CHEMISTRY LETTERS, pp. 65-68, 1993.

The Simplest Structure of the Hydrogen-Bonded Mesogen Built from 4-Alkoxybenzoic Acid and 4-Alkylpyridine

Mitsuo FUKUMASA, Takashi KATO,*,† Toshiyuki URYU,† and Jean M. J. FRÉCHET††
Materials Development Research Laboratory, Nippon Mining Co., Ltd., Toda, Saitama 335
†Institute of Industrial Science, The University of Tokyo, Minato-ku, Tokyo 106
††Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301, U.S.A.

Newly designed hydrogen-bonded liquid crystals having the simplest mesogenic structure have been obtained by self-assembly of 4-alkoxybenzoic acid and 4-alkylpyridine. The complexes show nematic phases near room temperature. The nematic phase is broadened by mixing of several complexes within a homologous series.

Hydrogen bonding is a key interaction for molecular self-assembly and molecular recognition in nature. The use of hydrogen bonds has great potential for the design of functional materials. In 1988, we discovered that mesogenic structures could be obtained by self-assembly of carboxylic acid and pyridine fragments through the formation of intermolecular hydrogen bonds.1-10) A molecular complex with a well-defined structure is formed from independent and different molecules. The linear and rigid mesogenic structure is achieved through connecting a carboxylic acid and a pyridine via a single hydrogen bond. Hydrogen-bonded mesogens consisting of more than three aromatic rings have been found to exhibit significantly stable liquid crystalline phases.1-10) The mesophases of some of the complexes are stable over 200 °C.1-3,5,6) However, hydrogen-bonded mesogens that show a mesophase near room temperature are not easily prepared.

The objective of the present study is to obtain the hydrogen-bonded complexes with liquid crystalline properties near room temperature. The shortest and simplest hydrogen-bonded mesogen comprizing only

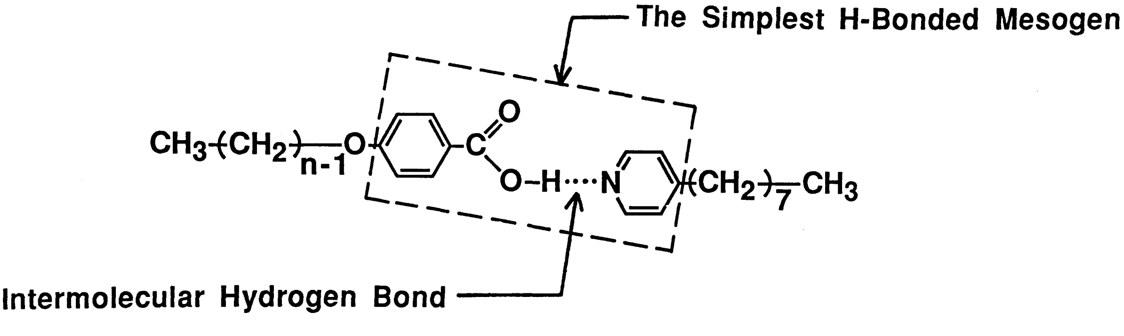

Fig. 1. The structure of the hydrogen-bonded mesogen formed by intermolecular hydrogen bonding between 4-alkoxybenzoic acid (**nOBA**) and 4-octylpyridine (**8Py**).

Table 1. Liquid crystalline behavior of hydrogen-bonded complexes from 4-alkoxybenzoic acid (**nOBA**) and 4-octylpyridine (**8Py**)

Complexes	Transition temperatures[a]				
6OBA-8Py	K	38	N	48	I
7OBA-8Py	K	43	N	49	I
8OBA-8Py	K	45	N	49	I
10OBA-8Py	K	42	N	46	I
12OBA-8Py	K	35	N	54	I

a) Transition temperatures (°C) on heating. K: crystal, N: nematic, I:isotropic.

two aromatic rings shown in Fig. 1 has been designed and built from 4-alkoxybenzoic acid (n-$C_nH_{2n+1}OC_6H_4COOH$: **nOBA**) and 4-octylpyridine (**8Py**)[11] for this purpose. In the complex structure, **nOBA** functions as H-bond donor and **8Py** operates as H-bond acceptor. A simple pyridine ring system is used as H-bond acceptor for the first time in our work with H-bonded mesogens. Equimolar complexes of **nOBA-8Py**s were prepared by direct mixing.[12]

