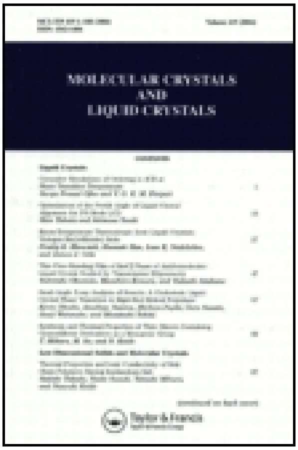

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A New Insight into the Hydrogen-bonded Liquid Crystals Built from Carboxylic Acids and Pyridyl Moieties

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A New Insight into the Hydrogen-bonded Liquid Crystals Built from Carboxylic Acids and Pyridyl Moieties

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The hydrogen-bonded complex of 4-hexyloxybenzoic acid and 4,4'-bipyridine (HOBA-BPy) was selected as an example to study the dynamic behavior of the hydrogen-bonded mesogens in liquid crystalline state by using temperature-variable FTIR (TV-FTIR). We found that there exist two dynamic equilibria of hydrogen bonding dissociation-association in the melting state of the complex, and the liquid crystallinity of the complex should be contributed from both of the two mesogens, HOBA···BPy···HOBA and $(HOBA)_2$ dimers.

Keywords Hydrogen bonds, liquid crystals, carboxylic acids, pyridyl moieties, temperature variable FTIR

INTRODUCTION

Benzoic acid derivatives have long been known to exhibit liquid crystallinity as a result of dimer formation in a process that involves the formation of *homo*-intermolecular hydrogen bonds [1–3]. In 1988, Kato et al. reported that mesogenic structures could be obtained by self-assembly of pyridine and carboxylic acid fragments through the formation of *hetero*-intermolecular hydrogen bonds [4–6]. Since then, the concept of building mesogenic structures through the hydrogen bond between the H-bond donor and acceptor moieties has been widely accepted and extended to a variety of mesogenic structures that form a novel family of liquid crystals [7–15].

Hydrogen bond is one kind of weak attractive force between a functional group A-H and an atom or group of atom B in the same or a different

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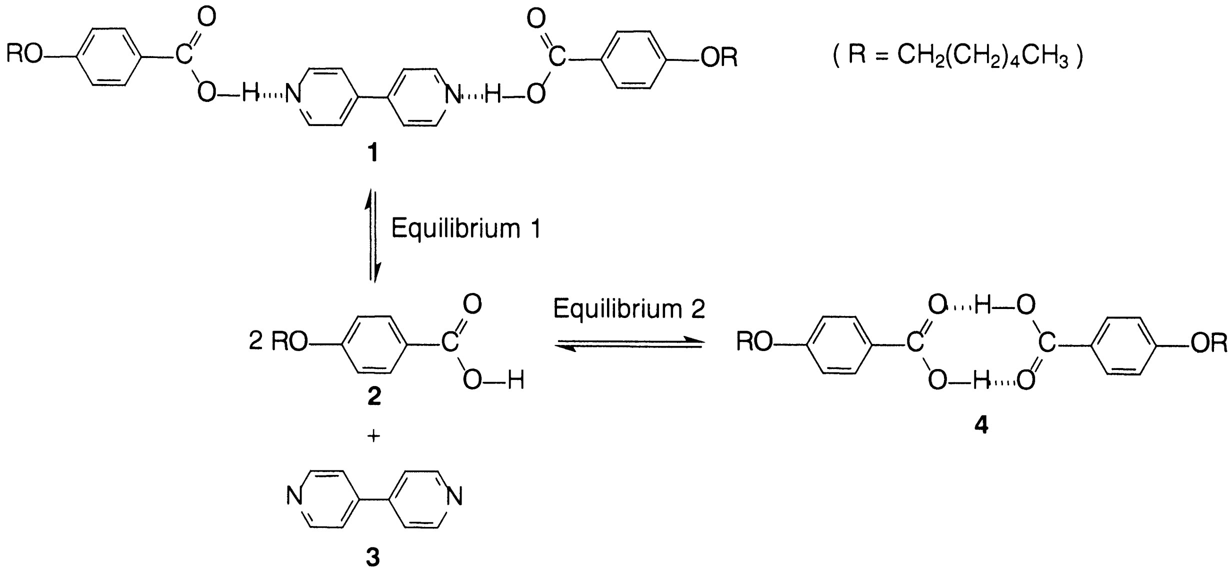
molecule [16]. The bond energy is in the order of 9–40 kJ/mol, which is far less than the energies of covalent bonds (200–400 kJ/mol). Hydrogen bonds can exist in the solid, liquid, and in solution, and even in the gas phase. But in solution, liquid, or gas phases hydrogen bonds can only exist in a dynamic form owing to their low bond energies, i.e., they rapidly form and break [17]. This characteristic of hydrogen bonds determines that hydrogen-bonded mesogens in liquid crystalline state are not immutable as compared to covalent bonded mesogens. The mesogens constantly disappear as the hydrogen bonds dissociate. In the meantime, new mesogens constantly form due to the hydrogen bonding association. In fact, the dynamic equilibrium of dissociation-association of hydrogen-bonded mesogens had been reported in carboxylic acid liquid crystals and liquid crystals built from carboxylic acids and pyridyl moieties as well [18–21]. But in the latter case it seems to be more complicated, considering that there are two kinds of possibilities of hydrogen bonding association, as depicted in Scheme 1 (4-hexyloxybenzoic acid (HOBA)-4,4′-bipyridine (BPy) complex was used as an example).

