Doubly Hydrogen-Bonded Liquid-Crystalline Complexes Obtained by Supramolecular Self-Assembly of 2,6-Diacylaminopyridines and 4-Alkoxybenzoic Acids

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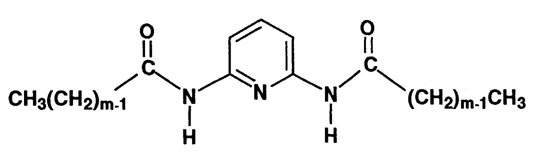
Doubly hydrogen-bonded complexes obtained by 1:1 supramolecular self-assembly of 2,6-diacylaminopyridines and 4-alkoxybenzoic acids exhibit liquid-crystalline behavior.

Molecular self-assembly process has become important to achieve architectures of liquid crystals as well as functional molecular systems. Recently, specific molecular interactions such as hydrogen bonds have been used for self-assembly of supramolecular liquid-crystalline materials.[1,2] For example, dissimilar mesogenic 1:1 complexes with well-defined structures are obtained by the formation of the single hydrogen bonds between carboxylic acid and pyridyl moieties.[1,3-7] Triple hydrogen bonds have also been used for the preparation of mesogenic complexes between uracil and 2,6-diaminopyridines.[2,8] In these cases, pyridine derivatives play a key role for the complexation through the formation of hydrogen bonding and the molecular self-assembly.

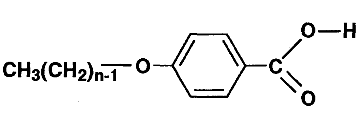
In the solid and the solution states, it is also established that double hydrogen bonds are formed by complexation between a 2-aminopyridyl unit and a carboxylic acid.[9-11] However, no liquid-crystalline complexes consisting of such double hydrogen bonds have been reported.

We here report a new type of supramolecular liquid-crystalline complexes obtained by self-assembly through the formation of double hydrogen bonds between 2-aminopyridine and benzoic acid moieties. As hydrogen bonding components containing a 2-aminopyridine unit, 2,6-diacylaminopyridines **1a** (m=4) and **1b** (m=7) were selected to form 1:1 complexes with benzoic acids. These compounds were prepared from 2,6-diaminopyridine and the corresponding acylchloride. Mp.: **1a**, 121 °C, **1b**, 108 °C. ^{1}H NMR for **1a** (CDCl$_3$, 27 °C, ppm) δ 7.91, 7.68, 7.56, 2.34, 1.70, 1.31, 0.88. Alkoxybenzoic acids (**2a,b**) with n=10 and 12 were complexed with the diacylaminopyridines. ^{1}H NMR spectrum was obtained for the 1:1 mixture of **1a** and **2b** in CDCl$_3$ solution at 25 °C. The proton resonance of the N-H group of **1a** at 7.59 ppm was shifted 0.57 ppm downfield, which shows that hydrogen-bonded 1:1 complex **1a/2b** is formed between **1a** and **2b**. Solid samples of molecular complexes were prepared by evaporation of solution containing an equimolar amount of **1** and **2** or by direct mixing of the mixture in molten state. Phase transitions were examined by DSC and visual observation on polarizing optical microscopy.

DSC thermograms for the 1:1 complex **1a/2b** consisting of **1a** and **2b** in heating and cooling runs are shown in Figure 1. It is noteworthy that the complex behaves as one single component. Moreover, no transition due to either of **1a** and **2b** is observed for the mixture. The complex melts sharply to an isotropic state at 88 °C on heating. Upon cooling, two exothermic peaks that can be ascribed to isotropic-mesophase and mesophase-crystalline transitions are seen for the complex. The enthalpy changes of these transitions are 11.6 and 40.8 kJ/mol, respectively. A mosaic texture with oblong sheets and a homeotropic texture appears for the complex (Figure 2). Some