The transition temperatures of the complexes are given in Table 1. The complexes exhibit enantiotropic nematic phases below 50 °C. For example, **6OBA-8Py** shows a nematic phase from 38 to 48 °C. A schlieren texture is clearly observed in the nematic phase (Fig. 2) and a droplet texture is seen at the isotropization transition.[13] These results confirm the formation of the complex shown in Fig. 1. In contrast, hydrogen-bonded complexes comprising three aromatic rings prepared from an alkoxybenzoic acid and a stilbazole usually exhibit significantly higher isotropization temperatures.[9,10] For example, the 1:1 complex of 4-hexyloxybenzoic acid (**6OBA**) and *trans*-4-octyloxy-4'-stilbazole (**8OSz**) shows mesophases from 91 to 159 °C.[9]

These results show that the linear structures of the H-bonded mesogen can be achieved through the intermolecular hydrogen bond that connects the two single nonmesogenic aromatic rings. The basic H-bonded mesogen consisting of two aromatic rings connected by a hydrogen bond is the simplest such mesogen reported to date. It also has the potential to afford nematogens with room temperature mesophases.

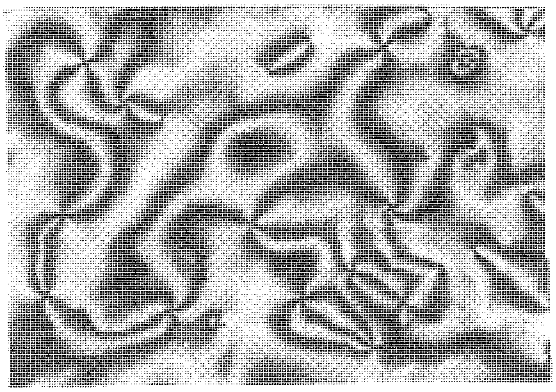

Fig. 2. Photomicrograph of a schlieren texture of a nematic phase for **6OBA-8Py** at 45 °C.

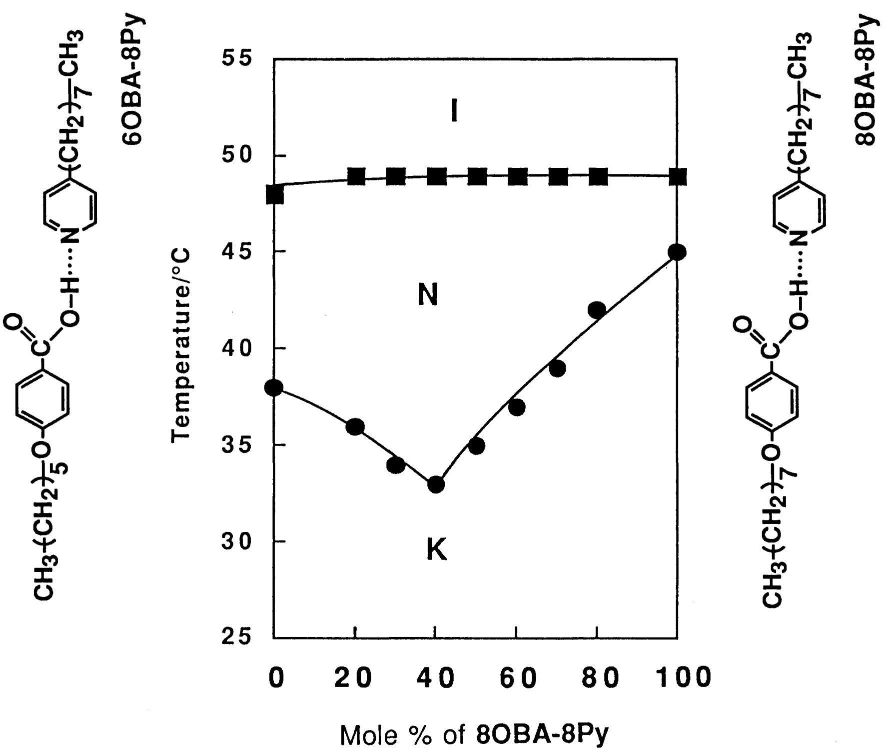

Fig. 3. Binary phase diagram of hydrogen bonded complexes of **6OBA-8Py** and **8OBA-8Py**.

