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Hydrogen bond-induced ferroelectric liquid crystals

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Hydrogen bond-induced ferroelectric liquid crystals

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Hydrogen-bonded dimers of 4-alkoxy-4′-stilbazole homologues (C_nOSB, proton acceptors) and the mono-(2-methylbutyl)ester of terephthalic acid (MBTA, proton donor) behaved like conventional thermotropic mesogens. For chiral MBTA mixtures, chiral nematic and blue phases were observed with $n=1$ and 2, and chiral smectic C phases were observed with $n \geqslant 5$. Achiral phases were observed for mixtures with racemic MBTA as proton donor. Transition temperatures and enthalpies are similar for the chiral and achiral systems.

1. Introduction

Ferroelectric liquid crystal materials have attracted a great deal of attention because of their application in liquid crystal displays. To achieve ferroelectric properties, a chiral entity must be incorporated in a biaxial smectic phase [1]. The chiral moiety can be either a non-mesogenic dopant or a mesogen [2]. In either case, synthetic procedures have to be employed to incorporate the chiral unit covalently in an appropriate molecule.

On the other hand, the existence of thermotropic mesophases stemming from hydrogen bond formation, i.e. non-covalent molecular association, is well-known in the case of 4-alkyl- and 4-alkoxy-benzoic acids, and more recently, a biaxial thermotropic nematic phase has been observed for a trisubstituted cinnamic acid [3]. It is believed that in these cases, the carboxyl groups are symmetrically linked by two hydrogen bonds, and the associated dimers are considered as a single component [4]. The formation of mesophases due to hydrogen bonds between dissimilar molecules is relatively rare, and hydrogen bonds are seldom employed as a direct means of designing new mesogens. Kato, Fréchet and co-workers have however, reported several studies in which mesophase temperature range was increased or new mesophases were induced for mesogen–mesogen or mesogen–non-mesogen mixtures by the formation of hydrogen bonds [5]. Also Brienne *et al.* have observed the formation of mesophases due to hydrogen bonds between two different non-mesogens [6].

It has also been shown that hydrogen bonds were formed and mesophases observed for mixtures of benzoic acid derivatives (proton donors) and 4-methoxy-4′-stilbazole (proton acceptor) [7]. All the proton donors and acceptor were non-mesogens.

In the present study, a non-mesogenic chiral proton donor, i.e. the mono-(2-methylbutyl) ester of terephthalic acid (MBTA), was synthesized and mixed with 4-alkoxy-4′-stilbazoles (C_nOSB, smectic B mesogens) in a 1 : 1 molar ratio. Blue phases, chiral nematic (N^*) and chiral smectic C (S_C^*) phases were observed for the mixtures depending upon the alkoxy chain length. The corresponding achiral phases were observed when racemic MBTA was employed.

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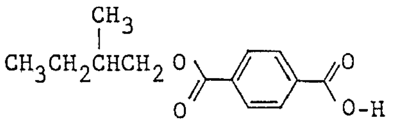
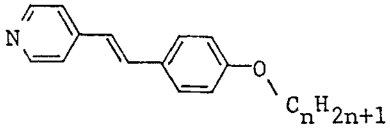


MBTA



C_nOSB

2. Experimental

The homologous series of C_nOSB ($n=1$ to 10, 12, 14 and 16) was synthesized according to [8, 9]. The racemic and optically active proton donors (IMBTA and AMBTA, respectively) were obtained by stirring a mixture of the corresponding 2-methyl-1-butanol (both from Fluka) and an excess of terephthaloyl chloride (Fluka) in dry pyridine at room temperature. Elemental analysis for ($C_{13}H_{16}O_4$): Calculated C: 66·10 per cent, H: 6·78 per cent. Found: IMBTA, C: 66·10 per cent, H: 6·88 per cent; AMBTA, C: 66·17 per cent, H: 6·92 per cent. The melting points were 157–159°C for IMBTA and 156–158°C for AMBTA. The proton NMR spectra agreed well with the required structures.

