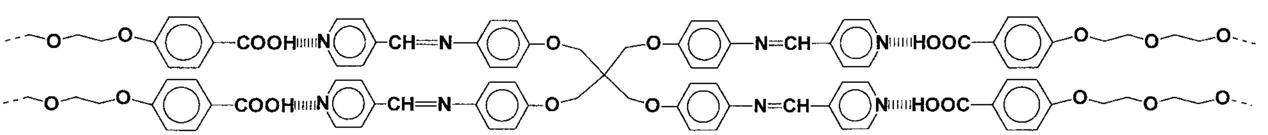
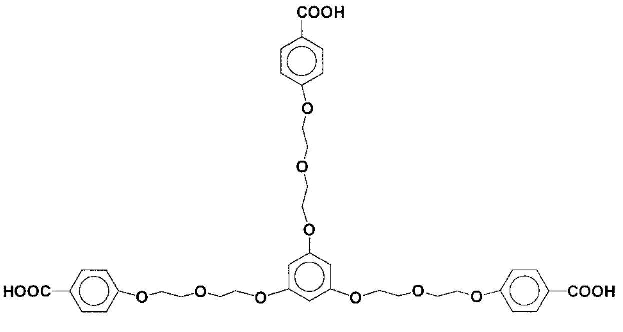


Figure 11. Supramolecular network derived from a pentaerythitol-based derivative with a flexible dicarboxylic acid. Reproduced by kind permission of the author and publishers [120].

Analogously, two tricarboxylic acids, **124** and **125**, when interacted with four bifunctional acceptors, **126–129**, afforded the respective complexes [121] with a 1 : 1 donor/acceptor group stoichiometry. For instance a smectic A phase was formed from the supramolecular complex originating from **124/128**, while a nematic phase was given by the complex **125/128** on cooling. Supramolecular networks, forming smectic and nematic liquid crystalline phases are shown schematically in figure 12.



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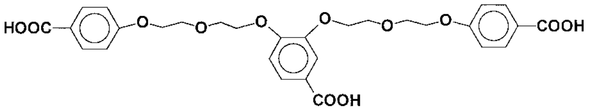

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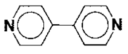

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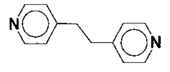

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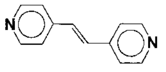

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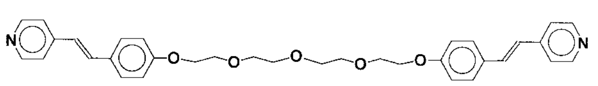
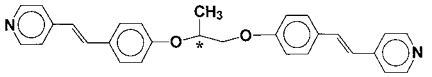


129

Furthermore, hydrogen-bonded networks were prepared [122] by the interaction of a chiral, bifunctional hydrogen-bonding acceptor, **130**, with achiral trifunctional hydrogen-bonding donors, **125** and its isomers **131–134**.

The chiral stilbazole dimer was complexed with the trifunctional acids in a 1 : 1 molar ratio. The interacting components were not mesomorphic, whereas all the complexes, except the one resulting from **130** and **134**, exhibited cholesteric (N*) phases. These results show that helical supramolecular networks may be formed from non-mesomorphic molecules. It is also interesting to note that the cholesteric texture was preserved in the glassy states of the networks.



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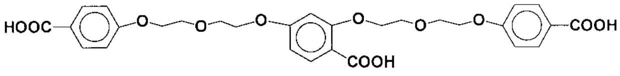

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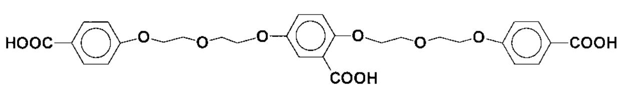

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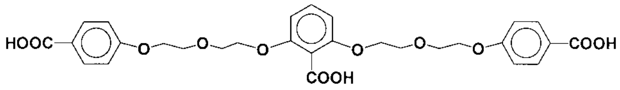

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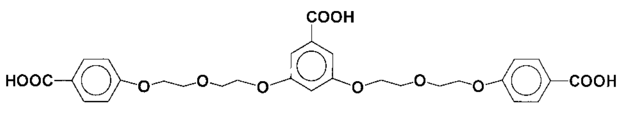


134

6. Liquid crystalline polymers induced by template-type interactions

Polymeric chains have been employed as ‘templates’ for the formation of liquid crystals through hydrogen-bonding interactions with mesogenic molecules. The term ‘template induced mesomorphism’ was introduced

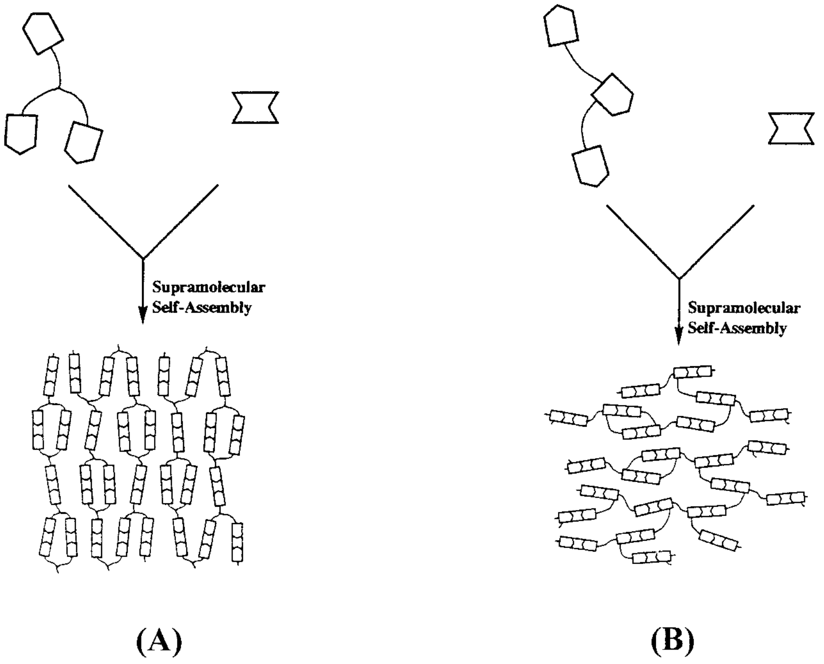
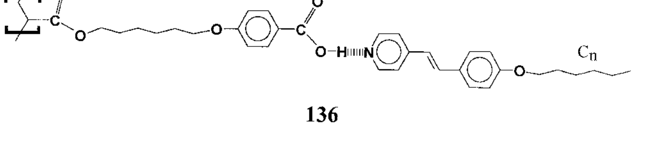


Figure 12. Supramolecular networks affording smectic (A) and nematic (B) liquid crystalline phases [121]. Reprinted with permission from *Chem. Mater.*, 1996, **8**, 961.

