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Mesophases induced by hydrogen bonds between non-mesogens

A di-proton acceptor and proton donors

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A non-mesogen, consisting of two stilbazole moieties as proton accepting end groups linked by a triethylene glycol unit, was synthesized. Monotropic smectic B phases were observed for mixtures with nonanoic acid up to tetradecanoic acid as proton donors. Enantiotropic nematic and, in some cases, monotropic smectic A phases were observed with 4-methyl-, 4-methoxy- and 4-halo-benzoic acids as proton donors. The stability of the induced mesophases decreased with 3- and 2-substituted benzoic acids. No mesophase was observed with aliphatic dicarboxylic acids as donors. The results are explained on the basis of the nature and molecular interactions involving the constituent molecules.

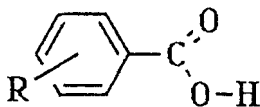
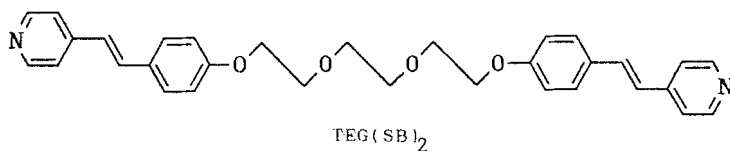
1. Introduction

The existence of mesophases due to the formation of the hydrogen bond is well-known in the cases of alkyl- and alkoxy-benzoic acids [1]. More recently, a biaxial nematic phase was observed for a trisubstituted cinnamic acid [2]. It is believed that the carboxyl groups are symmetrically linked by two hydrogen bonds in the mesophases of these mesogens.

The formation of mesophases due to hydrogen bonds, between dissimilar molecules is relatively rare. Kato, Fréché and their co-workers reported several studies in which the mesophase temperature range was enhanced or new mesophases were induced for mesogen-mesogen or mesogen-non-mesogen mixtures [3]. Brienne *et al.* also observed the formation of a mesophase due to hydrogen bonds between two different non-mesogens [4].

It has also been reported previously that mesophases were induced by the formation of hydrogen bonds between derivatives of benzoic acid (proton donors) and 4-methoxy-4'-stilbazole (proton acceptor) [5]. All the proton donors and acceptors were non-mesogenic and monofunctional in this case. We present here a new molecule, consisting of two stilbazole moieties as proton accepting end groups linked by a triethylene glycol unit, TEG(SB)₂, i.e. a non-mesogen capable of accepting two protons at the same time. Non-mesogenic proton donors employed were fatty acids, open chain aliphatic dicarboxylic acids and structural isomers of substituted benzoic acids. Nematic and smectic phases were induced depending upon the nature and geometric structures of the proton donors.

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R: H, CH₃, OCH₃, F, Cl, Br, I
 Symbol: BA, MBA, MOBA, FBA, CIBA, BrBA, IBA

2. Experimental

2.1. 1,2-Bis[2-(4-bromophenoxy)ethoxy]ethane

A mixture of 1,2-bis(2-chloroethoxy)ethane (Fluka) and two equivalent amounts of 4-bromophenol (Fluka), potassium carbonate and DMF was refluxed for 24 h. The crude product obtained after extraction with ether was recrystallized from *n*-hexane several times. The purified product had mp 67–70°C; Calculated for C₁₈H₂₀O₄Br₂, C: 46.9 per cent, H: 4.35 per cent. Found C: 47.04 per cent, H: 4.50 per cent; the proton NMR spectrum was consistent with the desired structure.

2.2. 1,2-Bis(2-{4-[2-(4-pyridyl)ethenyl]phenoxy}ethoxy)ethane

The procedure of the synthesis and purification of this di-proton acceptor followed those of [6, 7]. The di-stilbazolyl derivative of triethylene glycol (TEG(SB)₂) is a non-mesogen, mp 126–127°C; Calculated for C₃₂H₃₂O₄N₂ + $\frac{1}{2}$ H₂O C: 74.27 per cent, H: 6.38 per cent, N: 5.42 per cent. Found, C: 74.52 per cent, H: 6.38 per cent, N: 5.42 per cent, the proton NMR spectrum was consistent with the required structure.

