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Effect of the Molecular Orientation on the Stability of Hydrogen-Bonded Benzoic Acid Dimers. Infrared Study of Liquid-Crystalline 4-Alkylbenzoic Acids

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Liquid-crystalline benzoic acid derivatives, 4-pentylbenzoic acid and 4-hexylbenzoic acid, have been examined by infrared spectroscopy. These benzoic acids show nematic phases. In the crystalline state, only the dimeric form is observed. However, the monomeric non-hydrogen-bonded benzoic acid appears once the temperature reaches the crystal-nematic transition (melting) point. The fraction of the monomeric moiety increases upon heating and an abrupt increase is observed at the isotropization temperature. These results suggest that the stability of the hydrogen bonds is not simply a function of the temperature, but greatly depends on the molecular orientation.

Hydrogen bonding plays an important role regarding the assembly of molecules in nature. For thermotropic liquid crystals, hydrogen bonds between identical molecules have been used to induce mesomorphism.[1] For example, benzoic acid derivatives have long been known to form mesogenic dimers, due to the hydrogen bonds between two carboxylic acid groups.[2—4]

A new type of liquid-crystalline material built through molecular self-assembly via hydrogen bonds has been reported by Kato and Fréchet.[5—12] They found that mesogenic structures of molecular complexes could be obtained through intermolecular hydrogen bonds between carboxylic acid groups and pyridyl moieties. For this hydrogen bonding, carboxylic acids function as H-bond donors and pyridyl moieties operate as H-bond acceptors. It was shown that the hydrogen bonds between these donor and acceptor moieties could be greatly stabilized by molecular aggregation of liquid-crystalline states.[7,11,12] On the other hand, the hydrogen bonds between two carboxylic acid groups have been used to build new types of functional materials, such as polymeric liquid crystals[6,8] and crystalline materials for nonlinear optics.[13] For the design of H-bonded functional materials that have great potential for advanced technologies, it is important to understand the relationship between the molecular orientation and the stability of the hydrogen bonds. However, to our knowledge, no systematic work has been carried out regarding the effect of molecular aggregation on the stability of the H-bonded mesogenic benzoic acid dimers.

In the present study, liquid-crystalline benzoic acid dimers, 4-pentylbenzoic acid (**1**) and 4-hexylbenzoic acid (**2**) (Chart 1) were examined by infrared spectroscopy to obtain information about the stability of the hydrogen bonds at various phases. These compounds exhibit enantiotropic nematic phases.[2] The infrared spectra as a function of the temperature have been obtained for **1** and **2** from the crystalline state to the isotropic phase. Infrared measurements have also been performed for nonmesogenic 4-propylbenzoic acid (**3**).

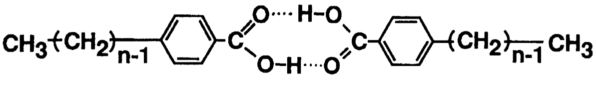
Experimental

Infrared measurements at elevated temperature were conducted on a JASCO Micro FT/IR-200 spectrometer equipped with a Mettler FP84 hot stage. The sample was heated at a rate of 10 °C min^{-1} from 70 to 168 °C. The resolution was 4 cm^{-1}. The sample between two KBr crystal plates was pressed to form a disk for the measurement. The thickness of the KBr disk was less than 1 mm. Samples that were heated to 20 °C higher than the melting point and then cooled to room temperature were used for the measurements.

Results and Discussion

Liquid-crystalline benzoic acids, 4-pentylbenzoic acid (**1**) and 4-hexylbenzoic acid (**2**), were examined using a micro-sampling FT/IR spectrometer equipped with a programmable hot stage. Benzoic acid **1** shows a nematic phase between 88 and 127 °C upon heating, due to the formation of a hydrogen-bonded dimer. Compound **1** exhibits the widest temperature range of the mesophase in the series of 4-alkylbenzoic acids.[2] A nematic phase is also observed for **2** from 97 to 114 °C. A nonmesogenic benzoic acid, 4-propylbenzoic acid (**3**) was also studied by infrared spectroscopy. Compound **3** shows a melting transition at 142 °C.

The infrared spectrum of **1** in the crystalline state at 70 °C in the range of 900—3400 cm^{-1} is shown in Fig. 1. In the crystalline state, benzoic acid derivatives form exclusively the hydrogen-bonded dimer.[14,15] The broad



1 : n=5
2 : n=6
3 : n=3

Chart 1.

