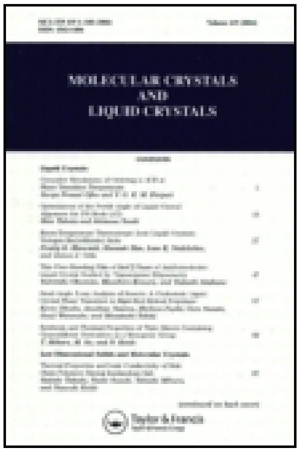

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Synthesis of New Phasmidic Liquid Crystals Induced by Intermolecular Hydrogen Bonding between Pyridine Moieties and Carboxylic Acids

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Synthesis of New Phasmidic Liquid Crystals Induced by Intermolecular Hydrogen Bonding between Pyridine Moieties and Carboxylic Acids

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New liquid crystals induced by intermolecular hydrogen bonding between 4-[3, 4, 5-tridocyloxy benzoyloxy)-4′-stilbazole (3DBSZ) and malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, maleic acid, fumaric acid, 3,4,5,-tridocyloxy-benzoic acid(3DBA) respectively were prepared, their liquid crystalline properties were investigated by using DSC, polarized optical microscopy and wide-angle X-ray diffraction. The results show that most of the complexes exhibit column phases. Furthermore, a new room temperature column complex was induced by the intermolecular hydrogen bonding between 3DBSZ and 3DBA.

Keywords: Phasmidic liquid crystals; hydrogen bonding; pyridines; carboxylic acids; DSC; X-ray diffraction

INTRODUCTION

Since T. Kato *et al.* prepared new liquid crystals induced by intermolecular hydrogen bonding between pyridyl moieties which are proton acceptors and carboxylic acid groups which are proton donors [1], many new liquid crystals such as molecular liquid crystals [2–7], polymer liquid crystals

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[8–16], ferroelectric liquid crystals [17–19], evenmore room temperature liquid crystals [20] have been prepared by using this method, because of the stability of intermolecular hydrogen bonding [19,21] and the synthetic directionality [18,20].

In this present study, new hydrogen bonded liquid crystals were prepared and investigated (see Fig. 1) by choosing 4-(3,4.5-tridocyloxy benzoyloxy)-4′-stilbazole (3DBSZ) and 4-(4-docyloxybenzoyloxy)-4′-stilbazole (10SZ) as proton acceptors and choosing 4-(3,4,5,-tridocyloxybenzoic acid (3DBA), 4-docyloxyebnzoic acid (10BA) and aliphatic diacids such as malonic acid (3DA), succinic acid (4DA), glutaric acid (5DA), adipic acid (6DA), pimelic acid (7DA), Suberic acid (8DA), maleic acid (4ZA), fumaric acid (4EA) as proton donors respectively.

The compounds 3DBSZ and 3DBA are non-mesogenic molecules bearing three docyloxy terminal groups. The complexes between 3DBSZ and *n*DA, 4EA, 4ZA, 3DBA are the first phasmidic liquid crystalline systems induced by intermolecular hydrogen bonding. In order to study the effect of different molecular structures on the phase behavior. We investigated series II and series III by changing the rigidity of pronton donors and the shape of complexes. The DSC and polarized optical microscopy studies show that all