It has been proven that there is only one kind of hydrogen bonding association (COOH···N) in the solid state of the complex because carboxylic acids form stronger hydrogen bonds with pyridyl moieties than with themselves [20, 21]. However, in the melting state this selectivity could be weakened by the enhanced molecular mobility resulting from the high temperature, by which means it might be possible to have the second equilibrium—the hydrogen bonding association of carboxylic acid dimers—to appear. Making sure whether or not the two dynamic equilibria coexist in the liquid crystalline phase of the complex is very important and necessary to our correct evaluation of the phase behavior and thermal stability of these kind of liquid crystals. It should be pointed out that in a similar study to ours Sidertous et al. [22] proved that the second equilibrium does appear at high temperature, essentially at isotropic or nematic phase of the complex, through the analysis of the infrared spectra at various temperatures. In this paper, we confirmed the coexistence of the two dynamic equilibria in the melting state of the complex (not only in isotropic or nematic phase, but also in smectic phase) using temperature variable FTIR (TV-FTIR) analysis of the carbonyl stretching band of COOH, which is sensitive to the variation of hydrogen bonds. In addition, the relative contribution to the liquid crystallinity of the complex from the two kinds of mesogens was roughly calculated. Since all the complexes of carboxylic acids with pyridyl units show similar behavior, HOBA-BPy complex was selected as an example for the purposes of this investigation.



SCHEME 1 Dynamic equilibria of the hydrogen-bonded complex of HOBA-BPy in melting state.

EXPERIMENTAL

Materials: 4-hexyloxybenzoic acid (Aldrich, 98%, m.p.: 105–153°C) and 4,4′-bipyridine (Merck, >99%, m.p.: 109–112°C) were both commercially available and used without further purification. Pyridine was obtained from Beijing Chemical Co., and dried and then distilled before use. The hydrogen bonded complex was prepared by an evaporation technique from a pyridine solution containing 4-hexyloxybenzoic acid and 4,4′-bipyridine (2:1 in molar ratio) followed by drying *in vacuo* at 60°C [20]. The complex shows a smectic C phase in the temperature range of 105–130°C, a smectic A phase in the range of 130–158°C, and then isotropic phase >158°C.

TV-FTIR spectra were recorded on a Nicolet 750 FTIR spectrometer (with resolution of $4\,\mathrm{cm}^{-1}$) equipped with a Mettler FP-84 hot-stage at a heating rate of $10°\mathrm{C\ min}^{-1}$. The sample for measurement was prepared by casting the pyridine solution of the complex (or pure HOBA) onto a KBr crystal, which was then dried *in vacuo* at 60°C for 20 h. Afterwards another KBr crystal was used to sandwich the sample. The sample was annealed at 120°C before measurement.