[123] several years ago by the authors of this review to describe a method for the formation of liquid crystals through ionic bonding. It continues to be a fruitful method for the formation of a diversity of liquid crystalline phases.

Carboxyl-pyridyl group interaction has been extensively employed for the stabilization or induction of liquid crystalline phases in polymers. Thus side group liquid crystalline polymers bearing a carboxyl group interact with the pyridyl group of 4-*trans*-stilbazole derivatives affording polymeric hydrogen-bonded complexes. Specifically, polymer **135** was formed [124] through the interaction of a polyacrylic acid derivative with a *trans*-stilbazole ester. In this case both of the interacting components exhibit mesomorphic behaviour. The polymer has a mesomorphic range of 140–155°C and the *trans*-stilbazole derivative of 168–216°C. These materials were miscible over the whole composition range and the binary mixture exhibits a broad mesophase range. The enhancement of the liquid crystalline phase is due to the formation of an elongated mesogenic unit involving a hydrogen-bonded moiety. A similar polymer was also interacted with various *trans*-4-alkoxy-4′-stilbazoles carrying terminal *n*-alkoxy groups ($n = 1$–8, 10); compounds of the general formula **136** were obtained [125]. Thermally stable smectic A phases were formed and the isotropization and melting temperatures showed the known odd–even effect associated with the terminal alkoxy group. The analogous monomeric (1 : 1 molar ratio) complexes were also prepared and as expected showed lower transition temperatures than the corresponding polymeric materials.



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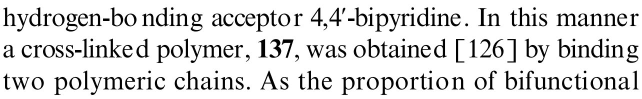
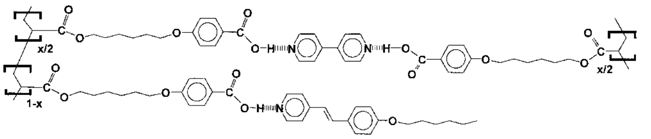


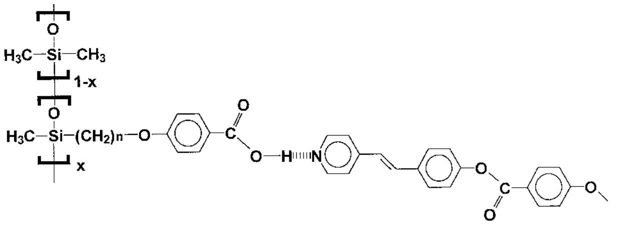
136

The previously employed polyacrylic acid derivative was also interacted with both the monofunctional *trans*-4-hexyloxy-4′-stilbazole acceptor and the bifunctional hydrogen-bonding acceptor 4,4′-bipyridine. In this manner a cross-linked polymer, **137**, was obtained [126] by binding two polymeric chains. As the proportion of bifunctional acceptor increases, so does the glass transition temperature, while the melting point shows a decreasing trend. Mesomorphic character is shown for the 1 : 1 complexes over the whole composition range of hydrogen-bonded components. The isotropization temperatures are observed at about 200°C for all these complexes. It is interesting to note that reversible non-covalent crosslinking is assumed, as evidenced by the reversibility of the smectic–isotropic transitions. On heating the isotropic phase, some of the hydrogen bonds between the carboxyl and bipyridyl groups are broken. On cooling the isotropic melt, some of the hydrogen bonds are reformed, affording the smectic phase again. It should be noted [125] that for covalently bonded and highly crosslinked polymers, molecular orientations are preserved in the solid phase and mesomorphic character is not observed.



137

Using the same strategy as before for enhancing or modifying liquid crystalline properties, poly(methylsiloxanes) and poly(methyl-*co*-dimethylsiloxanes) with a benzoic acid moiety in their side groups have been used. These polymers, which themselves exhibit liquid crystalline properties due to dimerization, interact through hydrogen bonding with the mesogenic *trans*-4-(4-methoxybenzoyloxy)-4′-stilbazole and the non-mesogenic *trans*-4-ethoxy-4′-stilbazole affording [127] polymers **138** and **139** (spacers $n = 5, 8, 10$), respectively. It should be noted that this persistent use of stilbazoles as hydrogen-bond acceptors is due to the high enthalpy value involved in the formation of the complexes between the carboxyl and pyridyl moieties [128]. In addition, the components show complete miscibility and high liquid crystalline thermal stability over the whole composition range. For non-oriented samples, XRD studies reveal smectic C or A phases for the various hydrogen-bonded complexes.



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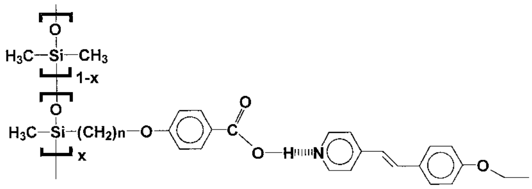
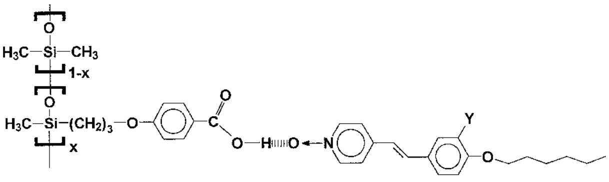


139

Polymers with potential practical applications in mind were also prepared by employing the methodology of interacting polymeric donors with acceptors bearing appropriate functional groups. Thus, polysiloxanes bearing a pendant propyloxybenzoic acid group as donor [129] were interacted with stilbazole-*N*-oxide as acceptor leading to the formation of the polymers **140** (**140a**, $x = 1.00$ and $Y = \mathrm{H}$; **140b**, $x = 1.00$ and $Y = \mathrm{F}$; **140c**, $x = 0.43$ and $Y = \mathrm{H}$; **140d**, $x = 0.43$ and $Y = \mathrm{F}$). These polymers exhibited smectic A or smectic C phases above their glass transition temperatures and since none of the components of the complexes was liquid crystalline, the observed phases reflect the formation of mesogenic complexes by hydrogen bonding. The strong dipole along the molecular long axes results, as expected, in the formation of liquid crystalline materials with strong positive dielectric anisotropy, a prerequisite for certain electro-optical applications.



