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Self-Assembly of a Twin Liquid Crystalline Complex through Intermolecular Hydrogen Bondings

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A new type of twin liquid crystalline complex having two terminal mesogenic units and a central flexible spacer has been formed through intermolecular hydrogen bonds between a nonmesogenic aliphatic diacid and mesogenic stilbazoles.

Hydrogen bonding is one of the most important interactions to regulate the order of molecular aggregates. For thermotropic liquid crystals, the magnitude and the direction of intermolecular hydrogen bondings are not generally appropriate for the mesomorphism except for a few systems.[1-8] In all of these cases, liquid crystallinities result from intermolecular hydrogen bonds between identical molecules. Recently we have reported[9,10] a new liquid crystalline complex through intermolecular hydrogen bonds between two independent and different components, that is, H-bonding donor and acceptor moieties. The single intermolecular hydrogen bonds between a 4-stilbazolyl group and a 4-alkoxybenzoic acid unit along the long axis of the molecules have formed a new and extended aromatic mesogen which strongly stabilizes a mesophase.[9,10] The objective of the present study is to determine if this hydrogen bonding can be used as a linkage connecting two identical mesogenic units themselves incapable of self-interaction through an aliphatic soft segment. Covalently bonded twin liquid cryatals have been reported[11,12] and they show unique thermotropic properties.

We now report a new type of self-assembly of twin liquid crystalline complexes built by using intermolecular hydrogen bonds. Nonmesogenic polymethylene diacids (nDA, n=5-9) and mesogenic trans-4-[(ethoxybenzoyl)oxy]-4'-stilbazole[9] (2Sz) (nematic, 165-213 °C) have been

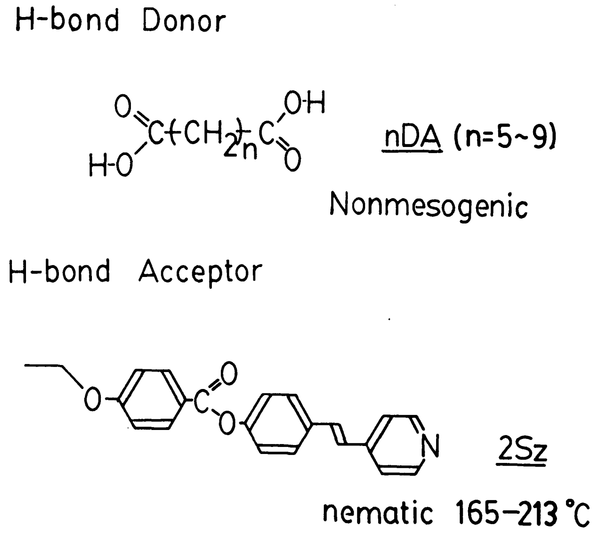

Table 1. Thermal properties of hydrogen-bonded complexes between nDA and 2Sz

n[a]	Transition temperatures[b]		
	K-S	S-N	N-I
5	146	182	230
6	156	196	230
7	138	179	218
8	152	188	220
9	141	185	218

a) Number of methylene carbons in nDA.

b) K:Crystal; N:Nematic; S:Smectic; I:Isotropic.

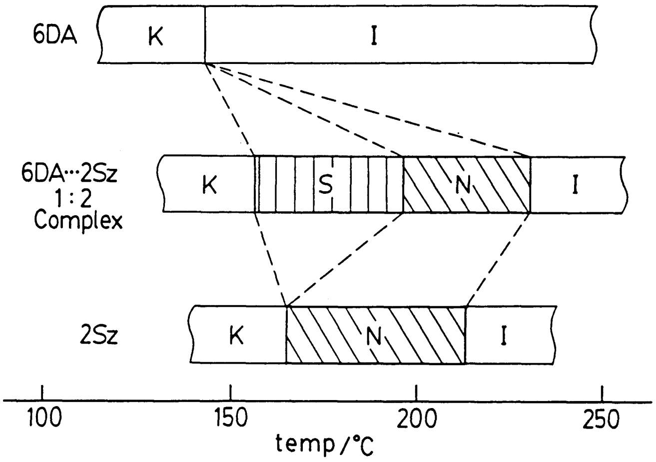

Fig. 1. Comparison of the mesomorphic range of the 1:2 complex between 6DA and 2Sz with that of each single component; K:Crystal; N:Nematic; S: Smectic; I:Isotropic.

selected as H-bond donor and acceptor moieties, respectively. These molecules were expected to form a twin type of liquid crystalline complex between the 4-pyridyl group of 2Sz and the two acid groups of nDA. Syntheses and thermal properties of 2Sz and its analogous compounds were reported previously.[9,10,13,14]

1:2 Mechanical mixtures of the various nDA and 2Sz were self-assembled into the twin liquid crystalline complexes through a simple slow evaporation of their solution in pyridine. This method has previously been used successfully to form the 1:1 H-bonded complex between 4-butoxybenzoic acid and 2Sz.[9] Thermotropic properties were measured by visual observations by polarizing microscope equipped with a hot stage (Mettler FP-84) and differencial scanning calorimetry (Perkin Elmer DSC-2).

