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Supramolecular ferroelectric liquid crystals. Hydrogen-bonded complexes between benzoic acids and chiral stilbazoles

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Supramolecular ferroelectric liquid crystalline complexes have been obtained from 4-alkoxybenzoic acids and optically active *trans*-4-substituted-4′-stilbazoles. Chiral smectic C phases are induced by the formation of supramolecular mesogenic structure through the selective intermolecular hydrogen bond between the achiral benzoic acids and the chiral non-mesogenic stilbazoles.

1. Introduction

A great effort has been focused on multicomponent systems based upon molecular recognition and self-assembly since this approach offers the way to design and develop a wide variety of materials with desired properties [1]. Hydrogen bonding is one of the principal intermolecular forces to enable the construction of such supramolecular structures. Recently, a number of supramolecular mesogenic materials have been obtained by molecular self-assembly through intermolecular hydrogen bonding [2–14].

The preparation of functional liquid crystalline materials capable of intermolecular hydrogen bonding is suited to the formation of H-bonded supramolecular complexes with ferroelectric properties [11, 12]. Ferroelectric liquid crystals have attracted much attention because of their potential for practical applications [15–17]. Supramolecular self-assembly of polysiloxanes having a side chain benzoic acid and a chiral stilbazole has resulted in the formation of side chain LC polymeric complexes that exhibit the smectic C* phase, while each component exhibits no ferroelectric liquid crystalline phase [11]. Low molecular mass hydrogen-bonded ferroelectric LC complexes have also been obtained by molecular association of a chiral benzoic acid and achiral stilbazoles [12]. These hydrogen-bonded complexes show a stable ferroelectric behaviour in the presence of an electric field. It is noteworthy that ferroelectricity is induced by the molecular self-assembly through intermolecular hydrogen bonds. Hydrogen-bonded liquid crystals are unique because the core is not built by only covalent bonds, and the molecular dynamics might therefore be different from those of normal covalently-bonded liquid crystals.

We report here upon the liquid crystalline and ferroelectric properties of the H-bonded complexes obtained by molecular self-assembly of the 4-alkoxybenzoic acids (*n*OBA) (where *n* is the number of carbon atoms in the alkyl chain) and chiral stilbazoles Me*Sz and MeO*Sz. The liquid crystalline properties of the complexes obtained from the *trans*-4-alkylcyclohexane carboxylic acids (*p*CHCA) (where *p* is the number of carbon atoms in the alkyl chain) and Me*Sz are also reported (see structures below).

2. Experimental

2.1. *Synthesis of chiral stilbazoles*

A mixture of *trans*-4-hydroxy-4′-stilbazole (2·55 g, 12·9 mmol), *S*-(+)-2-methylbutyl 4-toluenesulphonate (3·13 g, 12·9 mmol), (prepared from *S*-(-)-2-methylbutan-

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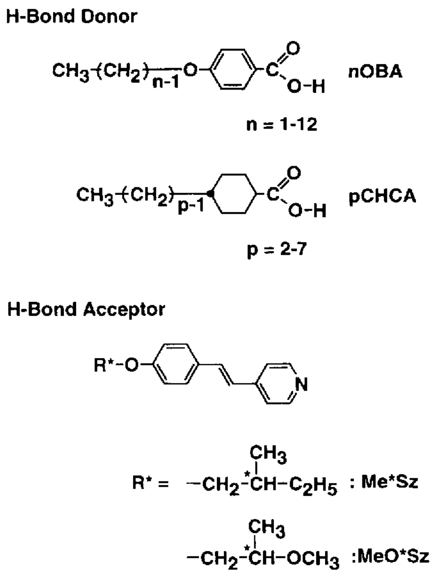


Scheme 1.