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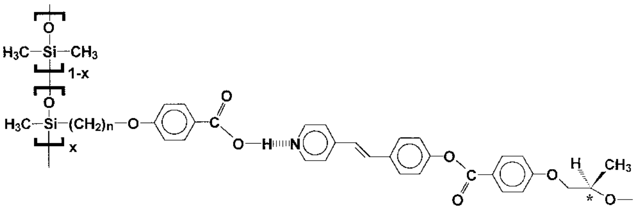
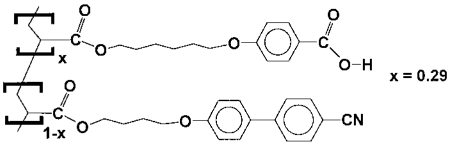


141

Ferroelectricity was induced when polysiloxanes bearing a pendant *p*-alkoxybenzoic acid group were complexed [130] with the optically active (*S*)-(–)-*trans*-4-(2-methoxypropyloxy)-4′-stilbazole forming a polymer **141** with spacer $n = 5$, $x = 0.29$; $n = 5$, $x = 0.43$; $n = 8$, $x = 0.29$; $n = 8$, $x = 0.43$. XRD data from annealed, non-oriented samples showed an intense ring, sometimes accompanied by its second order reflection which, together with the spontaneous polarization point to the formation of a smectic C phase comprising two overlapping hydrogen-bonded moieties. It should be noted that in this case the SmA → SmC* phase transition was only indicated by POM, but not by DSC.

Similarly, by interacting liquid crystalline copolymers **142** and **143** with the chiral compound **144**, liquid crystalline complexes were obtained. Specifically, at concentrations in the range 1–25 mol% of the chiral component, the cholesteric (N*) phase was induced [131]. Concerning the optical properties, the chiral nematic phase induced for these hydrogen-bonded complexes is comparable to that of conventional cholesteric copolymers in which the chiral group is covalently linked to the polymer chain.



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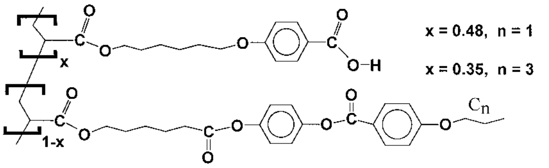

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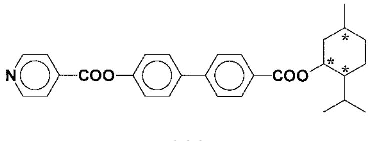
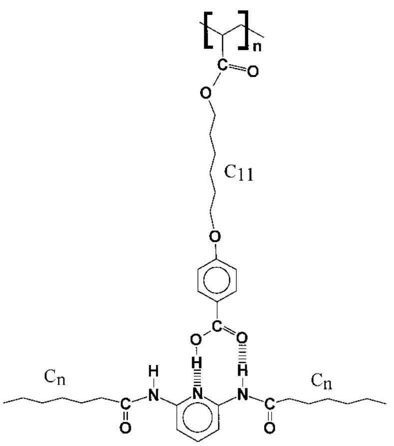


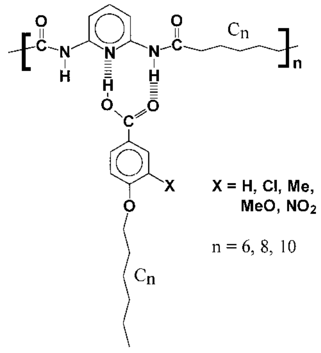
144

According to recent work, mesogens can also be attached to the polymeric chain through two hydrogen bonds. Thus, a polyacrylate derivative with a terminal carboxyl group interacts with certain 2,6-bis(acylamino)-pyridines affording supramolecular complexes, **145**, which exhibit monotropic liquid crystalline phases [132]. The mesogenic molecular structure reported is unique because the two alkyl chains of the acyl groups do not lie on the long axis of the aromatic core of the side group moiety which therefore does not have a simple rod shape.



145

Another mode of employing the 2,6-bis(acylamino)-pyridine moiety as a hydrogen-bonding component is to introduce it into the main chain of a polyamide polymer. A diversity of benzoic acid derivatives interact [133–135] with the above-mentioned moiety in the polymer backbone through a system involving two hydrogen bonds and afford polymeric complexes such as **146**. The structure of these complexes is again unique, as discussed before, because they share the features of side group and main chain polymers. Stable smectic A mesophases were obtained and a schematic supramolecular structure justifying the appearance of these phases is shown in figure 13.



146

Another method of preparing hydrogen-bonded liquid crystalline polymers [136] is by the interaction of two components both of which are polymeric. Thus, a main chain polyester bearing a lateral pyridylethenyl group

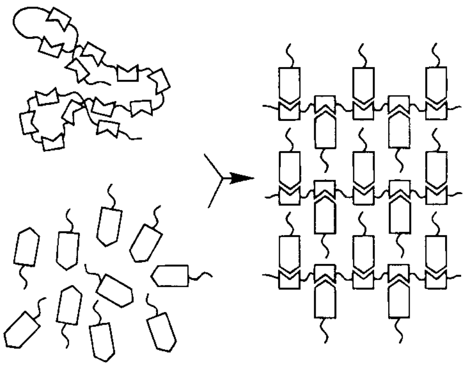
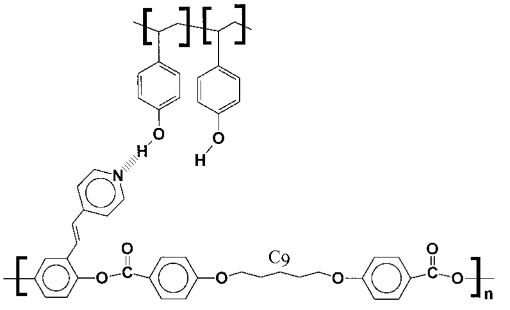