The mixtures of a 1 : 1 molar ratio of proton donor and C_nOSB were obtained by weighing and melting to form the homogeneous isotropic phase. The textures of the mesophases were characterized by polarizing optical microscopy (Nikon, OPTIPHOT-POL) in conjunction with a heating stage (Mettler, FP 80–82). Differential scanning calorimetry (Perkin–Elmer, DSC 2) was used for the measurement of the temperatures and enthalpies of the phase transitions. The proton NMR spectra were recorded with a Bruker WP100SY FTNMR spectrometer and vibrational spectra with a BIO-RAD FTS-40 FTIR spectrometer.

3. Results and discussion

All the results of the elemental analyses of the C_nOSB homologues were, for both individual elements (C, H, N) and total content, within 0·2 per cent of the calculated values. TLC showed that the materials gave a single spot with acetone/hexane as eluent. Only *trans*-isomers were observed by proton NMR (in $CDCl_3$) and FTIR (in KBr pellets) spectroscopy. The first four members of the series, $n=1$ to 4, are non-mesogens. Enantiotropic smectic B (S_B) phases were observed when $n=5$–10 and 12. A direct I–C transition was observed for $C_{14}OSB$ and $C_{16}OSB$ using a cooling rate of 5°C min^{-1}. However, a monotropic S_B texture, along with crystals, was observed upon quench cooling.

For the mixtures of AMBTA and the C_nOSB homologues all the phases are enantiotropic; the transition temperatures are listed in table 1. These results are also shown in figure 1. As can be seen from figure 1, the transition temperature of the mesophase to isotropic phase changes exhibit an even-odd effect, pronounced for the mixtures consisting of lower C_nOSB homologues, and damping out for mixtures with higher homologues. The crystal–mesophase transition temperatures decrease on ascending the series. Such behaviour is typical for pure, conventional thermotropic mesogenic homologues.

The mixture of C_1OSB exhibits smectic A (S_A), chiral nematic and blue phases. The platelet textures of the blue phases (see figure 2) existing between the N* and I phases,

Table 1. The phases and transition temperatures (°C) and enthalpies (kJ mol^{-1}) in parentheses for the mixtures of chiral terephthalic acid mono(2-methylbutyl) ester and 4-alkoxy-4′-stilbazole homologues (C_nOSB) in a 1:1 molar ratio.

n	Phase behaviour
1†	$C \xrightarrow[(32\cdot5)]{104} S_A \xrightarrow[(1\cdot3)]{120\cdot5} N^* \xrightarrow[(1\cdot1)]{138\cdot5} I$
2†	$C \xrightarrow[(24\cdot3)]{112\cdot5} S_A \xrightarrow[(2\cdot0)]{143} N^* \xrightarrow[(1\cdot3)]{149\cdot5} I$
3†	$C \xrightarrow[(23\cdot9)]{112} S_A \xrightarrow[(5\cdot6)]{143} I$
4	$C \xrightarrow[(22\cdot4)]{106\cdot5} S_A \xrightarrow[(6\cdot3)]{151} I$
5	$C \xrightarrow[(19\cdot5)]{93} S_C^* \xrightarrow[(0\cdot2)]{100} S_A \xrightarrow[(6\cdot2)]{150} I$
6	$C \xrightarrow[(18\cdot7)]{94\cdot5} S_C^* \xrightarrow[(0\cdot2)]{111\cdot5} S_A \xrightarrow[(8\cdot3)]{153} I$
7	$C \xrightarrow[(22\cdot8)]{101} S_C^* \xrightarrow[(0\cdot2)]{118} S_A \xrightarrow[(8\cdot2)]{152} I$
8	$C \xrightarrow[(20\cdot4)]{99\cdot5} S_C^* \xrightarrow[(0\cdot2)]{125} S_A \xrightarrow[(8\cdot8)]{154} I$
9	$C \xrightarrow[(23\cdot6)]{101} S_C^* \xrightarrow[(0\cdot3)]{127} S_A \xrightarrow[(9\cdot5)]{152} I$
10	$C \xrightarrow[(24\cdot5)]{98} S_C^* \xrightarrow[(0\cdot3)]{129} S_A \xrightarrow[(9\cdot5)]{151\cdot7} I$
12	$C \xrightarrow[(20\cdot2)]{83} S_C^* \xrightarrow[(0\cdot4)]{130} S_A \xrightarrow[(10\cdot2)]{149\cdot5} I$
14	$C \xrightarrow[(28\cdot0)]{78} S_C^* \xrightarrow[(0\cdot2)]{130} S_A \xrightarrow[(10\cdot0)]{148} I$
16	$C \xrightarrow[(40\cdot6)]{84} S_C^* \xrightarrow[(0\cdot2)]{130} S_A \xrightarrow[(8\cdot9)]{145\cdot5} I$