1-ol, 4-toluenesulphonylchloride) and caesium carbonate (14·6 g, 14·2 mmol) in 40 ml of DMF was stirred at room temperature for 48 h. The crude product was purified by column chromatography (silica gel, eluent: chloroform/methanol = 30/1) and recrystallized from acetone to yield *S*-(+)-*trans*-4-(2-methylbutoxy)-4′-stilbazole (Me*Sz). Yield 1·48 g (43 per cent). ^{1}H NMR ($CDCl_3$, 27°C, ppm) δ 8·54, (d, 2 aromatic H *ortho* to N, $J=5{\cdot}9$ Hz), 7·47 (d, 2 aromatic H *meta* to $-OCH_2-$, $J=8{\cdot}6$ Hz), 7·33 (d, 2 aromatic H *meta* to N, $J=5{\cdot}9$ Hz), 7·25 (d, 1 H, $-CH=CH-$, $J=16{\cdot}3$ Hz), 6·92 (d, 2 aromatic H *ortho* to $-OCH_2-$, $J=8{\cdot}6$ Hz), 6·86 (d, 1 H, $-CH=CH-$, $J=16{\cdot}3$ Hz), 3·85–3·82, 3·77–3·73 (m, 2 H, $-O-CH_2-$), 1·89–1·83 (m, 1 H, $-CH-$), 1·61–1·54, 1·31–1·24 (m, 2 H, $-CH_2-CH_3$), 1·03 (d, 3 H, CH_3-CH-, $J=6{\cdot}8$ Hz), 0·98 (t, 3 H, CH_3-CH_2-, $J=7{\cdot}5$ Hz). The synthesis of *S*-(-)-*trans*-4-(2-methoxypropoxy)-4′-stilbazole (MeO*Sz) was reported in a previous paper [11].

2.2. *Preparation of the hydrogen-bonded complexes*

Hydrogen-bonded complexes were prepared [2, 4] by evaporation from pyridine or THF solution containing the required amounts of the H-bonding donor and acceptor moieties, followed by drying *in vacuo* at 60°C.

2.3. *Characterization*

^{1}H NMR spectra were obtained using a Jeol GX 270 FT NMR. DSC measurements were conducted with a Mettler DSC 30 and a Perkin-Elmer DSC7. The initial heating scans were not used. An Olympus BH2 polarizing microscope equipped with a Mettler FP82HT hot stage, and a Zeiss Labpol microscope equipped with a Linkam TH600 hot stage and PR600 controller were used for the visual observations. The spontaneous polarizations at various temperatures were measured from the hysteresis loop by the Sawyer–Tower method [18, 19].

3. Results and discussion

The general structure of the hydrogen-bonded complexes prepared from benzoic acid (*n*OBA) and chiral stilbazoles (Me*Sz and MeO*Sz) is shown in figure 1. The liquid crystalline properties of 1:1 non-chiral hydrogen-bonded complexes obtained from 4-alkoxybenzoic acid and *trans*-4-alkoxy-4′-stilbazole have been reported previously [13, 14]. The induction of mesophases was expected for the chiral H-bonded mesogens. 4-Alkoxybenzoic acids with $n \geqslant 4$ exhibit liquid crystallinity due to dimerization on heating. The chiral stilbazoles of Me*Sz and MeO*Sz are non-mesogenic and melt directly into the isotropic liquid at 98°C and 111°C, respectively. The H-bonded complexes were prepared from equimolar amounts of H-bonding donor and acceptor moieties. The thermal behaviour of a series of the H-bonded complexes of *n*OBA–Me*Sz for $n=1$–12 is shown in figure 2 and table 1. All of the complexes exhibit liquid crystalline phases. The hydrogen-bonded complex 1OBA–Me*Sz shows an enantiotropic chiral nematic phase and a monotropic smectic A phase, whereas the individual 'pure' component compounds, 1OBA and Me*Sz, are not liquid crystalline. A chiral smectic C phase is induced for the complexes with $n \geqslant 6$. For example, complex 8OBA–Me*Sz shows a S_C^* phase between 92 and 100°C, a S_A phase between 100 and 126°C, and a N* phase up to 130°C. An odd–even effect is seen for the clearing points of the complexes, while this effect reverses at $n=7$ and 8. We have reported upon the ferroelectric liquid crystalline complexes based on *S*-(+)-4-(2-methylbutoxy)benzoic acid (Me*BA) and *trans*-4-alkoxy-4′-stilbazoles (*m*OSz) [12] (see structure below). The complexes Me*BA–*m*OSz and *n*OBA–Me*Sz have the same H-bonded mesogenic core; however, the chiral group is introduced to the end group in the opposite position. The phase behaviour of