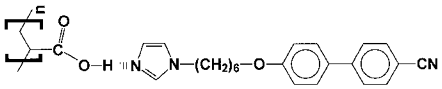
Figure 13. Schematic representation of supramolecular polymeric complexes derived from polyamides after their interaction through hydrogen bonding with benzoic acid derivatives [134]. Reprinted with permission from *Macromolecules*, 1998, **31**, 3551.

interacts with a non-mesogenic poly(vinylphenol) affording the supramolecular complex **147** which exhibits a homogeneous nematic phase.



147

Employing the extensively used polyacrylic acid and mesogenic derivatives bearing the imidazolyl moiety, the supramolecular liquid crystalline side group polymers **148** were obtained [137]. Additionally, liquid crystal networks were prepared by the interaction of polyacrylic acid with a mesogenic derivative with two terminal imidazolyl groups, affording polymeric complexes of structure **149**. In both cases smectic A phases were exhibited.



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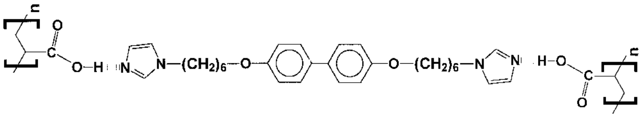
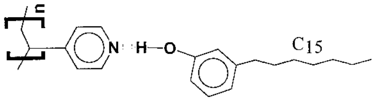


149

Poly(4-vinylpyridine) was also employed [138] as template for the induction of liquid crystallinity. The polymer was interacted with 3-pentadecylphenol forming a hydrogen-bonded polymeric complex **150**. The smectic-like structures observed were attributed to the microphase separation between the long aliphatic chain and the polar polymer chain to which the phenolic moiety was attached. Other phenolic donors have also been employed for the formation of side group liquid crystalline polymers [139]. Thus when poly(4-vinylpyridine)-*co*-(butyl acrylate) was interacted with 4-(4-nitrophenylazo)-phenol, 4-(4-methoxyphenylazo)phenol or 4-phenylazophenol, complexes **151** were formed. These exhibited nematic liquid crystalline phases as established by XRD and POM. The isotropization temperatures of the polymeric complexes for different Y varied in the sequence $NO_2 > H > OCH_3$.



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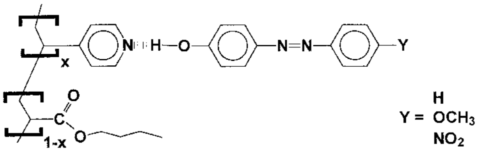
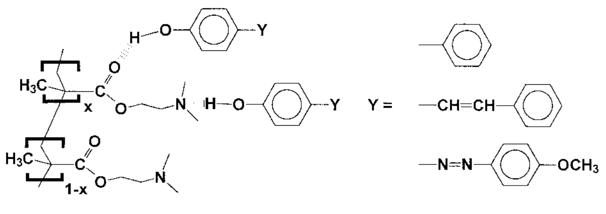


151

Poly[(2-dimethylamino)ethyl acrylate] and poly-(2-hydroxyethyl acrylate) were also employed as functional templates [140] bearing proton accepting and proton donating groups, respectively. They were reacted with rigid aromatic mesogenic groups and afforded complexes **152** and **153**, which, exhibited nematic phases, as established by XRD. It is interesting to note that for these complexes hydrogen bonding occurs not only with the tertiary amine group, but also with the ester carbonyl group.



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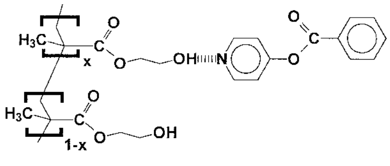
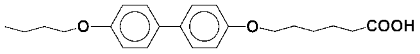


153

In the foregoing investigations, the mesogenic moieties of the polymers were formed primarily by hydrogen-bonding interaction between the complementary groups of the components, leading to the formation of an extended rigid-rod system; the liquid crystalline behaviour was attributed to this structural feature. Almost simultaneously, another strategy was being followed for the preparation of liquid crystals. According to this method the pyridyl moiety of poly(4-vinylpyridine) or poly(2-vinylpyridine) was interacted with a carboxyl group located at the end of an aliphatic spacer; at the other end of the spacer a mesogenic moiety was attached which contributed to the formation of the liquid crystalline phases of the complexes. Various acids have been employed for the formation of the polymers such as 6-(4-*n*-butylazobenzene-4′-oxy)hexanoic acid, **154** [141], 6-(4-*n*-butyl-oxybiphenyl)hexanoic acid, **155** [142–145], 4-*n*-octyloxybenzoic acid, **156** [146] or 6-(4-methoxyazobenzene-4′-oxy)hexanoic acid, **157** [147]. The thermal behaviour of the blends of the acids with poly(4-vinylpyridines) is essentially identical to that observed with structurally similar mesogenic carboxylic acids, and supports the view that molecular mixing occurs up to a certain concentration of the acid after which separation takes place [147]; hydrogen bonding formation is the driving force for the miscibility of the blends. A schematic representation of these supramolecular liquid crystalline polymers is shown in figure 14.