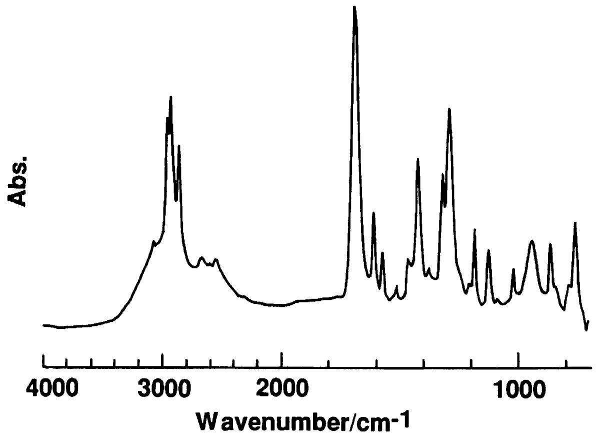


Fig. 1. Infrared spectrum of 4-pentylbenzoic acid (**1**) in the crystalline state at 70 °C.

band centered at 3000 cm^{-1} is assigned to the stretching band of the hydroxyl group (ν(OH)) involving the hydrogen-bonded dimer. The Fermi resonances[16] appear at 2540 and 2665 cm^{-1}, and the stretching carbonyl band at 1695 cm^{-1}. The band of the hydroxyl out-of-plane deformation vibration (γ(OH))[16,17] is observed at 941 cm^{-1}.

Figure 2 shows the infrared spectra for **1** in the range of 1500—1800 cm^{-1} as a function of the temperature from 70 to 168 °C. The band at 1736 cm^{-1} appears once the temperature reaches the melting (crystalline-nematic: K-N) transition temperature at 88 °C, while in the crystalline state the only carbonyl band of the dimer is observed at 1695 cm^{-1}. The 1736 cm^{-1} band is attributable to the C=O band of the non-H-bonded "monomeric" molecule.[15,17] It is noteworthy that the monomeric benzoic acid exists in the nematic state. On the contrary, for pyridine–benzoic acid complexes that form stronger hydrogen bonds than benzoic acid dimers, no monomeric benzoic acid was observed in the liquid-crystalline state, even over 150 °C.[7,11,12] For compound **1**, the intensity of the "free" carbonyl peak increases, while the aromatic ring peak at 1510 cm^{-1} shows no change in intensity. This observation suggests that the intensity change of the C=O peak is not caused by a change in the sample thickness. The proportion of the area of the 1736 cm^{-1} band (A_{1736}) to the total area of the carbonyl bands at 1736 and 1695 cm^{-1} ($A_{1736}+A_{1695}$) is represented by f_{1736},

$$f_{1736}=\frac{A_{1736}}{A_{1736}+A_{1695}}.$$

The area fraction (f_{1736}) against the temperature is plotted in Fig. 3. The value of f_{1736} increases from 0.014 to 0.062 in the nematic state.[19] An abrupt increase can be seen at the nematic-isotropic (N-I) transition at 127 °C. In the isotropic phase, a steady increase of f_{1736} is observed.

Figure 4 shows the infrared spectra of the C=O band region of 4-hexylbenzoic acid (**2**) at elevated temperatures. The increase in the "free" C=O peak is greatly dependent on the phase behavior, as is observed for **1**.

The infrared spectra for **3** as a function of the tem-

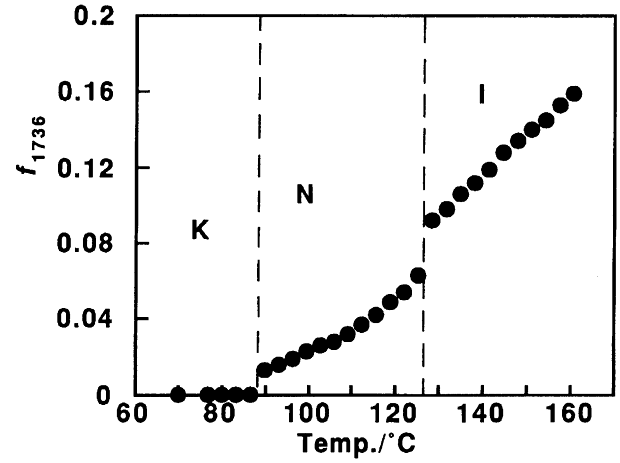


Fig. 3. Proportion of the "free" C=O peak to the total area of C=O peak of **1** as a function of the temperature.