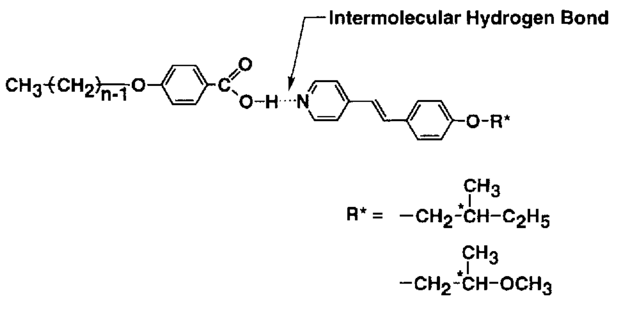


Figure 1. The general molecular structure of the hydrogen-bonded liquid crystalline complexes based on chiral stilbazoles.

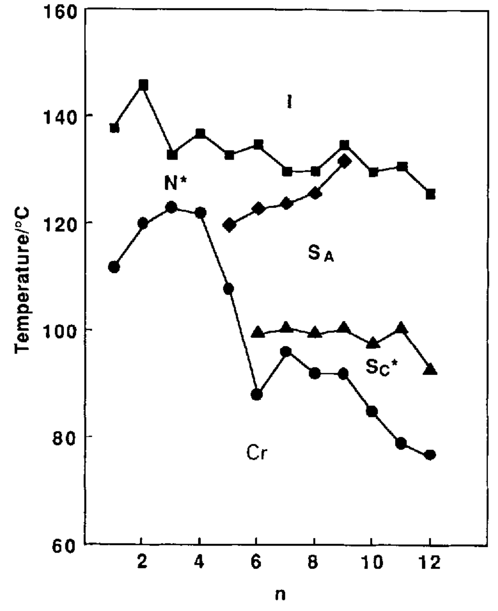
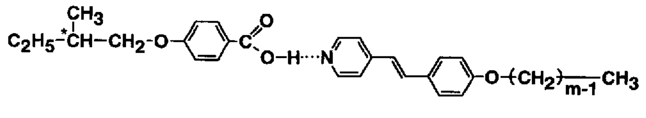


Figure 2. The plot of transition temperature against the number of carbon atoms (*n*) in the alkyl chain for the 1 : 1 hydrogen-bonded complex *n*OBA–Me*Sz series.



Scheme 2.

Me*BA–1OSz (Cr 114 N* 137 I) is similar to that of 1OBA–Me*Sz. Isotropization temperatures increase as *m* increases for the Me*BA–*m*OSz series, while they decrease with increasing *n* for the *n*OBA–Me*Sz compounds. Therefore, as the length of the alkyl chains increases, the difference in the clearing points between the *n*OBA–Me*Sz and Me*BA–*m*OSz complexes becomes larger. For example, 8OBA–Me*Sz clears at 130°C, while for Me*BA–8OSz the clearing temperature is 147°C. A smectic A phase is observed for the Me*BA–*m*OSz complexes with $m \geq 2$, while for *n*OBA–Me*Sz *n* must be 5 or greater before a S_A phase is exhibited. In contrast, a smectic C* phase is observed for the *n*OBA–Me*Sz complexes with $n \geq 6$, and for the Me*BA–*m*OSz complexes with $m \geq 7$. The complexes of Me*BA–*m*OSz with $m \geq 7$ show the chiral smectic C phase at a temperature of over 100°C, while the

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) (in parentheses) of the hydrogen-bonded complexes prepared from the 4-alkoxybenzoic acids (*n*OBA) and *S*-(+)-*trans*-4-(2-methylbutoxy)-4′-stilbazole (Me*Sz).