Mixtures with appropriate molar ratios of proton donor and TEG(SB)₂ were obtained by weighting the components and melting to form a homogeneous isotropic phase. Mesophase textures were characterized using polarizing optical microscopy (Nikon, OPTIPHOT-POL) in conjunction with a heating stage (Mettler FP 80–82). The transition temperatures were checked, and enthalpies of the phase transitions were obtained, by a differential scanning calorimetry (Perkin–Elmer DSC 2).

3. Results and discussion

The textures of the monotropic smectic B phases, as shown in figure 1, were similar to those of 4-alkoxy-4'-stilbazoles [7], and were observed for the mixtures of the di-proton acceptor with higher homologues of the fatty acids, i.e. from nonanoic to tetradecanoic acids. No mesophase was observed for the mixtures with lower homologues. The monotropic isotropic to smectic B and the smectic B to crystal transition temperatures are listed in table 1. In general, the I–S_B and S_B–C transition temperatures decreased slightly on descending the series, and the S_B textures of mixtures with undecanoic, decanoic and nonanoic acids persisted for hours at room temperature.

It is noted here that no mesophase was observed for mixtures with open chain dicarboxylic acids as proton donors.



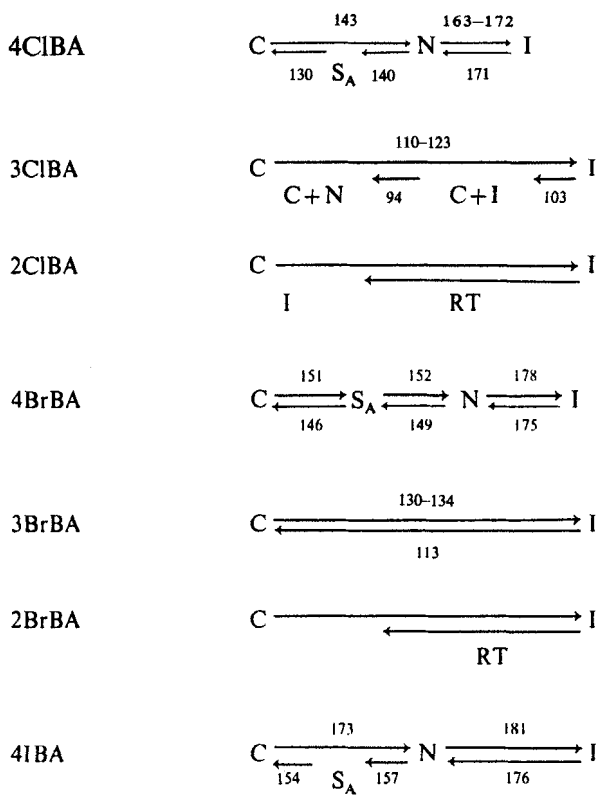
Figure 1. The texture of the smectic B phase, 56°C, obtained from the isotropic phase by cooling for the mixture of decanoic acid/TEG(SB)₂, with molar ratio 2:1.

Table 1. The induced monotropic mesophases and the corresponding transition temperatures (°C) for mixtures of fatty acids (C_nH_{2n}O₂) with the di-proton acceptor, TEG(SB)₂.