154



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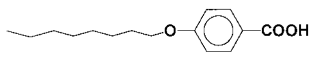

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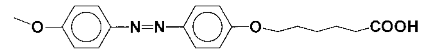

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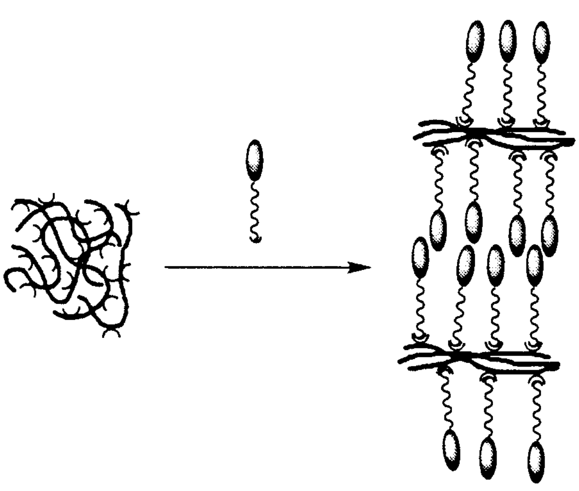
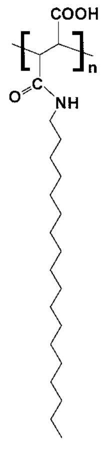


Figure 14. Schematic representation of the supramolecular structure of side group liquid crystalline polymers with the mesogenic moieties decoupled from the hydrogen-bonded system. Reproduced by kind permission of the authors and publishers [142].

As known for a long time [22], liquid crystalline behaviour is not displayed only by aromatic acids. According to preliminary reports certain amphiphilic-type acids exhibit mesomorphic character. Extending this work to polymers, the amphiphilic polymers **158–160**, which were prepared by the reaction of poly(maleic anhydride) [148, 149], or poly(acryloyl chloride) [150] with some long chain primary and secondary amines or ω-aminoundecanoic acid, exhibited liquid crystalline properties. By analogy with the dimers formed by aromatic acids, for instance cinnamic acid derivatives, the exhibition of liquid crystalline character was attributed to the formation of supramolecular structures resulting from the association, through hydrogen bonding of the carboxyl groups of the polymers. The observed smectic phases were attributed to the lamellar structure formed by the segregation of the aliphatic chains from the hydrogen-bonded carboxyl groups which face one another, as shown schematically for these polymers in figure 15 (structures A and B). However in addition to these facing A and B structures, one can envisage C and D structures formed by side-ways association in the polymers. As revealed by FTIR spectroscopy [150], these two supramolecular architectures coexist in the solid and liquid crystalline phases and the temperature of the sample determines which structure predominates.



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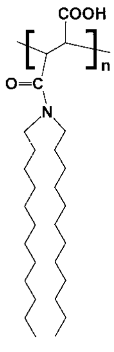

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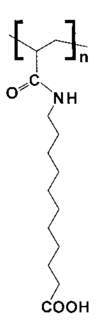

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On similar grounds, the functionalization of polymethylsiloxane with the 4-propoxybenzoic acid moiety was recently reported [151]. The polymer was dimerized,

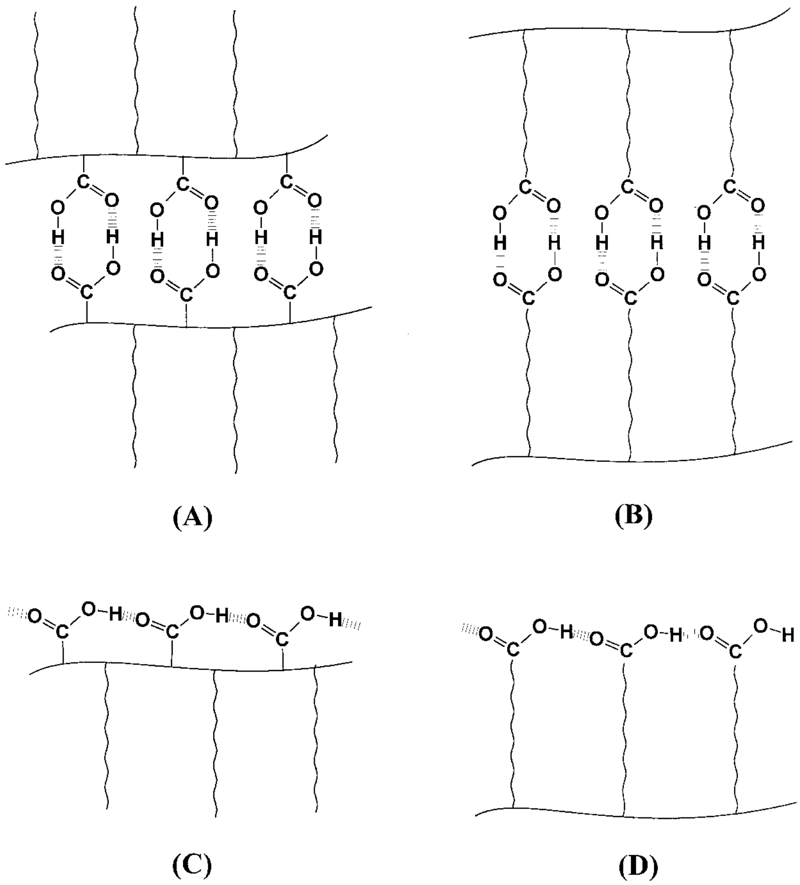
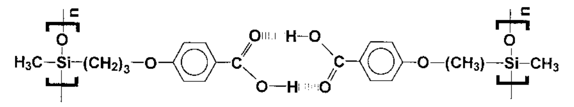


Figure 15. Schematic representation of hydrogen-bonded amphiphilic polymers [150]. Reprinted from *Polymer*, 1992, **33**, 4047 with permission from Elsevier Science.

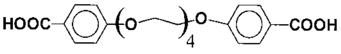
161, as established by FTIR spectroscopy, and exhibited a nematic mesophase, which on cooling afforded a stable hydrogen-bonded network, characterized by POM, DSC and XRD.



161

7. Main chain liquid crystalline polymers derived from bifunctional hydrogen-bond forming molecules

Intermolecular reactions analogous to covalent polycondensation may occur when complementary bifunctional molecules interact with each other through hydrogen bonding. Thus, when dicarboxylic acid **162** was interacted with the bipyridines **163–165**, three hydrogen-bonded main chain polymers were obtained. All three polymeric complexes exhibited [152] enantiotropic nematic mesophases, while their starting components exhibited no liquid crystalline behaviour. For complexes **162/163** and **162/165** the nematic–isotropic transition shows only a small hysteresis, while it is quite large (about 25°C) for the **162/164** complex. In addition the polymer resulting from **162** and **163** exhibited a smectic A phase as evidenced by the focal conic fan-type texture observed by POM.