† Blue phases were observed (see text).

are typical of those for BPI and BPII phases reported by Stegemeyer *et al.* [10]. The blue fog phase was also observed for this mixture. However, the temperature ranges of these blue phases have not yet been determined, partly due to the photochemistry of the protonated C_nOSB [11], and partly due to experimental factors concerned with the DSC.

The mixture of C_2OSB exhibited similar phases, but with wider S_A and narrower N* temperature ranges. The blue phases of this mixture appeared over a very narrow temperature range. The mixture of C_3OSB exhibited a S_A phase which, upon heating, transformed to the N* phase and the I phase at the same time. Phase transitions were reversible upon cooling. No blue phase was observed. Apparently, the N* and blue phases merge into S_A around C_3OSB, since only an S_A phase was observed for the C_4OSB mixture. For mixtures containing C_5OSB and higher members, chiral smectic C and smectic A phases were observed. The temperature range became wider for the former and narrower for the latter phases on ascending the series. Such behaviour is consistent with that for conventional homologous series of thermotropic mesogens.

The enthalpy values for the corresponding phase transitions are also listed in table 1. The values for S_A–N* and N*–I are of the order of 1–2 kJ mol^{-1} of mixture. These

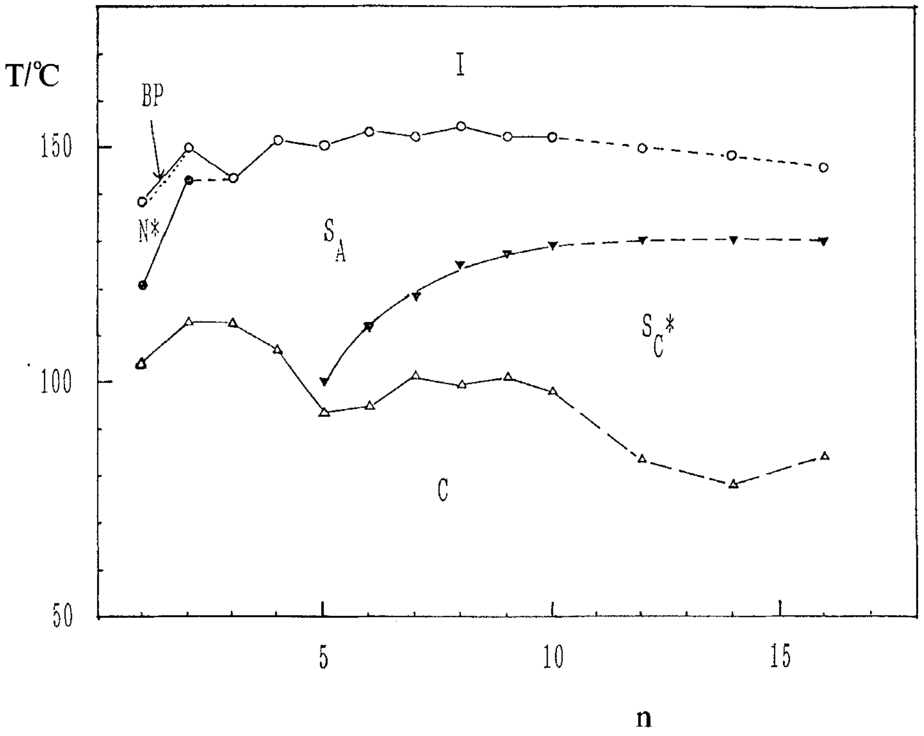


Figure 1. The mesophases observed for the mixtures consisting of chiral terephthalic acid mono-(2-methylbutyl)ester (proton donor) and 4-alkoxy-4′-stilbazole homologues (C_nOSB, proton acceptors) in a 1 : 1 molar ratio.

