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Self-Assembly of Liquid Crystalline Complexes Having Angular Structures through Intermolecular Hydrogen Bonding

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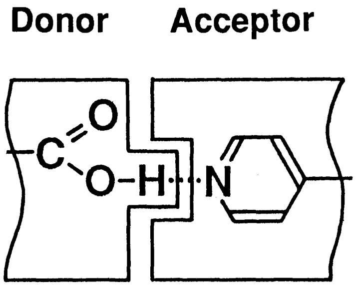
Novel liquid crystalline materials having angular structures with mesogens pointing in two directions have been prepared by complexation of phthalic or isophthalic acid and two molecules of a stilbazole through intermolecular hydrogen bonding.

In thermotropic liquid crystals, one of the typical mesogens is a rigid rod structure containing two or three p-phenylene units connected directly or through covalently bound functional groups that maintain a linear structure.[1)]

Recently, we have found that a novel family of liquid crystalline complexes is built through intermolecular hydrogen bonding.[2-6)] The complexes having linear structures show more stable mesophases than either of the individual components if the structure is designed properly. In the H-bonded liquid crystals, the hydrogen bond between a benzoic acid moiety and a pyridyl group functions like the connecting part of molecular "Lego" set, as shown below. Overall, this type of intermolecular hydrogen bonding affords mesogens with linear structures. We now report novel mesogenic structures incorporating a bent between two mesogenic fragments connected to a single bifunctional H-bond donor.

The hydrogen-bonded complexes were prepared from a mixture (1:2 mole ratio) of phthalic acid (**PA**), isophthalic acid (**IA**), or terephthalic acid (**TA**), which operates as the bi-functional hydrogen bond donor, and *trans*-4-alkoxy-4'-stilbazole[7,8)] (**nOSz**, n=7, 8, and 10) that acts as hydrogen bond acceptor. The solid complexes were obtained by a simple evaporation technique of a pyridine solution of the two components as was described previously.[2-6)]

The transition temperatures and enthalpies of transition for the complexes are given in Table 1.[9)] The complexes obtained



Molecular Lego

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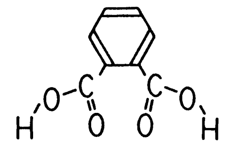
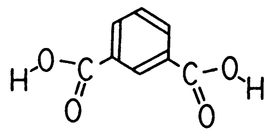
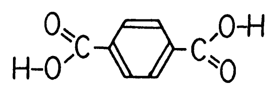
H-Bond Donor



PA

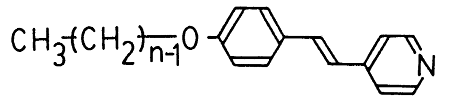


IA



TA

H-Bond Acceptor



nOSz (n=7, 8, 10)

Table 1. Thermal properties[a] of hydrogen-bonded complexes from benzenedicarboxylic acid and *trans*-4-alkoxy-4'-stilbazole[b]

Complex	Liquid crystalline behavior[c]					
PA-(7OSz)$_2$	K	102 (21.2)	N	123 (1.8)	I	
PA-(8OSz)$_2$	K	105 (23.3)	N	128 (2.3)	I	
PA-(10OSz)$_2$	K	98 (31.6)	N	135 (2.1)	I	
IA-(7OSz)$_2$	K	120 (26.8)	M	156 (18.9)	S	250 (decomp.)[d]
IA-(8OSz)$_2$	K	120 (27.3)	M	150 (23.5)	S	250 (decomp.)[d]
IA-(10OSz)$_2$	K	119 (26.1)	M	150 (20.7)	S	250 (decomp.)[d]
TA-(7OSz)$_2$	K	158 (63.3)	S	250 (decomp.)[d]		
TA-(8OSz)$_2$	K	153 (69.2)	S	250 (decomp.)[d]		
TA-(10OSz)$_2$	K	143 (65.3)	S	250 (decomp.)[d]		

a) Transition temperatures (°C) and enthalpies of transition (kJ/mol, in parenthesis).
b) **7OSz**: smectic 86-89 °C, **8OSz**: smectic 76-88 °C, **10OSz**: smectic 85-88 °C.
c) K: crystal, N: nematic, S: smectic, M: mesomorphic, I: isotropic.
d) Slow decomposition occurs at around 250 °C.

from the 1:2 mixture of phthalic or isophthalic acid and the stilbazole show liquid crystalline behavior despite the fact non-linear structures incorporating a bent angle between two connected mesogenic fragments are obtained. For example the 1:2 complex of phthalic acid and *trans*-4-heptyloxy-4'-stilbazole (**7OSz**), which will be denoted as **PA-(7OSz)$_2$**, exhibits a nematic phase between 102 and 123 °C, while **7OSz** shows smectic phases between 86 and 89 °C, and isophthalic acid itself is nonmesogenic. The enthalpy values of 1.8-2.3 kJ/mol for isotropization are typical for those for nematic-isotropic transitions. A droplet texture appears on the transition from the mesophase to the isotropic state. For complex **IA-(7OSz)$_2$**, melting behavior to a fluid mesomorphic state and a mesophase-mesophase transition are clearly observed at 120 °C and 156 °C, respectively, by optical polarizing microscopy. The mesomorphic state is more stable than that of **PA-(7OSz)$_2$**. DSC thermogram of **IA-(7OSz)$_2$** (Fig. 1) shows two endothermic peaks of the melting and the mesophase-mesophase transitions. These peaks are not observed for each of single component. No endothermic peak corresponding to isotropization is seen due to slow decomposition of the complexes. **TA-(nOSz)$_2$** that forms linear structure of the complex exhibits a smectic phase, the texture of which is similar to that of the high-temperature mesophase of **IA-(nOSz)$_2$**. These two mesophases show complete miscibility.