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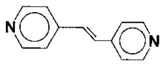

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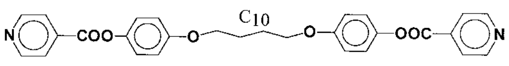

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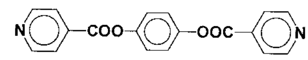
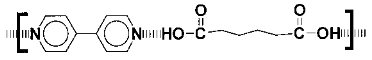


165

Also, 4,4′-bipyridyl and *trans*-1,2-bis(4-pyridyl)ethylene were used as bifunctional acceptors for interaction with either adipic or sebacic acid to form the polymeric complexes **166–169** which exhibited smectic liquid crystalline phases [153, 154] above their melting transitions. Main chain hydrogen-bonded thermotropic liquid crystalline polymers based on *trans*-1,2-bis(4-pyridyl)ethylene and 4-aminobenzoic acid were also prepared [155]. The latter acid has three hydrogen donor sites and it is therefore possible for a liquid crystalline network to be constructed. Polymer **170**, prepared by 1:1 complexation, had a lower liquid crystalline thermal stability than the polymer **171**, with a crosslinked hydrogen-bonded structure resulting from a 3:2 molar ratio of the components.



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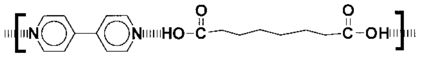

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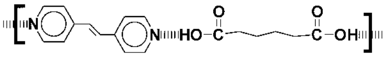

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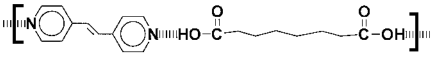

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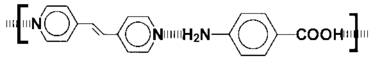

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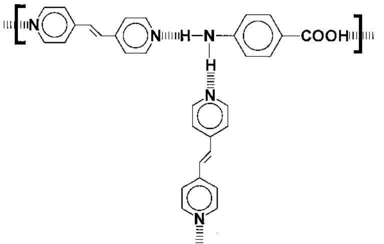
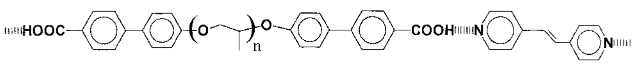


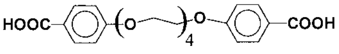
171

Hydrogen-bonding interaction of 4,4′-bipyridine and 4-[poly(propyleneoxy)propyloxy]-4′-bis(biphenylcarboxylic acid), with average degrees of polymerization for the poly(propylene oxide) coil ranging from 8 to 34, led to the formation of supramolecular rod-coil copolymers **172**. Depending on the length of the poly(propylene oxide) coils, a diversity of self-assembled microstructures [156] was induced. Following the melting transition, the rod–coil copolymers with poly(propylene oxide) coils of 8 and 10 repeating units exhibited a bicontinuous cubic mesophase of *Ia*3*d* symmetry, while the copolymers with a medium length poly(propylene oxide) coil (15, 17 and 21), exhibited columnar mesophases. Further increase of the coil to 27 and 34 repeating units suppressed liquid crystallinity and induced only crystalline polymers.



172

Further elaboration of the properties of main chain hydrogen-bonded liquid crystalline polymers [157] was obtained by the introduction of lateral substituents on the aromatic rings of the dicarboxylic acid components as a method of achieving lower temperature liquid crystals by reducing the tendency to crystallize with disruption of the lattice packing. The monomers employed for this study, **173–177**, are shown below.



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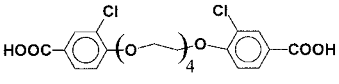

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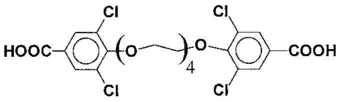

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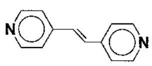

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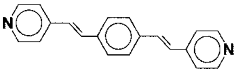
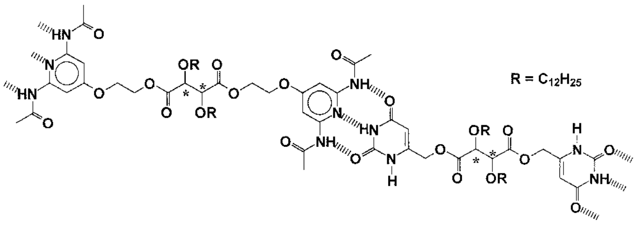


177

Main chain hydrogen-bonded polymers were also prepared from bifunctional components through multiple hydrogen-bonding interactions. Specifically, uracil (U) and 2,6-diacylaminopyridine (P) derivatives were introduced into tartaric acid (T) and the compounds were then allowed to interact [158] forming triply-hydrogen-bonded supramolecular polymers, **178**. Due to the presence of the chiral centres in tartaric acid, it was also possible to study the effect of chirality on the material properties.



178

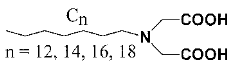
The components LP_2, LU_2, DP_2, MP_2 and MU_2 were prepared from L(+), D(−) and meso(M) tartaric acid and associated through their heterocyclic moieties. In fact, 1 : 1 mixtures of the complementary pairs ($\mathrm{LP}_2 + \mathrm{LU}_2$) and ($\mathrm{MP}_2 + \mathrm{MU}_2$) gave compounds with different properties from their components both in the bulk and in solution, as established by NMR and circular dichroism. The thermal transitions of the pure compounds and of their 1 : 1 mixtures were studied by DSC and POM. The pure compounds showed solid state polymorphic behaviour, whereas the 1 : 1 mixtures exhibited liquid crystalline behaviour from below room temperature to above 200°C. The optical textures were different for LL and MM mixtures, as shown for the mixtures ($\mathrm{LU}_2 + \mathrm{LP}_2$) and ($\mathrm{MU}_2 + \mathrm{MP}_2$). The X-ray patterns the of LL, DL and MM mixtures showed the formation of hexagonal columnar phases [159].

