Cooperation of Hydrogen Bonds for Mesophase Stabilization in Supramolecular Assemblies

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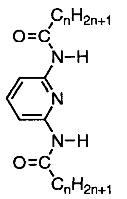
The supramolecular complexes of 2,6-bis(acylamino)-pyridines and mesogenic compounds containing carboxyl-terminated alkyl chains exhibit thermally stable mesomorphic behavior due to the cooperation of two different types of hydrogen bonds.

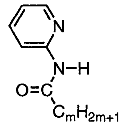
The use of hydrogen bonds for the design of molecular materials such as liquid crystals has recently attracted attention because a wide variety of dynamic functional systems are obtained by such approach.[1-11] Supramolecular mesomorphic complexes consisting of different and independent molecules have been designed and prepared by *hetero*-intermolecular hydrogen bonds. Recently, doubly hydrogen-bonded mesogenic complexes have been built through self-assembly of benzoic acids and 2,6-bis(acylamino)pyridines.[7-9] The formation of *homo*-intermolecular hydrogen bonds between identical molecules can also induce liquid crystallinity. One interesting example is mesomorphic bis(acylamino)benzenes.[12-14] In this case, the hydrogen bonding formation between amide linkages results in stacked molecular associations.

If we properly control cooperation of such several types of hydrogen bonds in molecular organization, new classes of molecular assemblies with dynamic functions will be obtained because in nature various interactions serve molecular organization and highly efficient chemical processes.

We report here a new self-assembled material where two different types of H bond interactions cooperate for mesophase stabilization. As hydrogen bonding components, 2,6-bis(acylamino)pyridines **1a**-**c** and 2-(acylamino)pyridines **2a**-**c** have been selected to form supramolecular complexes with compound **3**, which consists of a mesogenic core linked to a carboxylic acid moiety through a flexible spacer.[15] The formation of double hydrogen bonds between 2-aminopyridine and carboxylic acid moieties was expected for these compounds.[7-9,16,17] Complexes were prepared by evaporation of solution containing equimolar amounts of **1a**-**c** or **2a**-**c** and **3**.[2-4]



1a: n=6
1b: n=7
1c: n=15



2a: m=6
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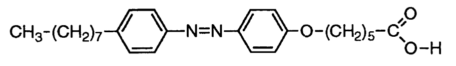

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Figure 1 shows DSC thermograms of complexes of **1c/3** (a) and **2c/3** (b) on cooling. Single sharp phase transitions are observed in the thermograms, which shows that the complexes of **1c/3** and **2c/3** behave as one single component as shown in Figure 2. Both isotropic-mesophase and crystallization temperatures of **1c/3** are higher than those of **2c/3**. It is noteworthy that a liquid-crystalline phase displayed by **1c/3** is more thermally stable than that of **2c/3** despite that complex **1c/3** has two acylamino groups that are not expected to contribute to liquid crystallinity. Table 1 presents the transition behavior of homologous series of the complexes. All complexes show similar tendency to **1c/3** and **2c/3**. Above 110 °C on heating, the mesophases of complexes **1a**-**c/3** are observed, while complexes **2a**-**c/3** exhibit no mesophase at this temperature range. In the mesophases, mosaic textures have been observed on the polarizing microscope, which suggests the

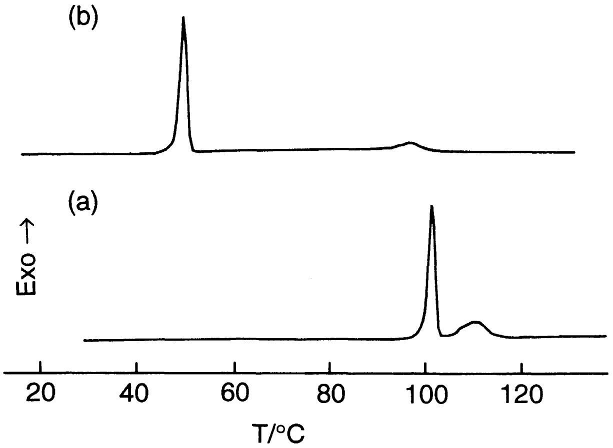


Figure 1. DSC thermograms of complexes of **1c/3** (a) and **2c/3** (b) on cooling.