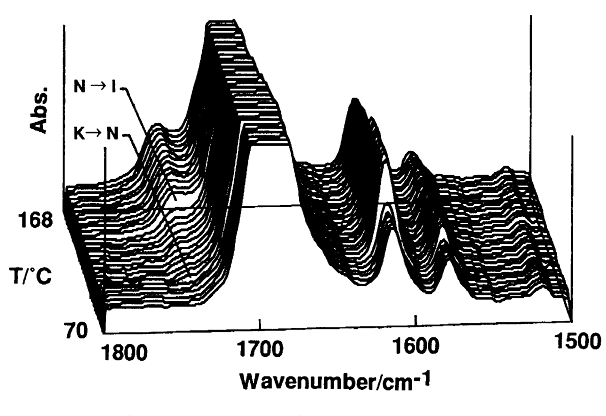


Fig. 2. Infrared spectra of liquid-crystalline 4-pentylbenzoic acid (**1**) in the 1500—1800 cm^{-1} range from 70 to 168 °C.

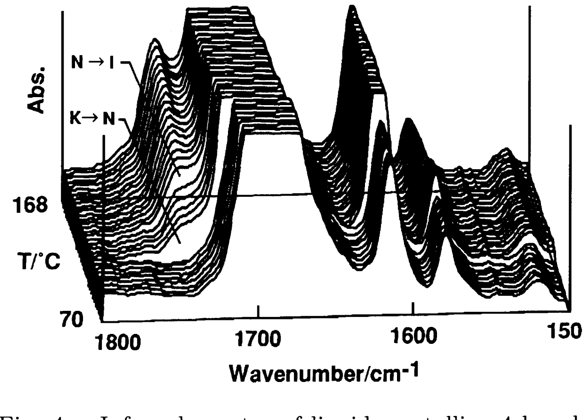


Fig. 4. Infrared spectra of liquid-crystalline 4-hexylbenzoic acid (**2**) in the 1500—1800 cm^{-1} range from 70 to 168 °C.

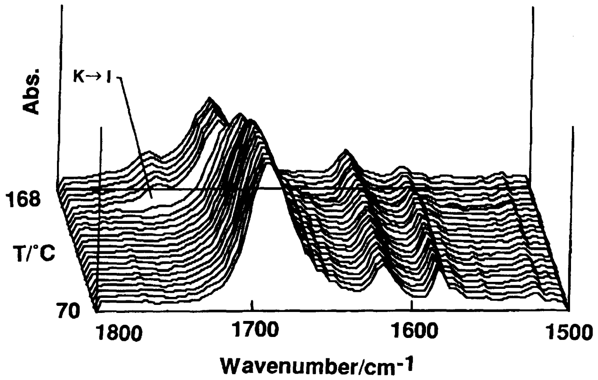


Fig. 5. Infrared spectra of nonmesogenic 4-propylbenzoic acid (**3**) in the 1500—1800 cm^{-1} range from 70 to 168 °C.

perature are shown in Fig. 5. In the crystalline state below 142 °C, no "free" carbonyl peak is observed in the spectra, while for **1** the "free" carbonyl peak of the monomeric molecule develops at above 88 °C.

These results suggest that the stability of the hydrogen bonds of the liquid-crystalline benzoic acid dimer is not simply a function of the temperature, but the molecular ordering greatly affects the stability of the hydrogen bonds.

Figure 6 shows the infrared spectra of **1** in the 700—1050 cm^{-1} region as a function of the temperature. The wavenumbers of the γ(OH) band as a function of the temperature are plotted in Fig. 7. The γ(OH) band observed at 941 cm^{-1} in the crystalline state at 74 °C shifts to lower frequencies in the nematic and isotropic states. In the nematic state, the band is observed at 934 cm^{-1}. After the nematic-isotropic transition, the band shifts to 922 cm^{-1}. Fischmeister showed[17] that there is a linear relation between the hydrogen bond (O–H···O) length and the γ(OH) frequency for carboxylic acid dimers, and that the γ(OH) frequency decreases as the hydrogen bond length of the carboxylic acid dimer increases. The present observation shows that the length of the hydrogen bond of the mesogenic benzoic acid dimer is dependent on the phase behavior.