1a: m=4
1b: m=7



2a: n=10
2b: n=12

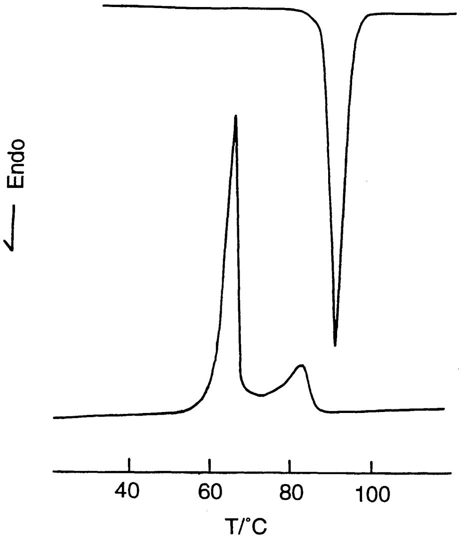


Figure 1. DSC thermogram of the 1:1 complex of **1a** and **2b**.

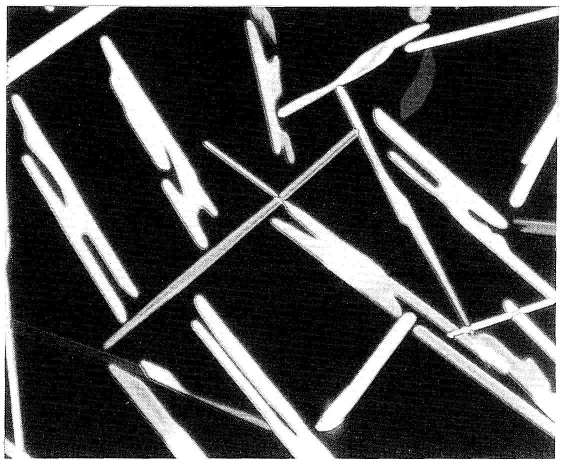


Figure 2. Photomicrograph of the 1:1 complex of **1a** and **2b** at 78 °C on cooling.

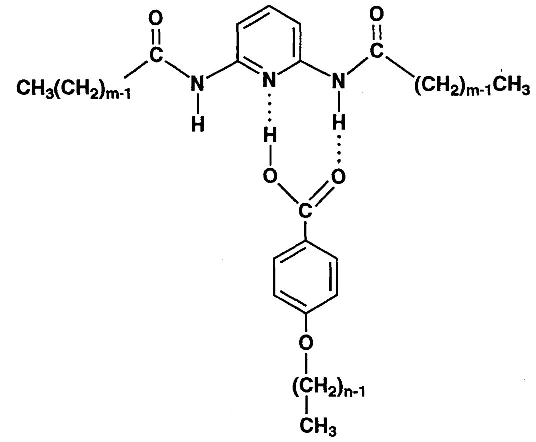


Figure 3. Molecular structure of the 1:1 complex of **1** and **2**.

Table 1. Transition temperatures of doubly hydrogen-bonded complexes of **1** and **2**

	transition temperatures / °C [a]							
Complex	heating			cooling				
1a/2a	K	85	I	I	83	S_B	71	K
1a/2b	K	88	I	I	86	S_B	67	K
1b/2a	K	83	I	I	78	S_B	68	K
1b/2b	K	82	I	I	78	S_B	69	K

[a] K: crystalline, S_B: smectic B, I: isotropic.

H shapes can be seen for the mosaic area. These are characteristics of a smectic B phase.[12] All complexes based on **1** and **2** show monotropic mesomorphic behavior and similar textures (Table 1). X-ray measurements could not be performed because of the crystallization from the monotropic mesophase. No smectic B phase was observed for each component of **1** and **2** on heating and cooling.

We attribute these results to the formation of a new type of liquid-crystalline molecular complex shown in Figure 3. The complex is built by supramolecular self-assembly of the benzoic acids and the 2,6-diacylaminopyridines. The structure of the molecular complex is not a simple rod shape and it is unique for calamitic liquid crystals. It is also of interest that nonmesogenic 2,6-diacylaminopyridines that are useful units for molecular recognition and molecular organization can function as a part of the mesogen.

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