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Hydrogen-bonded liquid crystals built from hydrogen-bonding donors and acceptors Infrared study on the stability of the hydrogen bond between carboxylic acid and pyridyl moieties

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Development of supramolecular hydrogen-bonded liquid crystals and its impact on liquid-crystalline and materials science

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A Commentary on the paper "Hydrogen-bonded liquid crystals built from hydrogen-bonding donors and acceptors. Infrared study on the stability of the hydrogen bond between carboxylic acid and pyridyl moieties", by Takashi Kato, Toshiyuki Uryu, Fumiko Kaneuchi, Chihiro Jin and Jean M.J. Fréchet. First published in *Liquid Crystals*, **14**, 1311–1317 (1993).

The design of liquid crystals has undergone a very rapid development in recent years [1–7]. New molecular shapes, and self-assembled structures, and unexpected properties have been found in liquid-crystalline materials. One of the growing areas is a supramolecular and non-covalent approach to the design of liquid-crystalline assemblies and complexes [5]. In these cases, specific intermolecular interactions such as hydrogen bonding [8–22], ionic interactions [23], and charge transfer interactions [24] that are stronger than van der Waals interactions drive the molecular assembly of liquid-crystalline structures. A variety of functional groups can be introduced as the parts of mesogenic components in these self-assembled materials. These new exotic liquid-crystalline materials have attracted considerable attention because of their great potential for new dynamic functions such as ion, charge, and mass transportation, photo-function, sensing, stimuli-responsive properties, and bio-function [5, 6].

Our 1993 paper was published in *Liquid Crystals* as part of the Proceedings of the International Liquid Crystal Conference held at Pisa, Italy in 1992 [21]. It is one of the papers that opened the new field of supramolecular liquid crystals. The supramolecular and non-covalent approaches to the design of liquid crystals and other related materials are now widely accepted and studied [12–20].

In 1989, Kato and Fréchet found that 1:1 complexation of benzoic acid and stilbazole leads to the formation of a well-defined structure of a hydrogen-bonded mesogen by the intermolecular hydrogen bonding between the carboxylic acid and the pyridine as shown in figure 1 (a) [8]. In this work, the molecular recognition process between different molecular species was successfully used to form a new mesogenic molecular structure for the first time. Before this discovery, only hydrogen-bonded compounds consisting of identical molecules, such as benzoic acids [25], sugars [26], and amides [27] had been known to exhibit mesomorphism. At almost the same time, Lehn and coworkers found that diaminopyridines and uracil derivatives form triply hydrogen-bonded liquid-crystalline complexes (see figure 1 (b)) [10]; they form columnar liquid-crystalline structures. Supramolecular side-chain [9] and main-chain [11] polymers that show liquid-crystalline order in bulk states have also been developed (see figure 1 (c), (d)). Until that time, supramolecular processes had been mostly studied in solution. These early studies by Kato and Fréchet [8, 9], and Lehn and coworkers [10, 11] have shown great possibilities as well as the importance of the use of hydrogen bonding not only in the design of liquid crystals but also in the design of condensed states of soft materials such as polymers, low-molecular-weight organic molecules, and composites. The field of supramolecular materials has evolved between the fields of supramolecular chemistry and materials science.

The supramolecular liquid crystals were developed in the following way. In March, 1988, Dr Takashi Kato joined the group of Professor Jean M. J. Fréchet at the Department of Chemistry, Cornell University as a postdoctoral research associate after he obtained his Ph.D. under the supervision of Professor Toshiyuki Uryu. Dr Kato studied the structure and properties of liquid-crystalline polyesters containing phenyl ester mesogenic groups [28]. Kato and Fréchet started a new project on the design and preparation of new liquid crystals involving hydrogen bonding. The basic idea is