1 : 1 H-bonded complex	Phase transition behaviour								
1OBA–Me*Sz	Cr	112 (28·8)	N*	138 (1·2)	I				
2OBA–Me*Sz	Cr	120 (29·3)	N*	146 (1·9)	I				
3OBA–Me*Sz	Cr	123 (56·3)	N*	133 (2·1)	I				
4OBA–Me*Sz	Cr	122 (28·6)	N*	137 (1·6)	I				
5OBA–Me*Sz	Cr	108 (22·4)	S_A	120 (0·2)	N*	133 (1·8)	I		
6OBA–Me*Sz	Cr	88 (22·4)	S_C^*	100 (—)[a]	S_A	123 (1·4)	N*	135 (4·0)	I
7OBA–Me*Sz	Cr	96 (29·4)	S_C^*	101 (—)[a]	S_A	124 (1·6)	N*	130 (3·7)	I
8OBA–Me*Sz	Cr	92 (31·1)	S_C^*	100 (—)[a]	S_A	126 (3·7)	N*	130 (4·4)	I
9OBA–Me*Sz	Cr	92 (38·4)	S_C^*	101 (—)[a]	S_A	132 (—)[b]	N*	135 (5·3)	I
10OBA–Me*Sz	Cr	85 (34·5)	S_C^*	98 (—)[a]	S_A	130 (7·0)	I		
11OBA–Me*Sz	Cr	79 (30·0)	S_C^*	101 (—)[a]	S_A	131 (6·7)	I		
12OBA–Me*Sz	Cr	77 (40·7)	S_C^*	93 (—)[a]	S_A	126 (9·9)	I		

Cr: crystal; S: smectic; N*: chiral nematic; I: isotropic.

[a] The peak could not be detected.

[b] The S_A–N* transition is overlapped with the isotropization peak.

complexes *n*OBA–Me*Sz with $n \geqslant 6$ exhibit the S_C^* phase between about 80 and 100°C. More ordered smectic phases, observed for the Me*BA–*m*OSz complexes, are not seen for the *n*OBA–Me*Sz series.

S-(-)-*trans*-4-(2-Methoxypropoxy)-4′-stilbazole (MeO*Sz) has been used as a chiral H-bonding acceptor component for ferroelectric low molecular mass complexes. In this structure, the CH_2 group of the *n*OBA–Me*Sz complex is replaced by an oxygen atom. Figure 3 and table 2 give the thermal properties of a series of the H-bonded complexes of *n*OBA–MeO*Sz for $n = 6$–8 and 10–12. A smectic C* phase is induced for the complexes with $n \geqslant 7$. Furthermore, the phase transition sequences (I–N*–S_A–S_C^* or I–S_A–S_C^*) for the two series (*n*OBA–Me*Sz and *n*OBA–MeO*Sz) are identical when $n \geqslant 7$. The isotropization temperatures of the *n*OBA–MeO*Sz series are lower than those of the *n*OBA–Me*Sz series. An optical photomicrograph of the smectic C* phase of the complex 12OBA–MeO*Sz taken at 72°C on cooling is shown in figure 4. The periodic lines associated with the helical pitch of the chiral smectic C phase are observed. The ferroelectric side chain H-bonded polymer obtained by the formation of intermolecular hydrogen bonds between H-bonding polysiloxanes and MeO*Sz [11] exhibits the S_C^* phase at over 100°C.

