CHEMISTRY LETTERS, pp. 2003-2006, 1990.

Hydrogen-Bonded Liquid Crystals. A Novel Mesogen Incorporating Nonmesogenic 4,4'-Bipyridine through Selective Recognition between Hydrogen Bonding Donor and Acceptor

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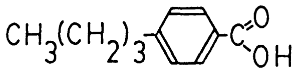
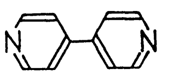
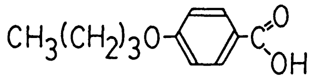
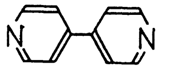
Selective recognition between a benzoic acid derivative and nonmesogenic 4,4'-bibyridine through intermolecular hydrogen bonds results in a novel molecular structure with liquid crystalline properties, in which 4,4'-bipyridine functions as a core unit.

Recently, we have reported a novel family of liquid crystals in which independent and different molecules are self-assembled through selective recognition between hydrogen bonding donor and acceptor moieties.[1-3] The hydrogen bond formed between a benzoic acid and a pyridyl group components of the liquid crystalline complex has shown high thermal stability and functions as an important part of the liquid crystalline complex.

Our strategy has been to build new molecular assemblies through selective intermolecular H-bonding interactions. Hydrogen bonding is one of the important interactions in nature that plays an important role for molecular recognition and molecular assembly. However it is not easy to design and control this interaction to assemble supramolecular structures. The objective of the present communication is to demonstrate how H-bonding may be used to assemble a nonmesogenic rigid molecule as a core into a well-defined complex, with a stable linear structure, that exhibits liquid crystalline behavior.

4,4'-Bipyridine (**4,4'-BPy**) has been selected as the rigid H-bonding acceptor that is capable of recognizing H-bonding donor molecules at each of its pyridyl ends. 4-Butylbenzoic acid (**4BA**) and 4-butoxybenzoic acid (**4OBA**) have been used as H-bonding donors. Complexes (2:1 mole ratio of a benzoic acid and 4,4'-bipyridine) were prepared by slow evaporation from

Table 1. Liquid Crystalline Properties of Hydrogen-Bonded Complexes[a)]

H-Bond donor	H-Bond acceptor	2:1 H-Bonded complex
 nematic 102–116 °C (**4BA**)	 nonmesogenic (**4,4'-BPy**)	K_1 93 K_2 104 S 147 I
 nematic 147–160 °C (**4OBA**)	 nonmesogenic (**4,4'-BPy**)	K_1 130 K_2 134 S 150 N 159 I

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

pyridine solution.

Table 1 shows the thermal behavior of the 2:1 complexes. Sharp phase transitions and homogeneous mesophases are clearly observed for both complexes. For **(4BA)$_2$-BPy** complex, only a smectic phase that is not observed for either single component is seen and this mesophase is stable up to 147 °C. This transition is 31 deg. higher than that of N-I transition of **4BA** dimer. The **(4OBA)$_2$-BPy** complex exhibits smectic (134-150 °C) and nematic (150-159 °C) phases. The phase transitions of the complex are clearly observed in the DSC thermogram (Fig. 1).

These results show that 4,4'-bipyridine functions as a core unit in the liquid crystalline complex as shown in Fig. 2.

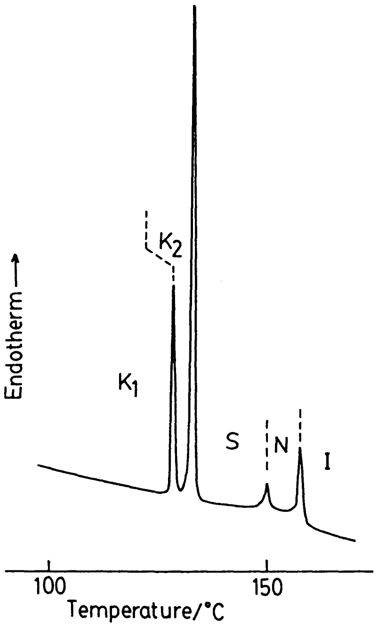


Fig. 1. DSC thermogram of the H-bonded complex between **4OBA** and **4,4'-BPy** on heating.

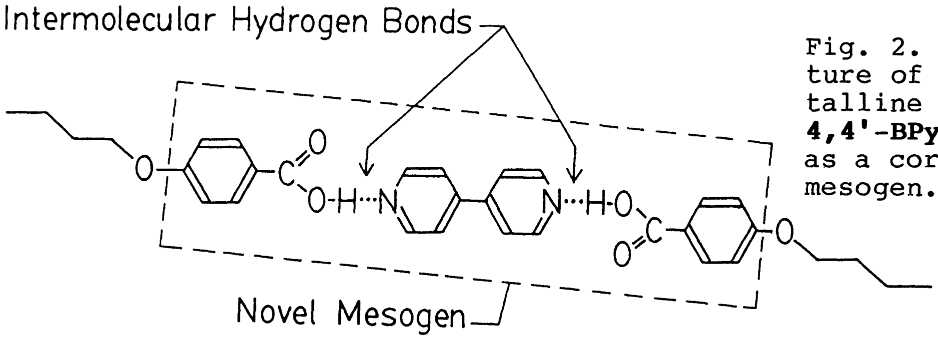


Fig. 2. Proposed structure of the liquid crystalline complex in which **4,4'-BPy** functions as a core unit in the mesogen.

In the complex, a novel mesogen is formed through intermolecular hydrogen bonding. Multiple H-bonds that contribute to the rigidity of complexes have been used by others to organize molecular structures.[4,5] However, in our system, the liquid crystalline behavior suggests strongly that the linear structure is achieved and therefore that high rigidity is obtained at either end of the core through involvement of a single hydrogen bond.