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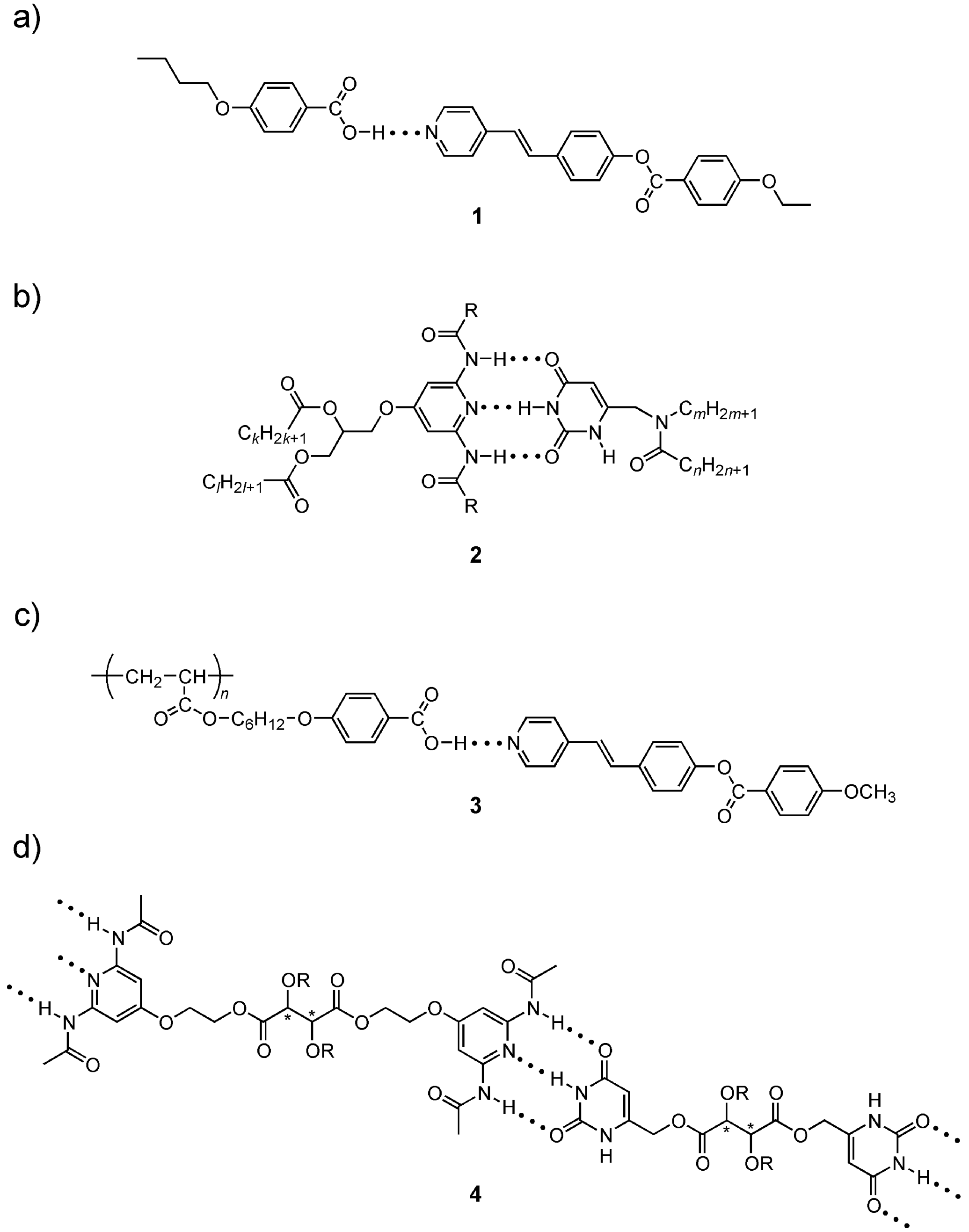

Figure 1. Supramolecular hydrogen-bonded mesogenic molecules: (a) low molecular weight complex by Kato and Fréchet in 1989 [8]; (b) low molecular weight complex by Lehn and coworkers in 1989 [9]; (c) side-chain polymeric complex by Kato and Fréchet in 1989 [10]; (d) main-chain polymeric complex by Lehn and coworkers in 1990 [11].