The mixture of **6OBA-8Py** and **8OBA-8Py** has been prepared to depress the melting point and widen the temperature range of the liquid crystalline state. Figure 3 shows the phase diagram of **6OBA-8Py** and **8OBA-8Py**. Wide mesophase ranges are seen for the mixture. In particular, the 6 : 4 mixture of **6OBA-8Py** and **8OBA-8Py** shows a nematic phase from 33 to 49 °C on heating. The DSC thermogram[14] of the 6 : 4 complex is shown in Fig. 4. Two endothermic peaks corresponding to the melting and isotropization transitions are observed clearly. A quaternary mixture of the complexes has been prepared to further depress the melting temperature. A mixture of **5OBA-8Py**, **6OBA-8Py**, **7OBA-8Py**, and **8OBA-8Py** in the ratio of 3.5 : 3.0 : 1.5 : 2.0 exhibits a nematic phase between 25 and 48 °C upon heating.

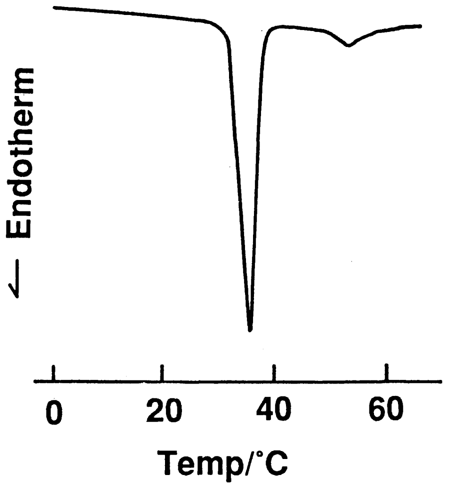

Fig.4. DSC thermogram of the 6:4 mixture of **6OBA-8Py** and **8OBA-8Py**.

The present results may widen the applicability of the hydrogen-bonded liquid crystalline materials for advanced technologies. Systematic studies on the mesomorphicity and physical properties of the H-bonded complexes based on alkylpyridines are now in progress.

References

1) T. Kato and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **111**, 8533 (1989); J. M. J. Fréchet and T. Kato, US Patent 5037574 (1991).
2) T. Kato and J. M. J. Fréchet , *Macromolecules*, **22**, 3818 (1989); **23**, 360 (1990).
3) T. Kato, A. Fujishima, and J. M. J. Fréchet, *Chem. Lett.*, **1990**, 919.
4) T. Kato, P. G. Wilson, A. Fujishima, and J. M. J. Fréchet, *Chem. Lett.*, **1990**, 2003.
5) T. Kato, H. Adachi, A. Fujishima, and J. M. J. Fréchet, *Chem. Lett.*, **1992**, 265.
6) U. Kumar, T. Kato, and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **114**, 6630 (1992).
7) U. Kumar, J. M. J. Fréchet, T. Kato, S. Ujiie, and K. Iimura, *Angew. Chem., Int. Ed. Engl.,* in press.
8) T. Kato, H. Adachi, N. Hirota, A. Fujishima, and J. M. J. Fréchet, *Contem. Top. Polym. Sci.*, in press.
9) T. Kato, H. Kihara, A. Fujishima, T. Uryu, and J. M. J. Fréchet, *Macromolecules*, in press.
10) T. Kato, T. Uryu, F. Kaneuchi, C. Jin, and J. M. J. Fréchet, *Liq. Cryst.*, submitted for publication.
11) 4-Octylpyridine was prepared using the method of Comins and Abdullah. D. L. Comins and A. H. Abudullar, *J. Org. Chem.*, **47**, 4315 (1982). The product was purified by vacuum distillation. B p 112-116 °C (2 mmHg). ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H), 1.26 (m, 10H), 1.62 (m, 2H), 2.59 (t, 2H), 7.10 (d, 2H), 8.47 (d, 2H).
12) An equimolar mixture of H-bond donor and acceptor moieties was once heated to isotropic temperature range and cooled below room temperature.
13) A polarizing microscope (Olympus BH2) equipped with a Mettler FP82HT hot stage was used for visual observations.
14) A heating rate of 2 deg/min was used for the DSC measurement.

(Received September 22, 1992)