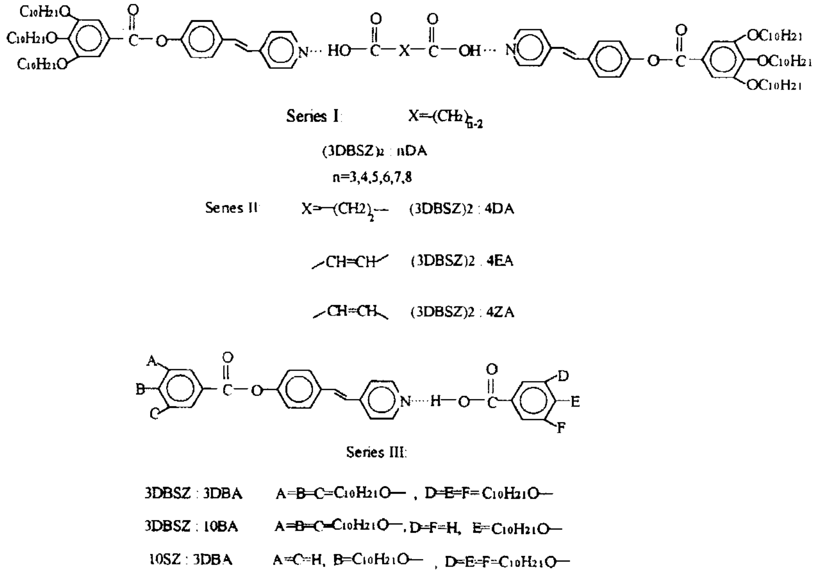

FIGURE 1 The molecular structures of the hydrogen bonded complexes investigated in this paper.

of the complexes except $(3DBSZ)_2$:3DA, $(3DBSZ)_2$:4DA, 3DBSZ:10BA are liquid crystals.

EXPERIMENTAL

Synthesis of Proton Donors and Acceptors

The compounds *n*DA, 4EA and 4ZA are commercial products, they are purified by recrystallization prior to use.

The 3,4,5-tridocyloxybenzoic acid (3DBA) were prepared according to a known procedure [22]. m.p is 50–52°C, IR: 1652.0 cm^{-1} (=C=O), ^{1}HNMR: 7.32(s, 2H, ArH), 4.02 (t, 6H, —OCH_2—), 1.90–1.28(48H, alkyl), 0.88 (t, 9H, —CH_3). Elemental analysis calculated for $C_{37}H_{66}O_5$, C: 75.20 percent, H: 11.26 percent; Found: C: 75.03 percent, H: 11.09 percent.

The 4-hydroxy-4′-stilbazole was synthesized according to ref [9].

The 4-docyloxybenzoic acid was prepared according to a known procedure [23], then it was recrystallized three times from glacial acetic acid m.p: 92–149°C(lit [23], mp 92–149°C).

The 4-docyloxybenzoyloxy-4′stilbazole (10SZ) was prepared according to the following procedure: the 4-hydroxy-4′stilbazole (3.0 g 15.2 mmol) was dissolved in 80 ml dry pyridine, then a solution of 20 ml dry THF containing 18 mmol 4-docyloxybenzoyl chloride obtained by reaction of 4-docyloxy benzoic acid and thionyl chloride was added dropwisely, the mixture was stirred at room temperature. After 24 h, it was poured into large amount of ice-water, the precipate was collected and purified by recrystallization once from ethanol, then twice from cyclohexane. The final product 10SZ is a liquid crystal. Cr 108.7°C (S_1 89.8°C) S_A 175.0°C I [24], IR: 1722.4 cm^{-1} (=C=O), ^{1}HNMR: 8.59 and 7.37 (4H, d, pyridyl), 7.02 and 7.30 (4H, d, trans —CH=CH—), 6.98, 7.26, 7.59 and 8.15 (8H, d, phenyl), 4.05 (2H, t, —OCH_2—), 1.27–1.84 (16H, alkyl), 0.89 (3H, d, —CH_3). Anal.calcd for $C_{30}H_{35}NO_3$: C 78.74 percent, H 7.71 percent, N 3.06 percent, Found C 78.57 percent, H 7.78 percent, N 3.27 percent.

The 4-(3,4,5-tridocyloxybenzoyloxy)-4′-stilbazole (3DBSZ) was synthesized according to the similar procedure of 10SZ, m.p. 73–75°C. IR: 1732.0 cm^{-1} (=C=O), ^{1}HNMR: 8.69 and 7.62 (4H, d, pyridyl), 7.42 and 7.36(4H d, phenyl), 7.32 and 7.00 (2H, d, trans —CH=CH—), 7.23 (2H, s, phenyl), 4.05 (6H, t, —OCH_2—), 1.84–1.28 (48H, m, —$(CH_2)n$—), 0.88 (9H, t, CH_3). Anal.Calcd for $C_{50}H_{75}NO_5$: C 77.98 percent, H 9.82 percent, N 1.82 percent, Found: C 77.75 percent, H 10.27 percent, N 2.01 percent.

Formation of the Hydrogen Bonded Complexes

The mixtures of 2:1 molar ratio or 1:1 molar ratio which could be seen in Figure 1 of proton acceptors and donors were dissolved in dry pyridine, then the pyridine was evaporated under vacuum at 60–65°C. The material obtained after cooling to r.t was used for liquid crystalline investigation.