Hydrogen-bonded complexes containing an alicyclic component have been obtained from mixing *trans*-4-alkylcyclohexane carboxylic acid (*p*CHCA) (*p* is the

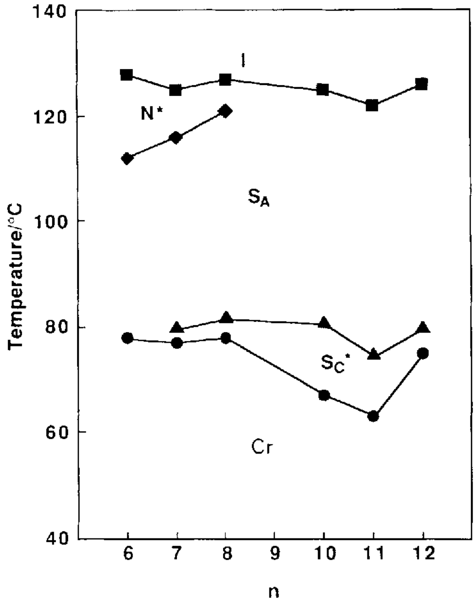


Figure 3. The plot of transition temperature against the number of carbon atoms (*n*) in the alkyl chain for the 1 : 1 hydrogen-bonded complex *n*OBA–MeO*Sz series.

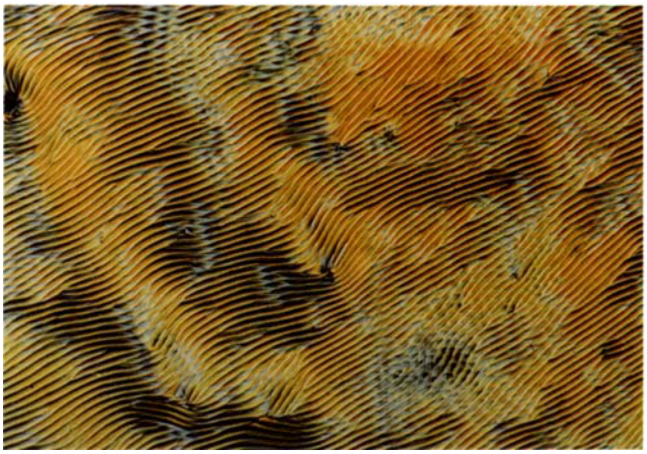


Figure 4. Photomicrograph of the chiral smectic C phase of the H-bonded complex 12OBA–MeO*Sz taken at 72°C on cooling.

Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) (in parentheses) of the hydrogen-bonded complexes prepared from the 4-alkoxybenzoic acids (*n*OBA) and *S*-(−)-*trans*-4-(2-methoxypropyloxy)-4′-stilbazole (MeO*Sz).

1 : 1 H-bonded complex	Phase transition behaviour								
6OBA–MeO*Sz	Cr	78 (19·4)	S_A	112 (0·5)	N*	128 (2·7)	I		
7OBA–MeO*Sz	Cr	77 (18·7)	S_C^*	80 (—)[a]	S_A	116 (2·4)	N*	125 (3·6)	I
8OBA–MeO*Sz	Cr	78 (20·1)	S_C^*	82 (—)[a]	S_A	121 (2·6)	N*	127 (4·1)	I
10OBA–MeO*Sz	Cr	67 (17·9)	S_C^*	81 (—)[a]	S_A	125 (6·1)	I		
11OBA–MeO*Sz	Cr	63 (17·1)	S_C^*	75 (—)[a]	S_A	122 (8·1)	I		
12OBA–MeO*Sz	Cr	75 (39·5)	S_C^*	80 (—)[a]	S_A	126 (8·2)	I		

Cr: crystal; S: smectic; N*: chiral nematic; I: isotropic.

[a] The peak could not be detected.

number of carbon atoms in the alkyl chain) and Me*Sz. The thermal properties of a series of the H-bonded complexes *p*CHCA–Me*Sz are given in table 3. Only the smectic A phase is observed for this series.

It should be noted that the mesogen units consist of different and independent components held together through (non-covalent) H-bonding. Therefore, the mixture of the two components can be prepared using non-stoichiometric compositions. This concept has been used effectively to control the specific properties of the H-bonded LC systems [2, 4]. Figure 5 shows the binary phase diagram for 10OBA and Me*Sz on heating. Chiral nematic and smectic C* phases are induced on mixing. A smectic C* phase is observed up to 50 mol % of Me*Sz. Between 60 and 80 mol % of Me*Sz, only the smectic A phase is observed. The temperature range of the smectic C* phase is at a maximum at a concentration of 25 mol % of Me*Sz. This mixture exhibits a smectic C* phase between 72 to 124°C, and a subsequent chiral nematic phase up to 138°C.