RESULTS AND DISCUSSION

During the melting process of the complex, there was a set of changes in the infrared spectra including O-H stretching and C=O stretching. The variation of the intensity of C=O stretching band ($\nu_{C=O}$) was most remarkable, and that accurately reflects the hydrogen bonding dissociation/association process. Therefore, we focused our analysis on the intensity variation of $\nu_{C=O}$.

For the HOBA···BPy···HOBA complex structure, the carbonyl group is in "free" state. For the HOBA dimeric structure, the carbonyl group is hydrogen-bonded with hydroxyl of another COOH. In both cases, $\nu_{C=O}$ falls in the range of $1680\text{–}1690\,\mathrm{cm}^{-1}$ (in following text, $\nu_{C=O}$ refers to the carbonyl stretching at $1680\text{–}1690\,\mathrm{cm}^{-1}$). But in the latter case, the intensity of $\nu_{C=O}$ is remarkably higher [23, 24]. It should be noted that the IR absorption at around $1730\,\mathrm{cm}^{-1}$ is attributed to the monomeric HOBA [25, 26]. For comparison purposes, the TV-FTIR spectra of the pure HOBA and HOBA-BPy complex are shown in Figures 1a and 1b, respectively.

It is noteworthy that the intensity variation of the $\nu_{C=O}$ for pure HOBA and HOBA-BPy complex is just opposite. In the case of pure HOBA, the intensity of $\nu_{C=O}$ decreases as the sample is melted. While in the case of

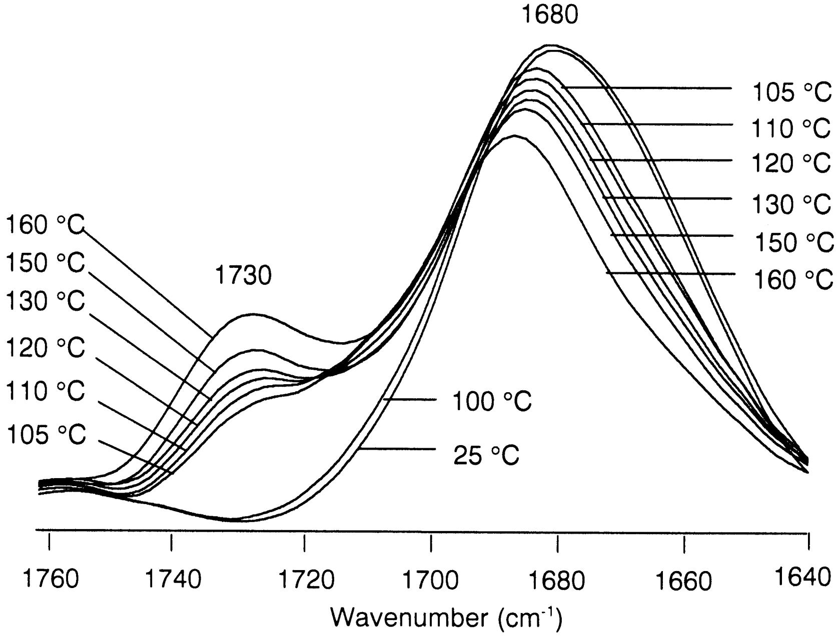


FIGURE 1a TV-FTIR spectra of pure 4-hexyloxybenzoic acid (HOBA).

HOBA-BPy complex, the intensity of $\nu_{C=O}$ increases as the sample is melted. The experiments were repeated many times, and the results were reproducible. In addition, similar results had been reported in other complexes by Kato et al. [7, 20, 21]. For the former case it is easy to understand because there is only one equilibrium in the melting state of pure HOBA. Hydrogen bonding dissociation definitely results in the reduction of the dimeric structures. As a result, the intensity of $\nu_{C=O}$ will accordingly decrease. The appearance of IR absorption of monomeric HOBA also confirms the occurrence of the dissociation of dimers. For the latter case, it should be the same if there is only one equilibrium as well. Therefore the only possible explanation for the intensity enhancement of $\nu_{C=O}$ is the occurrence of the second equilibrium. The second equilibrium gives rise to $(HOBA)_2$ dimers, which may somewhat compensate the reduction of HOBA···BPy···HOBA complexes due to the first equilibrium. As mentioned above, the intensity of $\nu_{C=O}$ of the $(HOBA)_2$ dimer is higher than that of HOBA···BPy···HOBA complex, which means that the overall intensity of $\nu_{C=O}$ could, on the contrary, increase.