Following the preceding rather extensive discussion on monomeric and polymeric supramolecular liquid crystals resulting from the interaction of pyridyl and carboxyl groups, a modellization [160] of the above systems has been proposed and may now be briefly mentioned. The mesogenic complexes are characterized as ‘living systems’ since their bonding properties are determined by non-covalent interactions; and due to the weak hydrogen-bonding interactions involved, the complexes form, separate and recombine at the melt temperature. In the models presented for a ‘living’ low molecular mass nematic and a ‘living’ liquid crystalline polymer, nematic effects are considered to induce hydrogen bonding between the components, resulting in discontinuous jumps in the concentration variables at the nematic–isotropic transition. Within this context the recent article by Ciferri [161] sets the framework for the formation of supramolecular liquid crystalline polymers, distinguishing between the closed type with binding sites internally compensated and the open type characterized by units with binding sites exposed to the surface and thus capable of extended growth. In the latter case a cooperative enhancement of growth occurs simultaneously with the formation of the ordered phase. The theoretical basis for the growth coupled to orientation mechanism, used to explain the formation of linear micelle aggregates, may apply to most types of supramolecular polymerization.

8. Liquid crystals formed by combined hydrogen bonding and ionic interactions

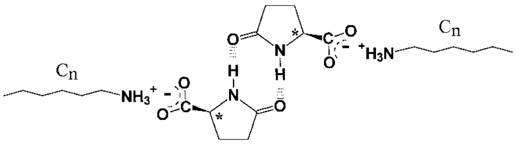
The formation of liquid crystals can also be induced by a two-level process, i.e. by combining hydrogen bonding with ionic interactions. Ionic interactions can either strengthen the rather weak hydrogen bonds or act independently of the hydrogen bonding; in both cases however, they can contribute to the formation of liquid crystalline materials. Examples of both types of complex formation will be cited.

The smectic liquid crystalline character of long chain iminodiacetic acids [162, 163], **179**, results from their dimerization induced by hydrogen bonding and ionic interactions. The zwitterionic character [164] of the iminodiacetic acids, as well as the presence in the molecules of proton donor and acceptor groups leading to the formation of a multiple hydrogen bonding system, result in the formation of a lamellar structure in conjunction with long alkyl chains. It should be noted, that in the crystalline state the hydroxy group does not act as an acceptor, since carbonyl and carboxyl groups are better acceptors than hydroxy groups [164]. The Bragg *d*-spacings [163] were found to be shorter than the length of the complex as determined by molecular modelling. One may therefore assume that either there is an overlapping of the aliphatic chains or that the molecules are tilted within the layers.



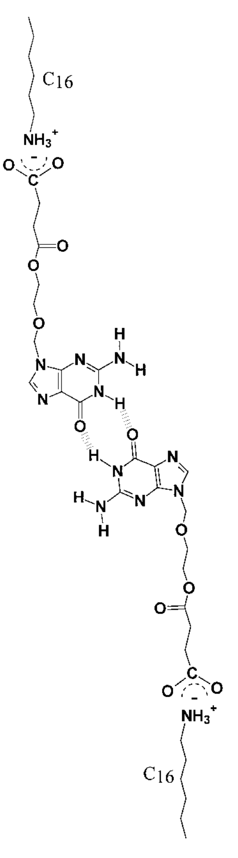
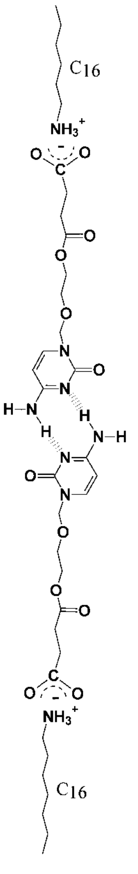
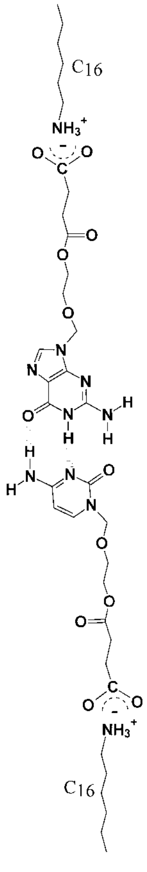
179

An example of liquid crystalline complexes for which hydrogen bonding and ionic forces act independently, involves the formation of pyroglutamate amphiphilic salts [165]. Specifically, when pyroglutamic acid was neutralized by long chain aliphatic amines, self-dimerization occurred, affording the compounds **180** which exhibited smectic A phases. Thus, the smectic liquid crystalline character of the *n*-alkylammonium pyroglutamates was attributed to combined salt formation and dimerization of the pyroglutamate moiety through hydrogen bonding. The head groups were arranged in double layers for the *n*-alkylammonium pyroglutamates, while the molecules of the di-*n*-alkylammonium derivatives formed single layers.



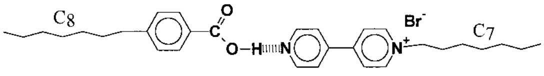
180

Another recent example along these lines is the preparation [166] of liquid crystals originating from self- or hetero-dimerization of *n*-hexadecylammonium salts of certain carboxylic guanine and cytosine derivatives. Specifically, these guanine and cytosine derivatives form, in a first stage, alkylammonium salts, G and C, which self-dimerize affording **181** and **182**. By mixing the complementary salts, a G-C heterodimer, **183**, was obtained. Smectic A mesophases were obtained for both the self-associating alkylammonium salts, as well as for their hetero-associating complex.

181 **182** **183**

Furthermore, by interacting 1-heptyl-4-(4-pyridyl)-pyridinium bromide with various acids, complexes such as **184** and **185** were obtained [167, 168] which, in certain cases, exhibited smectic A phases. The maximum phase stability in the liquid crystalline phase was at a composition differing significantly from the expected 1 : 1 molar ratio of the interacting components; the layer thickness as measured by XRD was smaller than that determined from molecular modelling. The ionic Coulomb forces do not interfere directly with the hydrogen-bonding interactions and according to preliminary experiments, a particular packing behaviour of the components in the smectic A layers has been indicated.