the introduction of hydrogen bonding in the binary liquid crystal mixtures consisting of components capable of hydrogen bonding. The combination of stilbazole and benzoic acids was successful in the induction and stabilization of the liquid-crystalline phases displayed by hydrogen-bonding proton donors and acceptors. It was known that the pyridyl group with phenol and benzoic acids enhanced the miscibility of polymer blends due to the formation of stable hydrogen bonds [29]. Stilbazoles were chosen because they have the pyridyl group at the end of their rod-like structure. At that time, liquid-crystalline stilbazoles had been documented [30] and metallomesogens containing stilbazoles were also reported [31].

The 1993 paper [21] reports variable temperature infrared studies on the state of hydrogen bonding in a

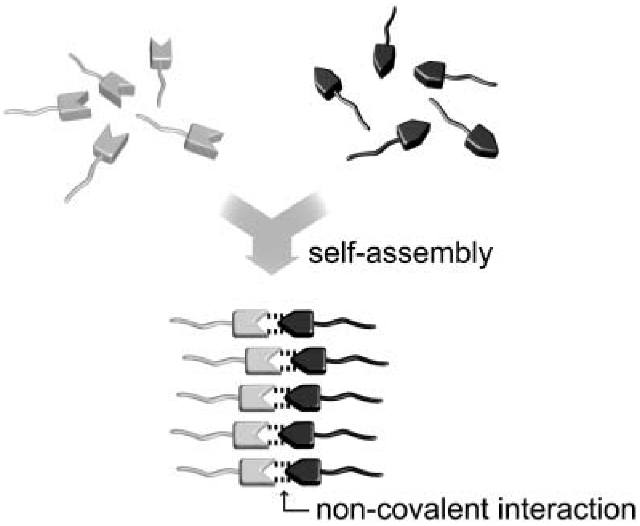

Figure 2. Supramolecular assembly of liquid-crystalline complexes through specific non-covalent interactions.

hydrogen-bonded supramolecular complex consisting of 4-hexyloxybenzoic acid and *trans*-4-propoxy-4′-stilbazole. The results have indicated that the hydrogen bond formed between pyridines and benzoic acids is quantitatively formed and stabilized in the liquid-crystalline ordered condensed states, while a small amount of free benzoic acid forms from the benzoic acid dimer even in the ordered states. The collaboration with Ms Kaneuchi and Ms Jin at Japan Spectroscopic Co. Ltd (JASCO) is greatly appreciated in obtaining these results using a microscopic infrared spectrometer (JASCO Micro FT/IR-200 spectrometer) equipped with a heating hot stage (Mettler FP84). One of the interesting properties of the supramolecular hydrogen bonded mesogens is their high thermal stability. The results indicate the stabilization effects of ordered condensed states of liquid crystals on hydrogen bonds. Molecular interactions in these condensed states are very different from those observed for host-guest chemistry in dilute solutions where each complex exists as a single component that is surrounded only by solvent molecules. Variable-temperature infrared studies were shown to be a powerful tool to study the states of hydrogen bonding. These measurements were also applied to other supramolecular hydrogen-bonded materials [32].

It should be pointed out that the fact that the supramolecular hydrogen-bonded mesogen behaves like a covalently-bonded component of a mesogen has suggested a new concept and strategy for the use of non-covalent approaches to material design. In the