CHARACTERIZATION

The textures of the mesophases were characterized by polarized optical microscopy (Jeiss Jena optical microscope) in conjunction with a heating stage. DSC measurements were conducted using a Perkin-Elmer DSC-2 with a heating rate of 5°C/min. Wide-angle X-ray diffraction was performed by using a Philip PW-1700 systems. Infrared spectra were obtained using a Nicolet-5DX FTIR spectrometer with maximum resolution of 2 cm^{-1}. ^{1}HNMR spectra were obtained using a Unity 400 NMR instrument operating at 400 MHz in the solution of $CDCl_3$. Element analyses were performed with a Perkin-Elmer 240 C microanalyser.

RESULTS AND DISCUSSIONS

The intermolecular hydrogen bonding can be identified by infrared spectra. Here an example (see Fig. 2) is given, the wavenumber of carboxylic carbonyl of 3DBA is 1692.0 cm^{-1}, but for the complex 3DBA:3DBSZ, it is 1711.2 cm^{-1}. The wavenumber change is 19.2 cm^{-1}, this significant change shows that the intermolecular hydrogen bonding between pyridyl and carboxylic unit has formed. And the bands centered at 2450 cm^{-1} and 1950 cm^{-1} for all complexes are also the strong identification of unionized type intermolecular hydrogen bonding [21, 25].

According to the results of DSC and polarized optical microscopy study. Table I gives the phases and phase transition temperatures for all of the proton donors, acceptors and their complexes. We find that the phase transition temperatures for all of the complexes are very different from their original proton donors and acceptors. This results suggest that the intermolecular hydrogen bonded complexes behave as a singal composition.

For series I, the proton donors (nDA), and proton acceptor (3DBSZ) are nonmesogens, on the contrary, when $n \geqslant 5$, their 1:2 complexes show liquid crystal properties. Furthermore the clearing points for all of the complexes

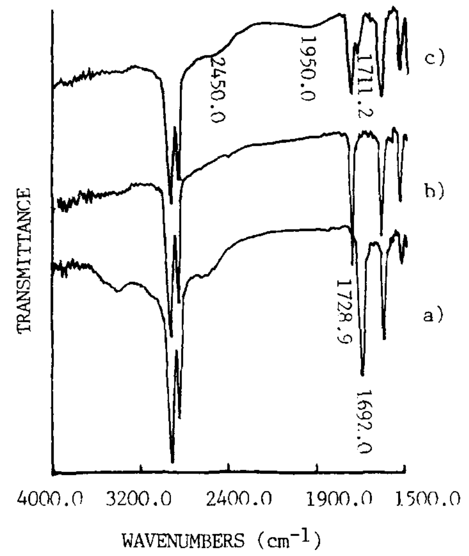

FIGURE 2 FTIR spectra of 3DBA(a), 3DBSZ(b) and 3DBSZ:3DBA at 25°C.

TABLE I The phases and transition temperatures of the proton donors, proton acceptors and their complexes

compounds	*transition temperature (°C)*	*complexes*	*transition temperature (°C)*
3DA	Cr 135–137 I	$(3DBSZ)_2$:3DA	Cr 58.2 I
4DA	Cr 188–190 I	$(3DBSZ)_2$:4DA	Cr 80.8 I
5DA	Cr 95–97 I	$(3DBSZ)_2$:5DA	Cr 53.3 ϕ 59.5 I
6DA	Cr 152–154 I	$(3DBSZ)_2$:6DA	Cr 57.0 ϕ 64.8 I
7DA	Cr 103–105 I	$(3DBSZ)_2$:7DA	Cr 59.5 ϕ 63.1 I
8DA	Cr 142–144 I	$(3DBSZ)_2$:8DA	Cr 48.6 ϕ 81.6 I
4EA	Cr 299–300 I	$(3DBSZ)_2$:4EA	Cr 66.7 ϕ 109.5 I
4ZA	Cr 140–142 I	$(3DBSZ)_2$:4ZA	Cr 66.1 ϕ 119.2 I
3DBA	Cr 50–52 I	3DBSZ:3DBA	Cr −20 ϕ 44.4 I
3DBSZ	Cr 73–75 I	3DBSZ:10BA	Cr 62.0 I
10SZ	Cr 108.7(S_1 89.8) S_A 175.0 I	10SZ:3DBA	Cr 42.2 ϕ 80.4 I
10BA	Cr 92.0 S 122 N 149 I		