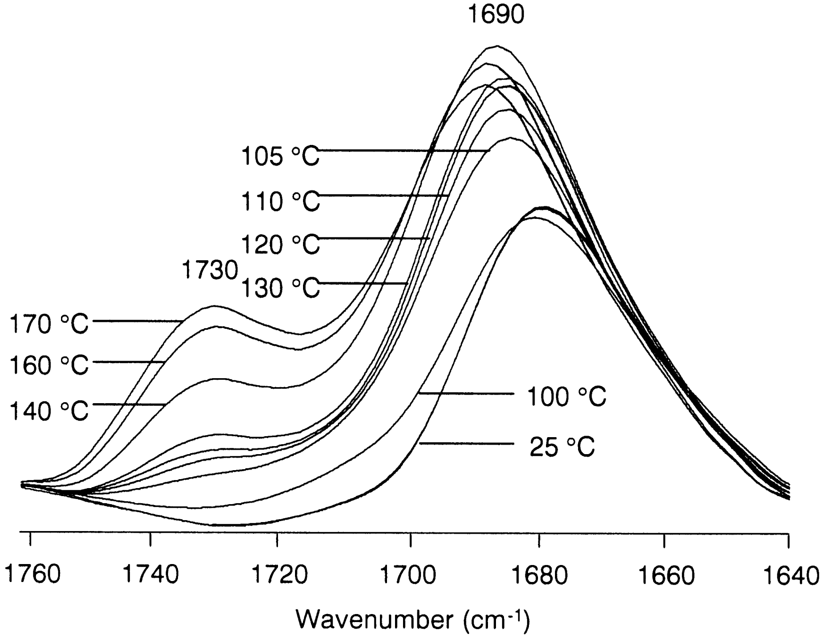


FIGURE 1b TV-FTIR spectra of the hydrogen-bonded complex of 4-hexyloxy benzoic acid and 4,4′-bipyridine (HOBA-BPy).

With the rise of temperature, the intensity of $\nu_{C=O}$ continues to increase, which means that more dimers are formed. We can take a further step and roughly estimate the relative ratio of the two mesogens in the melting state of the complex in terms of the intensity of $\nu_{C=O}$. We assume the intensity of $\nu_{C=O}$ of the mesogen (**1**) at solid state of HOBA-BPy complex as I_1, the intensity of $\nu_{C=O}$ of the mesogen (**4**) at solid state of pure HOBA as I_2. I_1 and I_2 are calibrated by referring to the intensity of ν_{as} (C-O-C) at around $1255\,\text{cm}^{-1}$, which is not affected by the addition of BPy. Since the intensity of IR absorption is proportional to the amount of sample, which here represents the sum of the two mesogens, the overall intensity of $\nu_{C=O}$ in the melting state of the complex could be represented as

$$I = xI_1 + (1 - x)I_2, \tag{1}$$

where x represents the content (percent) of mesogen (**1**), and $1 - x$ represents the content of mesogen (**4**). The Equation (1) is transformed into

TABLE 1 The relative content of mesogen (**1**) and mesogen (**4**) in liquid crystalline state of the HOBA-BPy complex

			Relative content (%)	
Temperature (°C)	*Mesophase*	*Intensity of* $\nu_{C=O}$[#]	*Mesogen (***1***)*	*Mesogen (***4***)*
105	S_C	0.40	82	18
110	S_C	0.42	75	25
120	S_C	0.45	70	30
130	S_C	0.46	68	32
140	S_A	0.51	56	44

[#] Calibrated value.

$$x = (I - I_2)/(I_1 - I_2). \tag{2}$$

By this equation, the relative content of the two mesogens were obtained. The results are listed in Table 1. The data are quite rough. The accuracy could be improved by using high resolution FTIR or high temperature NMR.