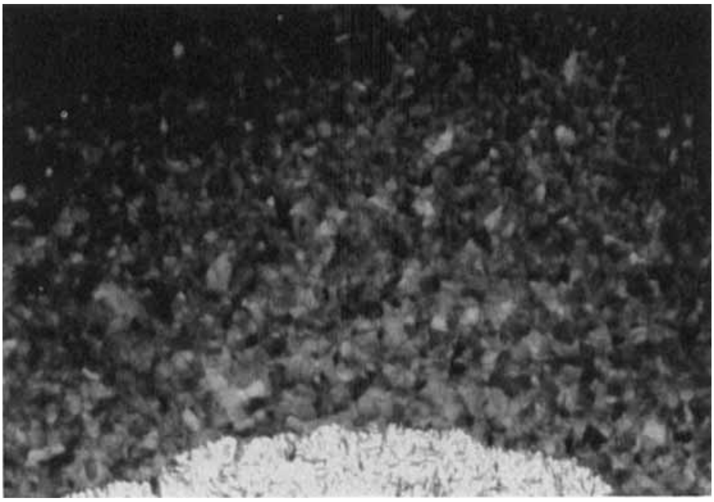
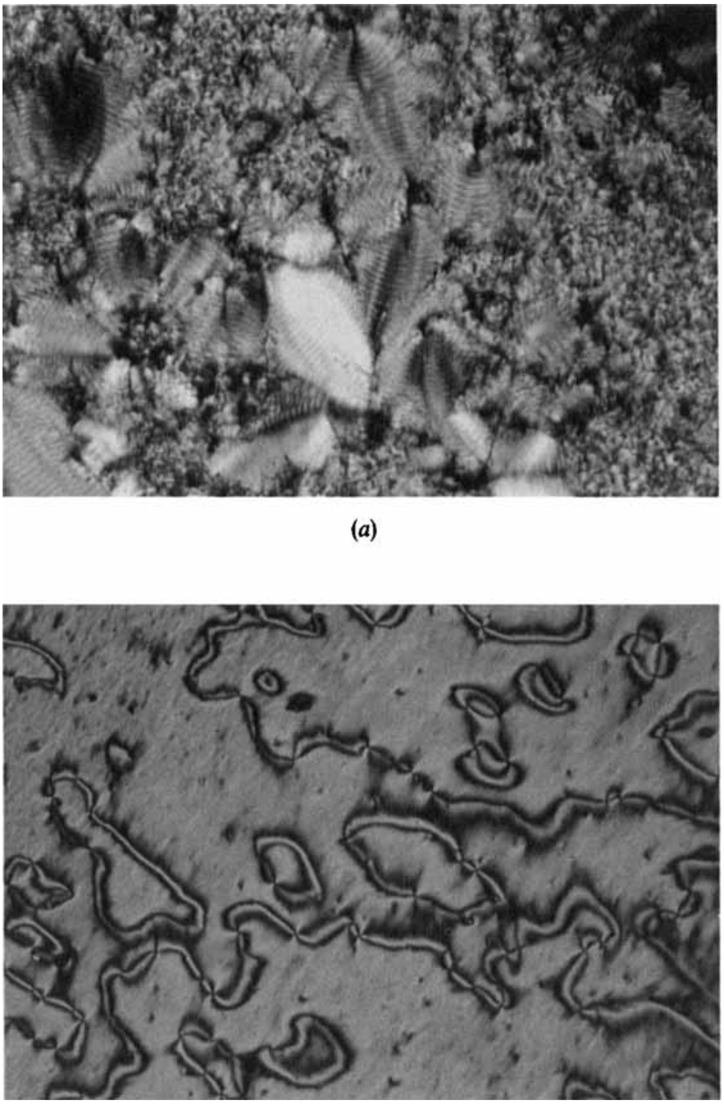


Figure 2. The platelet appearance of the blue phases observed for the mixture of chiral terephthalic acid mono-(2-methylbutyl) ester and 4-methoxy-4′-stilbazole in a 1 : 1 molar ratio at ~137°C.