Cr: crystal, I: isotropic phase, S: smetic phase, N: nematic phase, ϕ: column phase.

are lower than the melting points of proton donors, this may be caused by the low melting point of 3DBSZ. The textures for the complexes $(3DBSZ)_2$: *n*DA ($n = 5, 6, 7, 8$) are grainy, this kind of texture isn't well-characterized liquid crystalline texture although it may be smectic [26, 10] or column phase [27]. Mathete *et al.* [27, 28] pointed out if there were three long chains at each end of the phasmidic compounds, their liquid crystal phases should be column phases, so we think the phasmidic complexes are columnar liquid crystals. Figure 3 gives the X-ray diffraction diagram of one complex $(3DBSZ)_2$:5DA at 57°C, the strong diffraction peak (34.69 Å) along with other three weak sharp diffraction peaks (20.00 Å, 16.26 Å and 10.24 Å) in small angle region are the identification of column phase [29]. Figure 4 shows the phase diagram for series I. From Figure 4, we can see the clearing points for these complexes exhibit an odd-even effect, this results also suggest that the complexes hebave as a single composition.

The complex $(3DBSZ)_2$:4DA isn't liquid cryatal, but considerating increasing the length of mesogenic group is profit to form liquid crystal, so we choose two rigid 4ZA and 4EA to connect the two 3DBSZ molecules, indeed the complexes $(3DBSZ)_2$:4ZA and $(3DBSZ)_2$:4EA are column liquid crystals. And the clearing points for $(3DBSZ)_2$:4ZA and $(3DBSZ)_2$:4EA are higher than that of $(3DBSZ)_2$:4DA, this may be caused by the higher rigidity of $(3DBSZ)_2$:4ZA and $(3DBSZ)_2$:4EA. But we didn't find any obvious difference of transition temperatures between $(3DBSZ)_2$:4ZA and $(3DBSZ)_2$:4EA, this result implies that the cis, trans structures of the two compounds don't affect the phase behaviour siginificantly for the two complexes. Figure 5 gives the X-ray diffraction diagram of the complexes $(3DBSZ)_2$:4EA and $(3DBSZ)_2$:4ZA at 90°C respectively. The first diffraction peak for $(3DBSZ)_2$:4EA is 47.08 Å. But for complex $(3DBSZ)_2$:4ZA, the first diffraction peak is 42.65 Å, this difference may be caused by the difference of cis and trans structures.

The above study is about series I and series II, the two series are hydrogen bonded liquid crystals between two pyridyl units and a diacids. In series III, hydrogen bonded liquid crystals between a pyridyl unit and a carboxylic

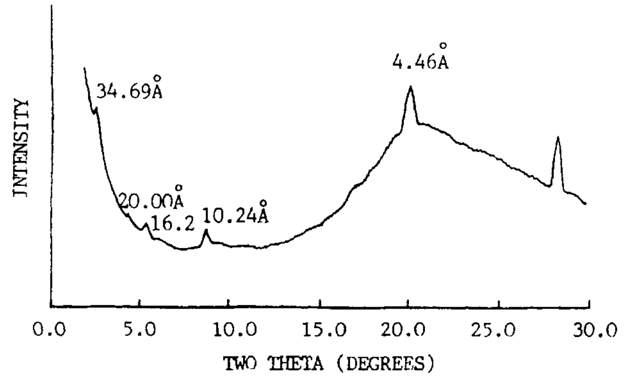

FIGURE 3 The X-ray diffraction diagram for $(3DBSZ)_2$:5DA at 57°C.