CONCLUSION

Based on the above data, it is concluded that in the liquid crystalline state of the complex

1. The selectivity of hydrogen bonding association becomes weaker with the rise of temperature.
2. The content of mesogen (**4**) is unexpectedly high, especially at high temperature, which means that the contribution of mesogen (**4**) to liquid crystallinity of the complex should not be neglected when studying this class of liquid crystals. This concept should be applicable to all hydrogen bonded systems built from carboxylic acids and pyridyl moieties or other *hetero*-hydrogen-bonded liquid crystals.

REFERENCES

1. G. W. Bennett and B. Jones, *J. Chem. Soc.*, 420–425 (1939).
2. G. W. Gray and B. Jones, *J. Chem. Soc.*, 4179–4180 (1953).
3. G. W. Gray, *Molecular Structure and Properties of Liquid Crystals* (Academic Press, New York, 1962) p. 148.
4. T. Kato and J. M. J. Frechet, *J. Am. Chem. Soc.*, 111, 8533–8534 (1989).

5. T. Kato and J. M. J. Frechet, *Macromolecules*, 22, 3816–3819 (1989).
6. J. M. J. Frechet and T. Kato, U.S. Patent 5 037 574 (1991).
7. T. Kato and J. M. J. Frechet, *Macromol. Symp.*, 98, 311–326 (1995).
8. T. Kato, *Handbook of Liquid Crystals*, D. Demus, J. W. Goodby, G. W. Gray, H. W. Spiess, and V. Vill, eds. (Wiley-VCH, Weinheim, 1998) p. 969.
9. J.-M. Lehn, *Makromol. Chem., Macromol. Symp.*, 69, 1–17 (1993).
10. C. M. Paleos and D. Tsiourvas, *Angew. Chem., Int. Ed. Engl.*, 34, 1696–1711 (1995).
11. E. Fan, C. Vincent, S. J. Geib, and A. D. Hamilton, *Chem. Mater.*, 6, 1113–1117 (1994).
12. D. S. Lawrence, T. Jiang, and M. Levett, *Chem. Rev.*, 95, 2229–2260 (1995).
13. J. L. M. van Nunen, B. F. B. Folmer, and R. J. M. Nolte, *J. Am. Chem. Soc.*, 119, 283–291 (1997).
14. C. G. Bazuin, F. A. Brandys, T. M. Eve, and M. Plante, *Macromol. Symp.*, 84, 183–196 (1994).
15. C. Lin, Y. S. Lin, Y. T. Chen, I. Chao, and T. W. Li, *Macromolecules*, 31, 7298–7311 (1998).
16. P. Schuster, G. Zundel, and C. Sandorfy, *The Hydrogen Bond: Recent Developments in Theory and Experiments* (North-Holland Publishing Co., Amsterdam, 1976).
17. J. March, *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure*, 4th ed. (John Wiley & Sons, New York, 1992) p. 76.
18. L. Cui, J. N. Liu, P. Xie, and R. B. Zhang, *Liq. Cryst.*, 26, 605–608 (1999).
19. S. K. Kang, E. T. Samulski, P. Kang, and J. Choo, *Liq. Cryst.*, 27, 377–385 (2000).
20. T. Kato, J. M. J. Frechet, P. G. Wilson, T. Saito, T. Uryu, A. Fujishima, C. Jin, and F. Kaneuchi, *Chem. Mater.*, 5, 1094–1100 (1993).
21. T. Kato, T. Uryu, F. Kaneuchi, C. Jin, and J. M. J. Frechet, *Liq. Cryst.*, 14, 1311–1317 (1993).
22. Z. Sideratou, D. Tsiourvas, C. M. Paleos, and A. Skoulios, *Liq. Cryst.*, 22, 51 (1997).
23. J. Wenograd and R. A. Spurr, *J. Am. Chem. Soc.*, 79, 5844–5848 (1957).
24. G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* (W. H. Freeman and Company, San Francisco, 1960) p. 137.
25. A. Azima and C. W. Brown, *Spectrochim. Acta A*, 31, 1475–1479 (1975).
26. H. Xu, N. Kang, P. Xie, R. B. Zhang, and D. F. Xu, *Liq. Cryst.*, 27, 169–176 (2000).