FT-IR spectrum of **IA-(7OSz)$_2$** in a smectic phase at 130 °C is shown in Fig. 2. The O-H bands observed at 1940 and 2510 cm^{-1} confirm the existence of hydrogen bonding between the dicarboxylic acid and

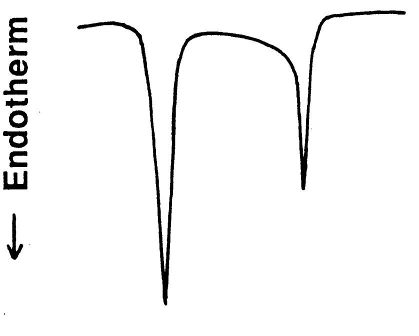


Fig. 1. DSC thermogram of H-bonded complex **IA-(7OSz)$_2$** on heating.

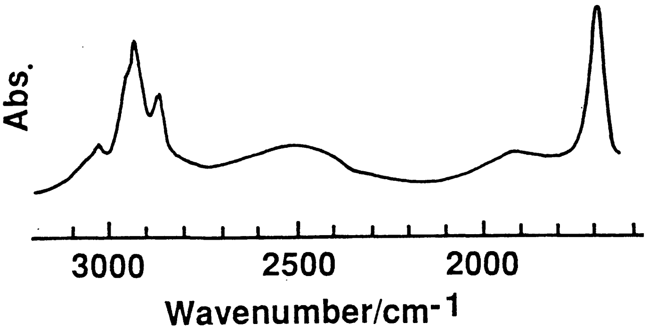


Fig. 2. FT-IR spectrum of H-bonded complex **IA-(7OSz)$_2$** in a mesophase at 130 °C.

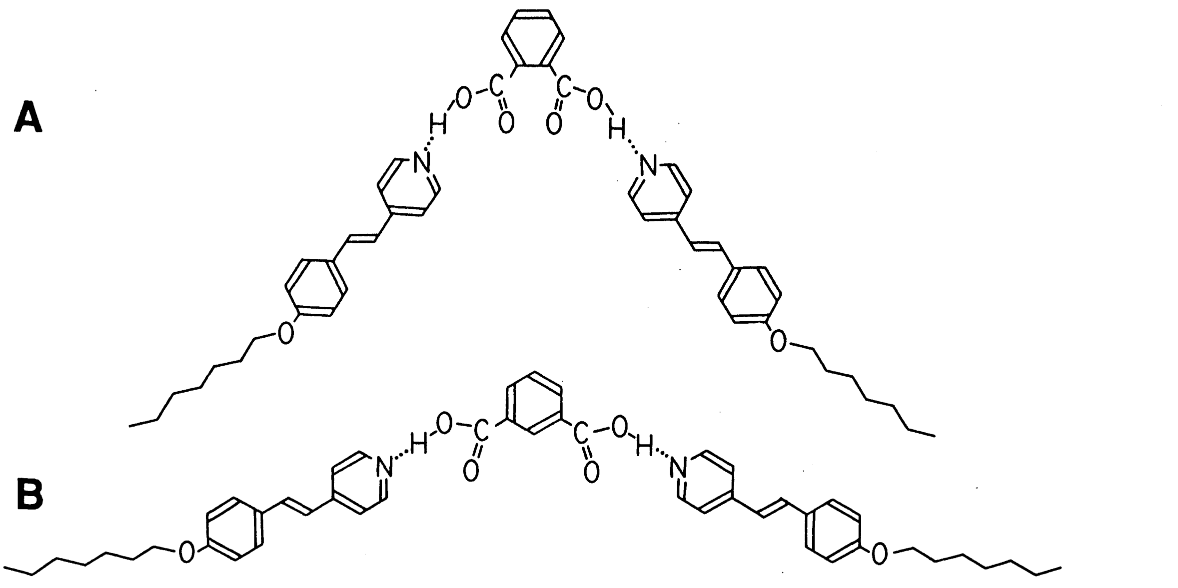


Fig. 3. Proposed structures of non-linear liquid crystalline H-bonded complexes: (A) **PA-(7OSz)$_2$**; (B) **IA-(7OSz)$_2$**.

stilbazole moieties.$^{10-12)}$

The mesomorphicity of the complexes reveals that the non-linear structures built through intermolecular hydrogen bonding between phthalic or isophthalic acid and a stilbazole function as novel mesogens, as illustrated in Fig.3. In liquid crystals that consist of only covalent bonding, non-linear structural units such as 1,2- or 1,3-phenylene units have been considered to be imcompatible with the formation of liquid crystalline phases.$^{13)}$ It is noteworthy that in the design of hydrogen-bonded liquid crystals, non-linear phenylene units can be used as a core part of the mesogen. The present results may widen the variety of molecular structures of liquid crystalline materials.

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