<i>n</i>	Phase behaviour
14	$ \begin{array}{c} \xrightarrow{80-85.4} \\ \text{C} \xrightarrow{\hspace{1.5cm}} \text{I} \\ \xleftarrow{64} \quad \text{S}_B \quad \xleftarrow{82.7} \end{array} $
13	$ \begin{array}{c} \xrightarrow{84} \\ \text{C} \xrightarrow{\hspace{1.5cm}} \text{I} \\ \xleftarrow{53} \quad \text{S}_B \quad \xleftarrow{81.7} \end{array} $
12	$ \begin{array}{c} \xrightarrow{82.2} \\ \text{C} \xrightarrow{\hspace{1.5cm}} \text{I} \\ \xleftarrow{46} \quad \text{S}_B \quad \xleftarrow{81.1} \end{array} $
11	$ \begin{array}{c} \xrightarrow{80} \\ \text{C} \xrightarrow{\hspace{1.5cm}} \text{I} \\ \xleftarrow{<RT} \quad \text{S}_B \quad \xleftarrow{78.2} \end{array} $
10	$ \begin{array}{c} \xrightarrow{76.2} \\ \text{C} \xrightarrow{\hspace{1.5cm}} \text{I} \\ \xleftarrow{<RT} \quad \text{S}_B \quad \xleftarrow{74} \end{array} $
9	$ \begin{array}{c} \xrightarrow{75} \\ \text{C} \xrightarrow{\hspace{1.5cm}} \text{I} \\ \xleftarrow{<RT} \quad \text{S}_B \quad \xleftarrow{74.1} \end{array} $

Table 2. The induced mesophases and the corresponding transition temperatures for mixtures consisting of the di-proton acceptor, TEG(SB)₂, and structural isomers of benzoic acid derivatives.

Donors	Phase behaviour
BA	$ \begin{array}{c} \text{C} \xrightarrow{124} \text{I} \\ \text{C+S}_A \xleftarrow{98} \quad \text{N} \xleftarrow{115} \end{array} $
4MOBA	$ \begin{array}{c} \text{C} \xrightarrow{133} \text{N} \xrightarrow{175} \text{I} \\ \xleftarrow{120} \quad \xleftarrow{174} \end{array} $
3MOBA	$ \text{C} \xrightleftharpoons{106-110} \text{I} $
2MOBA	$ \text{C} \xrightleftharpoons{\quad} \text{I} $
4MBA	$ \begin{array}{c} \text{C} \xrightarrow{129} \text{N} \xrightarrow{160} \text{I} \\ \xleftarrow{117} \quad \xleftarrow{155} \end{array} $
3MBA	$ \begin{array}{c} \text{C} \xrightarrow{100} \text{I} \\ \xleftarrow{66} \text{S}_A \xleftarrow{70.5} \text{N} \xleftarrow{85} \end{array} $
2MBA	$ \begin{array}{c} \text{C} \xrightarrow{80-105} \text{I} \\ \xleftarrow{65} \quad \text{N} \xleftarrow{73.5} \end{array} $
4FBA	$ \begin{array}{c} \text{C} \xrightarrow{140} \text{N} \xrightarrow{155} \text{I} \\ \xleftarrow{107} \quad \xleftarrow{150} \end{array} $
3FBA	$ \begin{array}{c} \text{C} \xrightarrow{120-133} \text{I} \\ \xleftarrow{110} \quad \text{N} \xleftarrow{115} \end{array} $
2FBA	$ \begin{array}{c} \text{C} \xrightarrow{110-117} \text{I} \\ \xleftarrow{96} \quad \text{N} \xleftarrow{98} \end{array} $



The induced mesophases and the corresponding transition temperatures for mixtures with benzoic acid derivatives as proton donors are listed in table 2. Those mixtures containing simply benzoic acid as proton donor exhibited monotropic nematic and smectic A phases, and crystalline phases. All mixtures consisting of 4-halo-, 4-methyl- and 4-methoxy-benzoic acids exhibited enantiotropic nematic phases. Monotropic smectic A (focal-conic texture on cooling from the nematic phase at 5°C min^{-1}) phases were observed for the mixtures with chloro, bromo and iodobenzoic acids. An example is shown in figure 2. However, with faster cooling rates ($>30^\circ\text{C min}^{-1}$), all the mixtures with 4-substituted benzoic acids exhibited I-N-S_A (focal-conic texture, followed by crystallization) transitions.

For the cases with 3- and 2-substituted benzoic acids, only the methyl- and fluoro-benzoic acids were observed to give monotropic nematic phases (cooling rate 5°C min^{-1}). However, nematic textures, followed by crystallization, were observed with faster cooling rates ($>30^\circ\text{C min}^{-1}$) for all the mixtures studied here, except for 2-methoxybenzoic acid. For the mixture consisting of 2-methoxybenzoic acid a direct I-C transition occurred.