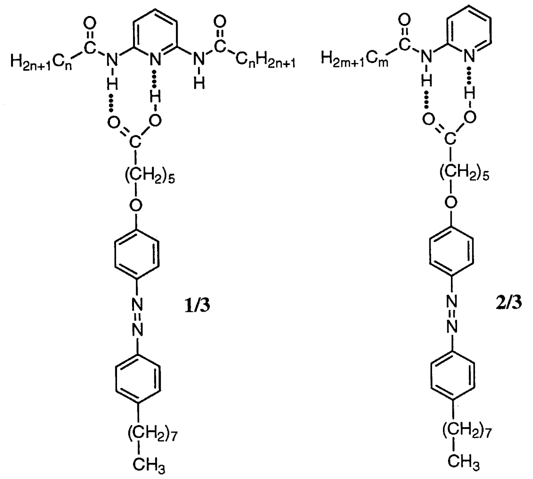
Table 1. Transition temperatures of the supramolecular complexes of aminopyridines and a mesogenic molecule[a]

Complex	Phase behavior / °C									
	Heating					Cooling				
1a/3	K	102	S	120	I	I	112	S	92	K
2a/3	K	47	S	110	I	I	102	S	-33	K
1b/3	K	101	S	122	I	I	113	S	93	K
2b/3	K	34	S	104	I	I	97	S	-31	K
1c/3	K	111	S	123	I	I	111	S	101	K
2c/3	K	67	S	107	I	I	97	S	49	K

[a] K: crystalline, S: smectic, I: isotropic.

existence of ordered smectic phases. The enthalpy changes of isotropization for **1c/3** and **2c/3** are 12.6 and 8.9 kJ/mol, respectively.

It has been reported that the formation of hydrogen bonding between the amide groups for mesomorphic bis(acylamino)-benzenes[12-14] and poly(*p*-phenyleneterephthalamide)[18] promotes the stack of aromatic rings. We attribute the stabilized mesomorphic behavior of **1/3** to the supramolecular association through hydrogen bonds shown in Figure 3. For complex **1/3**, one amide group of **1** is used for the formation of the hydrogen bond with the carbonyl moiety of **3**. Another amide group may form hydrogen bonding with the N-H and C=O groups of adjacent amide moieties, which causes the formation of H bonding chain leading to the stack of the pyridyl rings. This molecular association should contribute to the stabilization of the organized structure. The infrared spectrum for complex **1c/3** supports the existence of this structure. In the carbonyl band region, two peaks are observed at 1670 and 1706 cm^{-1}. The 1670 cm^{-1} band is due to the carbonyl of the amide group of **1c** that participates in hydrogen bonding to the N-H group of the neighboring amide linkage. The band at 1706 cm^{-1} is ascribed to two carbonyl bands: the free carbonyl band of another amide linkage of **1c** and the H-bonded carbonyl band of the carboxylic acid of **3** which interacts with the N-H group for supramolecular complexation. The area of the C=O band at 1670 cm^{-1} to that at 1706 cm^{-1} has a ratio of 1 to 2, which agrees to the proposed structure in Figure 3. Recently, we have reported significant mesophase stabilization of a supramolecular polyamide.[9] The effect of the formation of hydrogen bonding between amide linkages shown in Figure 3 may also contribute to this stabilization.



1/3 **2/3**

Figure 2. Structure of supramolecular complexes **1/3** and **2/3**.

The present study shows that the combination of different hydrogen bonding patterns is useful for the design of functional molecular assemblies.

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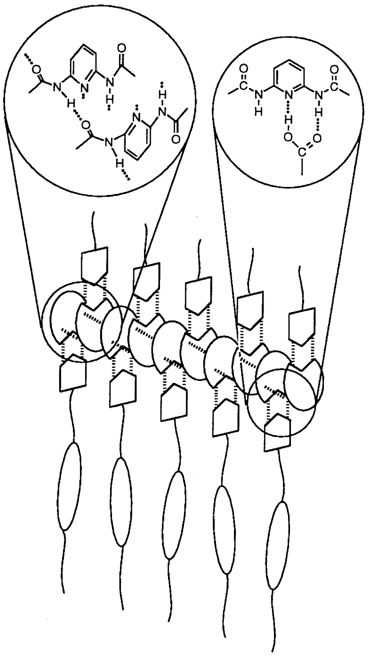

Figure 3. Schematic illustration of molecular association for supramolecular complex derived from **1** and **3**.

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15 Compounds 1 and 2 were prepared from 2,6-bis(amino)- and 2-aminopyridines and corresponding acylchlorides, respectively. Mp.: **1a**, 114 °C; **1b**, 108 °C; **1c**, 114 °C; **2a**, 54 °C; **2b**, 34 °C; **2c**, 70 °C. Compound 3 was commercially available from Dojindo Laboratories. Mp.: 3, 133 °C.
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