(*a*)

(*b*)

Figure 3. (*a*) The fingerprint texture of the chiral smectic C phase observed for the mixture of chiral terephthalic acid mono-(2-methylbutyl) ester and 4-octoxy-4′-stilbazole in a 1 : 1 molar ratio at 114·6°C. (*b*) The schlieren texture of the smectic C phase for the same achiral mixture.

values are comparable with those reported previously for the N–I transitions of mixtures of benzoic acid derivatives with C_1OSB [7], and with those for conventional thermotropic mesogens. The values for the S_A—I transitions for mixtures of C_3OSB, C_4OSB and C_5OSB are about 6 kJ mol^{-1} of mixture. The corresponding values for mixtures with C_6OSB through to $C_{16}OSB$ are in the range of 8–10 kJ mol^{-1} of mixture. All these values are comparable with those for conventional thermotropic mesogens and slightly less than the enthalpy values of the smectic B to isotropic transitions for pure C_nOSB's (for example, a value of 12·23 kJ mol^{-1} was measured for C_8OSB).

Table 2. The phases and transition temperatures (°C) and enthalpies (kJ mol^{-1}) in parentheses for the mixtures of racemic terephthalic acid mono (2-methylbutyl) ester and 4-alkoxy-4′-stilbazole homologues (C_nOSB) in a 1 : 1 molar ratio.

n	Phase behaviour
1	$C \xrightarrow[(27{\cdot}2)]{104} S_A \xrightarrow[(1{\cdot}1)]{119} N \xrightarrow[(0{\cdot}8)]{138} I$
5	$C \xrightarrow[(14{\cdot}6)]{94} S_C \xrightarrow[(0{\cdot}2)]{100} S_A \xrightarrow[(5{\cdot}3)]{150} I$
8	$C \xrightarrow[(22{\cdot}5)]{99} S_C \xrightarrow[(0{\cdot}2)]{123} S_A \xrightarrow[(8{\cdot}6)]{152{\cdot}5} I$
12	$C \xrightarrow[(19{\cdot}7)]{85} S_C \xrightarrow[(0{\cdot}3)]{128} S_A \xrightarrow[(9{\cdot}0)]{149} I$
16	$C \xrightarrow[(45{\cdot}5)]{86} S_C \xrightarrow[(0{\cdot}3)]{128} S_A \xrightarrow[(9{\cdot}7)]{146} I$

It is known that S_C–S_A or S_C^*–S_A phase transitions may be very weakly first order or, in some cases, second order or nearly so. The enthalpy values for these phase transitions are therefore very small. In agreement with these facts, the corresponding enthalpy values measured for these hydrogen-bonded dimers were in the range of 0·1–0·4 kJ mol^{-1} of mixture.

The S_A phase of the mixtures studied here exhibited spontaneously a pseudoisotropic (or homeotropic) texture, either on cooling or on heating. The S_A–S_C phase transition could therefore be easily identified optically by the formation (or vanishing) of the schlieren texture of the smectic C phase. For the chiral smectic C phase, the existence of finger print textures is a feature for identification. Figure 3 (*a*) shows an example. The helical structure could be unwound by application of an electric field (not shown here), and the periodicity of the texture was related to the helical pitch. Preliminary results showed that the pitch values increased on ascending the series, and were in the range of 5–20 μm. For comparison, the schlieren texture for the mixture IMBTA/C_8OSB is shown in figure 3 (*b*).

The mixtures containing the racemic proton donor exhibited similar phase transitions, except that the chiral phases were replaced by the achiral phases. The phases and the corresponding transition temperatures for some mixtures are listed in table 2. Also listed are the values of the corresponding transition enthalpies. From the values in tables 1 and 2, it is seen that the phases, and the transition temperatures and enthalpies are very similar for the mixtures of both series.

In summary, blue phases, chiral nematic and chiral smectic C phases were obtained by the formation of hydrogen bonds between the chiral mono-(2-methylbutyl)-ester of terephthalic acid and 4-alkoxy-4′-stilbazole homologues. The results presented here demonstrate that the properties of the hydrogen-bonded dimers are comparable to those of conventional thermotropic mesogens. These results indicate that the employment of the hydrogen bond is a most useful molecular design factor for the provision of new mesogens.

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