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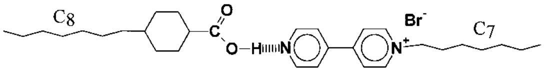
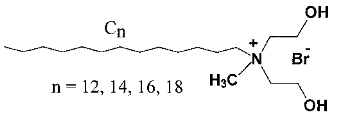


185

In a series of *N*,*N*-di(2-hydroxyethyl)-*N*-methyl-*N*-alkylammonium bromides, **186** (*n* = 12, 14, 16, 18), ionic and hydrogen bonding interactions act simultaneously [169] leading to the formation of supramolecular structures which exhibit liquid crystalline phases. Two smectic phases were identified, an ordered smectic T and a disordered smectic A. Both phases resulted from an alternate periodic stacking of polar sublayers of the ionic head groups and the lipophilic sublayers of the long alkyl chains in a disordered conformation. The smectic T phase has a two dimensional tetragonal symmetry and was for the first time observed and thoroughly characterized by Skoulios *et al.* [170] for dialkyl-dimethylammonium bromides. In the later work [169], dealing with compounds **186**, the presence of the two hydroxyethyl groups at the quaternary centre is decisive for the formation of the ordered smectic T phase. The exhibition of this phase is clearly attributed here to a hydrogen-bonded network that it is formed inside the polar sublayers between the hydroxy groups themselves and also between the hydroxy groups and the bromide anions. This network appears to fit perfectly the tetragonal arrangement [169] of the ionic quaternary ammonium groups. For this reason it should also be noted that in the smectic T phase, the ionic head groups were arranged inside the polar sublayers in a particularly dense fashion [169], figure 16. However, in the smectic A phase the ionic head groups are arranged in a disordered fashion with a normal packing density.



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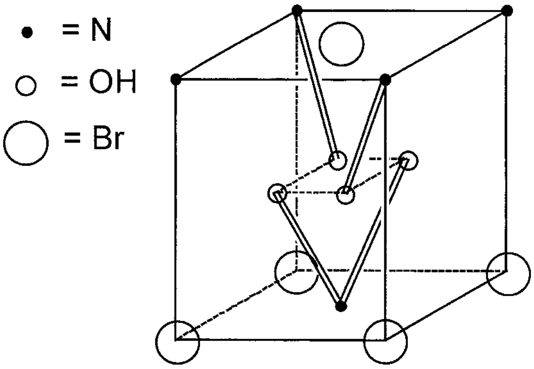

Figure 16. Arrangement of the ionic species and hydroxyethyl substituents (double lines) in the polar sublayer of the smectic T phase contained in one tetragonal unit cell [169]. Reprinted with permission from Arkas, M., Tsiourvas, D., Paleos, C. M., and Skoulios, A., *Chem. Eur. J.*, 1999, **5**, 3202.

9. Summary and concluding remarks

Molecular recognition of complementary molecules through hydrogen bonding constitutes an effective and facile method for the preparation of supramolecular thermotropic liquid crystalline materials. A diversity of hydrogen-bonded complexes resulting from the interaction of either mesomorphic or non-mesomorphic components has been prepared and these are discussed in this review. Following the first examples of hydrogen-bonded liquid crystals formed primarily by a single hydrogen-bonding interaction between carboxyl and pyridyl moieties, research activity has been extended to the preparation and characterization of other types of liquid crystal system as discussed in the foregoing chapters.

The central theme of hydrogen-bonded liquid crystals is the development of new complementary components or the use of existing ones for the formation of supramolecular complexes, which are then characterized as far as their liquid crystalline properties are concerned. In parallel, some investigations have been conducted concerning the theoretical aspects and practical applications of hydrogen-bonded liquid crystals. Thus, a mean-field theory of liquid crystalline ordering for hydrogen-bonded liquid crystals was proposed by Veytsman [171, 172], according to which, hydrogen bonds with a proper geometry enhance nematic ordering. The behaviour of the system proves to be completely different when the molecules form dimers or hydrogen-bonded polymers. In the latter case the molecules tend to form a completely ordered phase at low temperatures. The number of hydrogen bonds in the ordered phase and the isotropic melt is different. Another theory for hydrogen-bonded nematic liquid crystals, proposed by Jackson *et al.* [173, 174], also reached similar conclusions. It was shown that hydrogen bonding enhances the stability of the nematic phase and that the orientational ordering in the nematic phase enhances the hydrogen bonding. In addition, significant hydrogen bonding is indicated in the nematic phase at temperatures too high for hydrogen bonding to exist if the phase were isotropic.

In the area of applications of hydrogen-bonded liquid crystals in electro-optic devices, both smectogenic and nematogenic complexes have been employed. Thus, room temperature hydrogen-bonded liquid crystals derived from 4-alkoxybenzoic acid derivatives and alkyl pyridines align in twisted nematic cells and show electro-optic effects [27]. This observation suggests that hydrogen bonds are stable in electric fields. The induction of chiral smectic C phases and ferroelectric properties [40–43, 130, 175, 176] has also been observed for complexes prepared from chiral components. Furthermore, mixtures of hydrogen-bonded complexes with conventional liquid crystal materials were prepared [177], leading to various types of mesomorphic behaviour.

The requirement for stability, leading to even further diversification of hydrogen-bonded complexes, can be fullfilled by the choice of appropriate components. The interacting molecules, in addition to having a proper geometry and meeting the requirement of complementarity, may have to share the property of cooperativity [177] or secondary electrostatic interactions as set forth by Jorgensen *et al.* [179, 180]. According to a model proposed by the same authors, the most favourable case in relation to the stability of the supramolecular structure of the complexes is when all or at least most of the donor groups are located on one of the interacting molecules, while the acceptors are on the other. Work should certainly be addressed along these lines for the preparation of novel complementary components. Stabilization coupled with diversification of hydrogen-bonded complexes has also been achieved by combined ionic and hydrogen-bonding interactions. The first examples of this type of complex have already appeared in the literature and were included in the last chapter of this review. In this context, mention should be made of a report by Müllen *et al.* [181] on the use of combined hydrogen bonding and van der Waals interactions for the preparation of complexes.

The development of new complexes, with broad and stabilized mesophases will be a major objective of future work. We believe that the attempted categorization of hydrogen-bonded liquid crystals together with the examples discussed in this review will help newcomers to the field to undertake their own work in this exciting area of research.

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