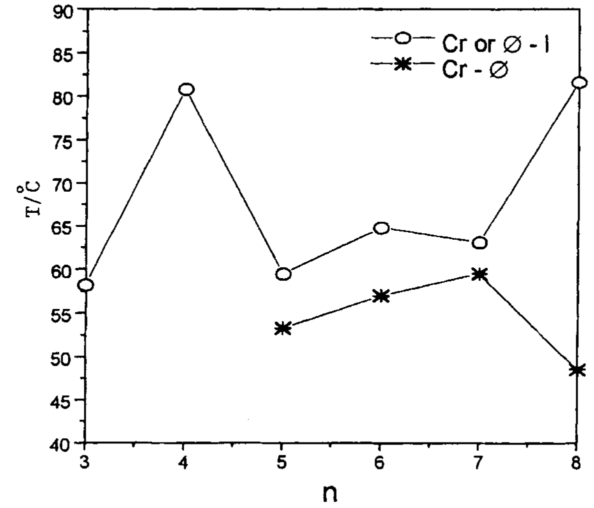

FIGURE 4 Phase diagram for series I.

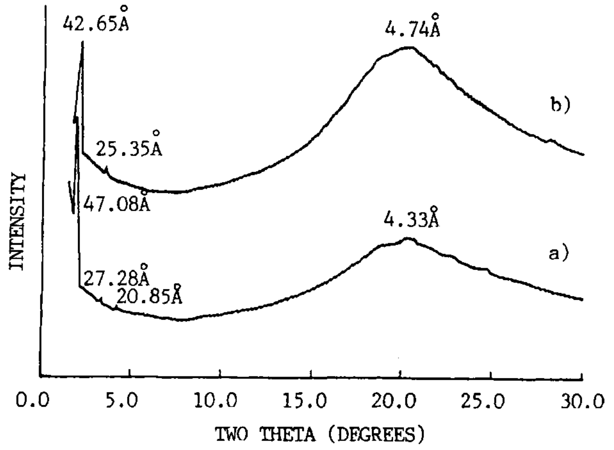

FIGURE 5 The X-ray diffraction diagrams for $(3DBSZ)_2$:4ZA(b) and $(3DBSZ)_2$:4EA(a) at 90°C respectively.

group were prepared by changing their terminal groups, in order to study the different molecular shapes on their phase bahavior. The complex 3DBSZ:10BA isn't liquid crystal though the proton donor 10BA is a liquid crystal, however the complex 10SZ:3DBA is a liquid crystal appeared with mosaic texture in the temperature range from 42°C to 80°C which is a typical texture of column mesophase [29, 30]. And it is very interesting that

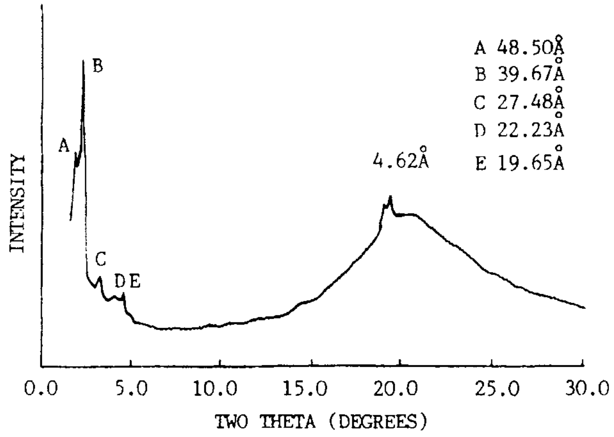

FIGURE 6 The X-ray diffraction diagram for 3DBSZ:3DBA.

a room temperature hydrogen bonded column liquid crystal was obtained by choosing a proton donor 3DBA and a proton acceptor 3DBSZ, both of which are nonmesogens with three terminal groups. The complex 3DBSZ:3DBA exhibit a column mesophase from lower than −20°C to 44.4°C with grainy texture. The lower transition temperature for this complex could be caused by the lower melting points of the two compounds. Figure 6 gives the X-ray diffraction diagram of 3DBSZ:3DBA at 35°C, its middle first diffraction peak (48.50 Å) and very strong second diffraction peak (39.67 Å) along with other three weak diffraction peaks (27.48 Å, 22.23 Å and 19.65 Å) are also the strong identification of column phase [29].

So in this paper, three new series column hydrogen bonded liquid crystals were investigated. We find that for series I, when the length of diacid is longer than 4 carbon column phases can be observed; for series II, increasing the rigidity of mesogenic group is profit to liquid crystal properties; for series III, when choosing appropritate proton donor and acceptor with low melting points, room temperature hydrogen bonded column mesophase can be prepared.

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