Table 3. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) (in parentheses) of the hydrogen-bonded complexes prepared from the *trans*-4-alkylcyclohexane carboxylic acids (*p*CHCA) and *S*-(+)-*trans*-4-(2-methylbutoxy)-4′-stilbazole (Me*Sz).

1:1 H-bonded complex	Phase transition behaviour				
2CHCA–Me*Sz	Cr	87 (52)	S$_A$	97 (14)	I
3CHCA–Me*Sz	Cr	96 (40)	S$_A$	105 (8·5)	I
5CHCA–Me*Sz	Cr	97 (39)	S$_A$	110 (14)	I
7CHCA–Me*Sz	Cr	93 (55)	S$_A$	110 (20)	I

Cr: crystal; S: smectic; I: isotropic.

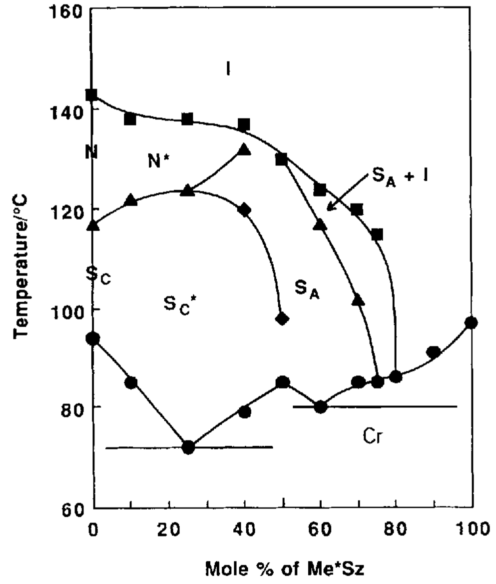


Figure 5. The binary phase diagram of 10OBA and Me*Sz.

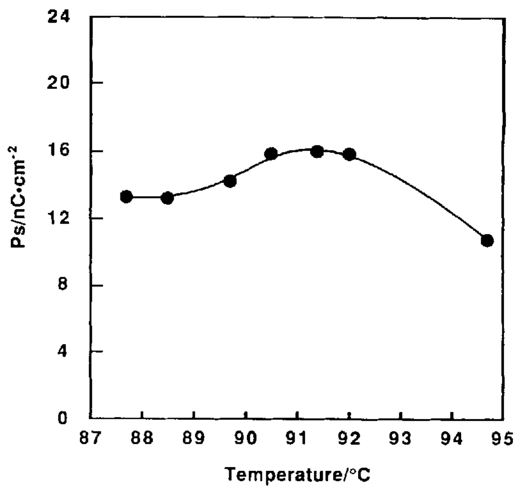


Figure 6. A plot of the temperature dependence of the spontaneous polarization for the H-bonded complex 8OBA–Me*Sz.

The ferroelectric properties of the complex 8OBA–Me*Sz were measured by the Sawyer–Tower method [18, 19]. The hysteresis loop was obtained in the smectic C* phase. It is interesting to note that a stable ferroelectricity has been induced for a supramolecular mesogenic structure built by non-covalent interactions. Figure 6 shows the values of the spontaneous polarizations for the complex 8OBA–Me*Sz as a function of temperature. The maximum value of 16 nC cm^{-2} was obtained at 91·4°C. Complex Me*BA–8OSz has a P_S value of 33 nC cm^{-2} [12]. These values are somewhat larger than those of conventional liquid crystals having a 2-methylbutoxy group as the chiral centre synthesized by only covalent bonds [15]. The structure of the complex consisting of 'soft' bonds between interacting molecular species may affect such ferroelectric properties.

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