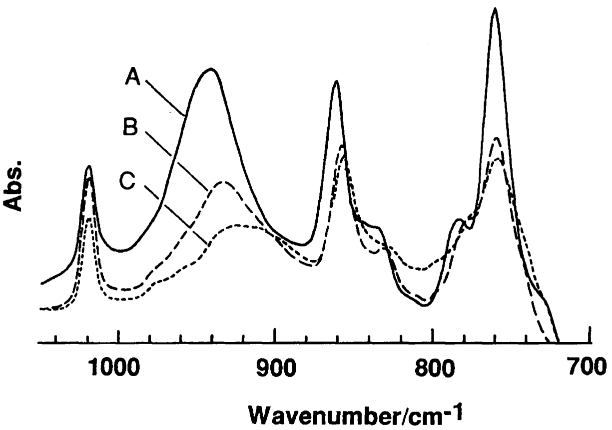


Fig. 6. Infrared spectra of **1** in the 700—1050 cm^{-1} range as a function of the temperature: (A) 74 °C; (B) 110 °C; (C) 140 °C.

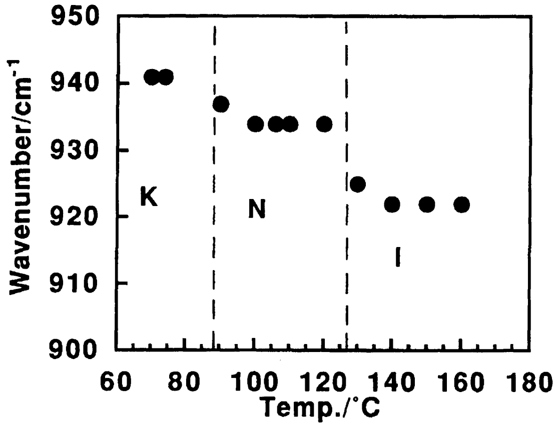


Fig. 7. Plots of the wavenumber of the γ(OH) band of **1** as a function of the temperature.

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References

1) R. Eidenschink, *Angew. Chem., Int. Ed. Engl., Adv. Mater.*, **28**, 1424 (1989).

2) C. Weygand and R. Gabler, *Z. Phys. Chem., Abt. B*, **B46**, 270 (1940).

3) G. M. Bennett and B. Jones, *J. Chem. Soc.*, **1939**, 420.

4) G. W. Gray and B. Jones, *J. Chem. Soc.*, **1953**, 4179.

5) T. Kato and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **111**, 8533 (1989).

6) T. Kato and J. M. J. Fréchet, *Macromolecules*, **22**, 3818 (1989).

7) T. Kato, P. G. Wilson, A. Fujishima, and J. M. J. Fréchet, *Chem. Lett.*, **1990**, 2003.

8) U. Kumar, T. Kato, and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **114**, 6630 (1992).

9) T. Kato, H. Kihara, T. Uryu, A. Fujishima, and J. M. J. Fréchet, *Macromolecules*, **25**, 6836 (1992).

10) M. Fukumasa, T. Kato, T. Uryu, and J. M. J. Fréchet, *Chem. Lett.*, **1993**, 65.

11) T. Kato, T. Uryu, F. Kaneuchi, C. Jin, and J. M. J. Fréchet, *Liq. Cryst.*, **14**, 1311 (1993).

12) T. Kato, J. M. J. Fréchet, P. G. Wilson, T. Saito, T. Uryu, A. Fujishima, C. Jin, and F. Kaneuchi, *Chem. Mater.*, **5**, 1094 (1993).

13) M. C. Etter and G. M. Frankenbach, *Chem. Mater.*, **1**, 10 (1989).

14) R. F. Bryan and J. J. Jenkins, *J. Chem. Soc., Perkin Trans. 2*, **1975**, 1171.

15) R. F. Bryan and L. Fallon, *J. Chem. Soc., Perkin Trans. 2*, **1975**, 1175.

16) V. P. Privalko, G. A. Puchkovskaya, E. N. Shermatov, and A. A. Yakubov, *Mol. Cryst. Liq. Cryst.*, **126**, 289 (1985).

17) I. Fischmeister, *Spectrochim. Acta*, **20**, 1071 (1964).

18) J. Y. Lee, P. C. Painter, and M. M. Coleman, *Macromolecules*, **21**, 346 (1988).
19) The absorptivity ratio of these carbonyl bands will be determined in the future study to evaluate the real mole fraction of the "free" carboxylic acid group.