These observations agree with the fact that the fluoro and methyl groups are the smallest among the substituents studied here. Hence the steric hindrance imposed by these substituents located in a lateral 3- or 2-position is not great enough to destroy completely the orientational order. Therefore, among the mixtures consisting of 3- and 2-substituted benzoic acids only with the fluoro- and methyl- benzoic acids form mesophases. Thus, the mixture with 2-methoxybenzoic acid did not show any mesophase.

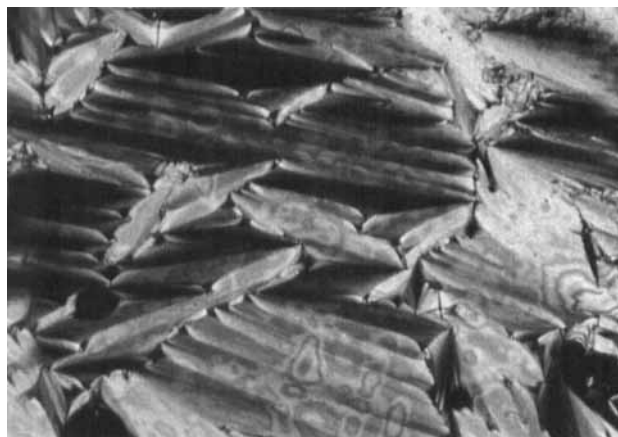


Figure 2. The focal conic texture of the smectic A phase, 136°C, obtained from the nematic phase by cooling, for the mixture of 4-chlorobenzoic acid/TEG(SB)₂, with molar ratio 2:1.

The occurrence of monotropic mesophases in these and other mixtures when faster cooling rates are used is a well established behaviour.

For the mixtures consisting of fatty acids, the occurrence of the smectic B phase, a more highly ordered smectic phase, instead of the nematic or smectic A phase, is understandable on the basis of the nature of the component molecules and the molecular interactions. The polarizability of the alkyl chain of a fatty acid is much less than that of the aromatic ring of benzoic acid. Therefore, for the mixtures consisting of fatty acids as proton donors, the hydrogen bonding interactions would be contributed to mainly by the highly conjugated π -systems, i.e. the stilbazole moieties. This situation resembles that for the 4-alkoxy-4'-stilbazoles, for which only highly ordered smectic phases (S_B) were observed [7]. The enthalpy values for the transitions for both cases are comparable. A value of 22.9 J g⁻¹ (or 22.1 kJ mol⁻¹ of mixture) was obtained from tetradecanoic acid/TEG(SB)₂, and 39.6 J g⁻¹ for pure 4-octoxy-4'-stilbazole. For those cases where the proton donor possesses more polarizable moieties, for example benzoic acid derivatives, the interactions for all the ring-containing components will be equally important. Considering these interactions, the bulkier geometric factors, and the dipole moments of the component molecules, nematic and smectic A phases seem the more probable to be observed. The enthalpy values measured for the I-N transitions for the 4-methoxybenzoic acid/TEG(SB)₂ and 4-fluorobenzoic acid/TEG(SB)₂ mixtures were 6.86 J g⁻¹ (or 5.54 kJ mol⁻¹ of mixture) and 3.4 J g⁻¹ (or 2.68 kJ mol⁻¹ of mixture), respectively. These values are of the same order as those obtained previously for mixtures of benzoic acid derivatives and 4-methoxy-4'-stilbazole [5].

In summary, the results presented here demonstrate that hydrogen bonds can be considered as useful for the design of new mesogens. The dependence of stability of the mesophase obtained upon the geometries of the interacting molecules appears similar to that for known thermotropic liquid crystal materials. The di-proton acceptor presented here is an example of a valuable monomer for the formation of polymeric liquid crystals. Although the straight chain dicarboxylic acids did not result in mesophase formation suitable di-proton donors could be employed for this purpose. We are currently working towards this objective.

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