Mesomorphic properties of the 1:2 mixture are given in Table 1. Each of the five binary mixtures behaved as one single component and exhibited both smectic and nematic phases while all the various diacids nDA are non-mesogenic and the stilbazole only shows a nematic phase. The mesophase of each mixture showed high thermal stabilities. Figure 1 illustrates comparison of the mesomorphic range of a mixture with that of each single component. After melting of the 1:2 mixture of 6DA and 2Sz at 156 °C, a focal conic texture due to a smectic phase was clearly observed up to 196 °C under a polarizing microscope. The transition from a nematic phase to an isotropic state occurred at 230 °C, which was higher than the nematic to isotropic transition of 2Sz itself. DSC thermograms also showed solid-smectic, smectic-nematic, and nematic-isotropic transitions. Figure 2 shows the plots of transition temperatures of mixtures as a function of the number of carbon atoms in the aliphatic diacids. The thermal behavior of each binary mixture reflects strongly the length of the aliphatic chain of the nonmesogenic diacid moiety. An odd-even effect is observed for this series of complexes as was reported for a series of twin liquid crystal formed through a covalent bonding between mesogens and a flexible spacer.[12)]

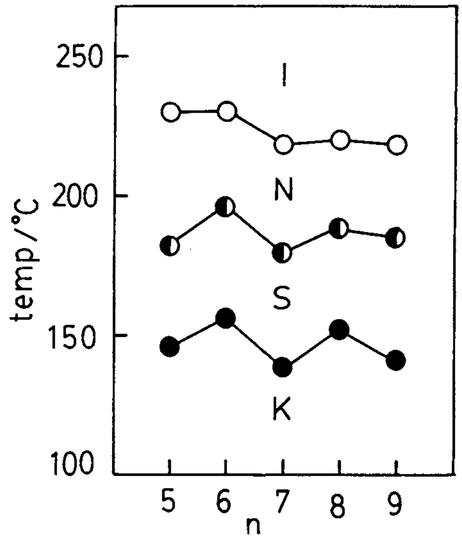

Fig. 2. Transition temperatures of the series of the complex between nDA and 2Sz.

We have attributed these results to the formation of the 1:2 hydrogen-bonded complex which behaves as a twin liquid crystalline component as shown in Fig. 3. The formation of such H-bonded complex is

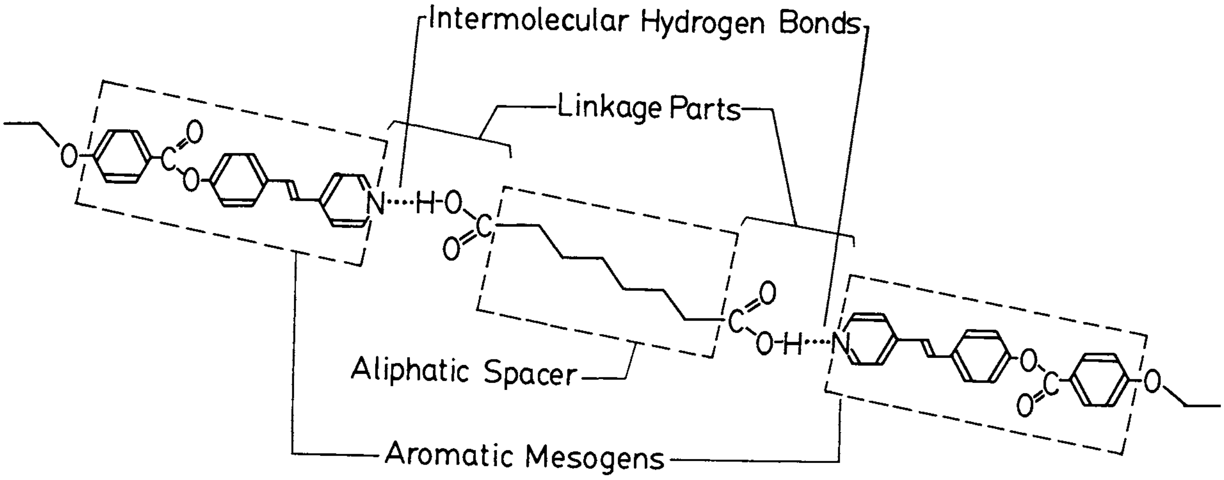

Fig. 3. Proposed structure of the 1:2 complex through intermolecular hydrogen bonds between 6DA and 2Sz.

supported by FT-IR measurements. For a simple mechanical mixture of 2Sz and 8DA, the band at 1700 cm^{-1} due to the carbonyl group of the carboxylic acid dimer is observed. After preparation of the mixture from pyridine solution, the band at 1700 cm^{-1} is shifted and overlaps with the band of the carbonyl group of 2Sz at 1725 cm^{-1}. This is due to the complexation between the carboxylic acid and the pyridine ring.[9,10]

In the structure of the complex between nDA and 2Sz, the intermolecular hydrogen bond is utilized as a linkage group which connects the mesogen and the flexible spacer portions of the twin liquid crystals and this hydrogen bonding shows high thermal stabilities. These results suggest that selective recognitions between H-bond donor and acceptor moieties have great potential in the preparation of new liquid crystalline system.

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