Hydrogen bonding between a proton donor (AH) and pyridine (Py) can be classified into three types as shown below.[6] For type I, no proton

$$\text{A-H} + \text{Py} \rightleftharpoons \underset{\text{(I)}}{\text{A-H}\cdots\text{Py}} \rightleftharpoons \underset{\text{(II)}}{(\text{A}\cdots\text{H}\cdots\text{Py})} \rightleftharpoons \underset{\text{(III)}}{\text{A}^-\cdots\text{H}^+\ \text{Py}} \rightleftharpoons \text{A}^- + \text{H}^+\text{Py}$$

transfer to pyridine occurs. In contrast, pyridine and hydrochloric acid form type III H-bonding. It has been reported[6,7] that for strong type I H-bonds, e.g., COOH····Py, the O-H stretching band appears below 3000 cm^{-1} whereas for weaker H-bonds, e.g., PhOH····Py it is observed at 3010 cm^{-1}.[6] For **$(4OBA)_2$-BPy**, the O-H bands are seen at 2450 and 1880 cm^{-1}, which is indicative of a strong H-bond.

Variable temperature FT-IR measurements were performed[8] on the **$(4OBA)_2$-BPy** complex to examine the effect of temperature on the hydrogen-bonded complex. Figure 3 shows the bands corresponding to carbonyl group and aromatic rings as a function of temperature. The carbonyl band is seen to shift to higher frequencies and becomes broader once the isotropization temperature has been reached at 159 °C. This may show that after the phase transition to isotropic the hydrogen bond becomes less stable because of disordering of the molecules. For a stilbazole-benzoic acid complex,[1,2] the H-bond was stable to over 200 °C in the mesophase. These phase transition temperatures are determined by the specific molecular structures of the complexes because the strength of the COOH····Py H-bond itself does not seem to be dif-ferent in these complexes. Therefore the contribution of H-bonding to stability may be strongly dependent on the states of molecular ordering.

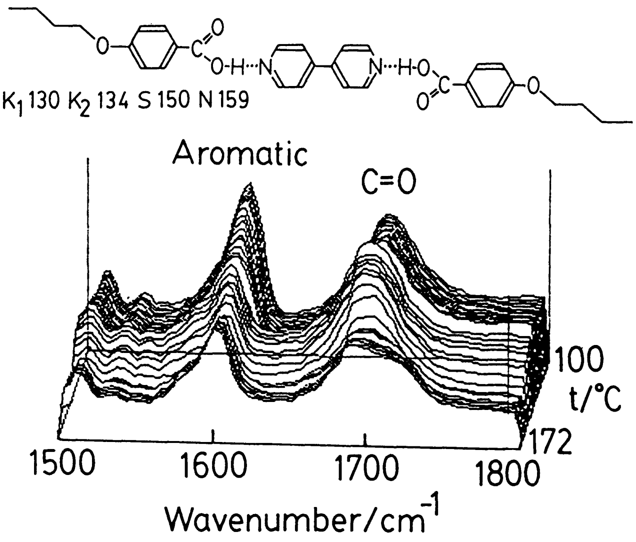


Fig. 3. Variable temperature FT-IR spectrum of the complex between **4OBA** and **4,4'-BPy**.

The novel type of H-bonded liquid crystals reported herein is of interest as they represent the first example of a linear mesogenic structure in which the nonmesogenic rigid unit plays an important role for mesomorphicity through intermolecular hydrogen bonds. A schematic illustration of self-assembly is shown in Fig. 4. This is a new type of molecular organization and recognition using selective intermolecular interactions.

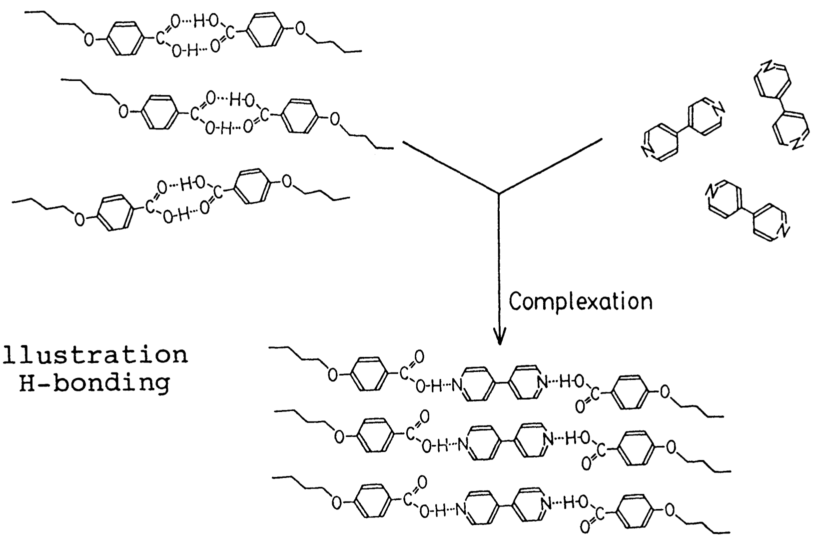


Fig. 4. Schematic illustration of self-assembly of H-bonding donor and acceptor.

The authors thank Ms. Chihiro Jin and Ms. Fumiko Kaneuchi of Japan Spectroscopic Co., Ltd. for their VT FT-IR measurements. Partial support of the Cornell Material Science Center (NSF-DMR 88-18558) is also acknowledged.

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8) Variable temperature FT-IR measurements were conducted on JASCO FT/IR-8300 and Micro-10 equipped with Mettler FP 84 hot stage.

(Received August 2, 1990)