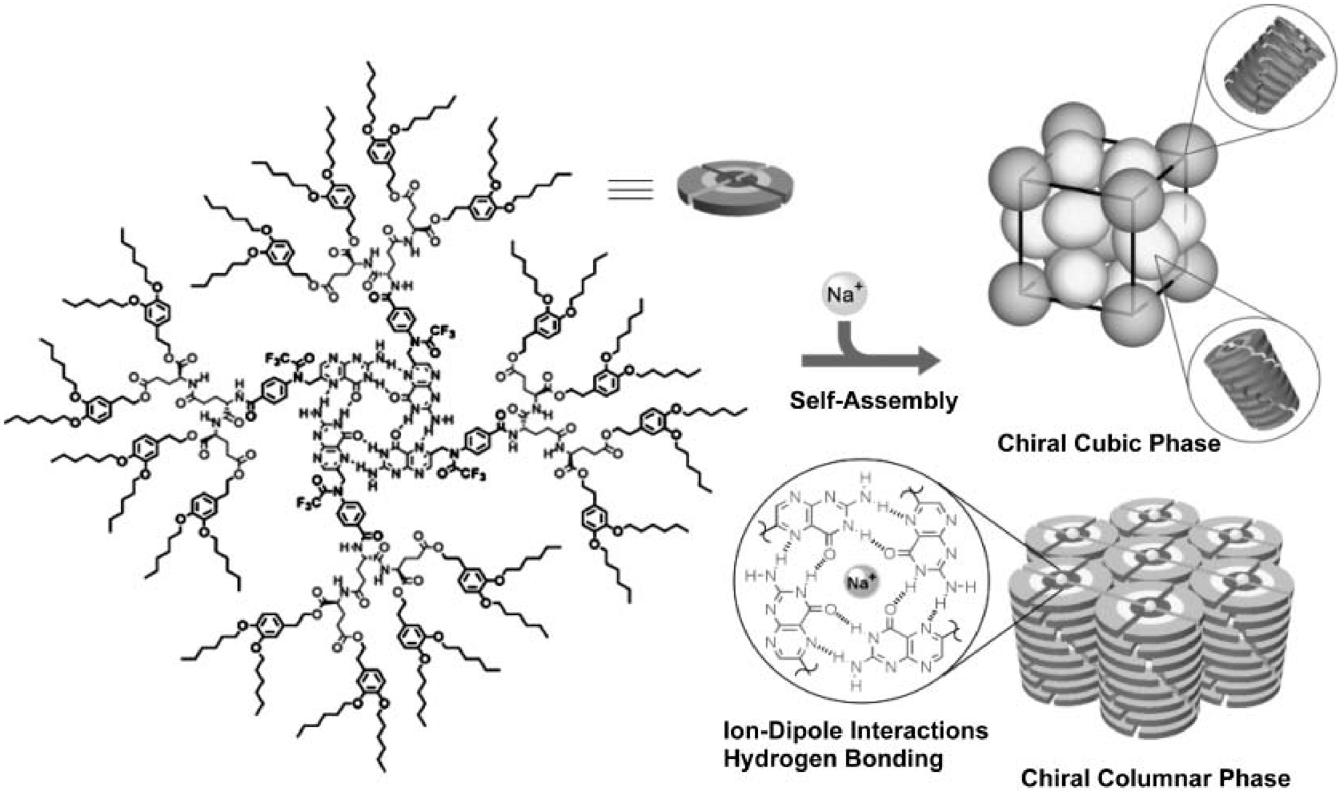

Figure 3. Formation of chiral cubic and chiral columnar phases induced by supramolecular assembly of folic acid derivatives and sodium triflate through hydrogen-bonding and ion-dipolar interactions [38].

design of liquid crystals, nematic and smectic mesogens [33], ferroelectric rod-like mesogens [34], bent-core mesogens [35], and disk-like complexes [36–39] were prepared. One of our recent materials is a liquid crystal based on folic acid. Folic acid derivatives form disk-like tetramers that lead to the formation of columnar and micellar cubic phases. It is of interest that the introduction of metal ions induces the formation of chiral micellar cubic and chiral columnar phases, as shown schematically in figure 3 [38].

The concept that functional molecular units, like mesogens, can be prepared by supramolecular assembly through non-covalent bonding has initiated the field of supramolecular polymers [9, 11–21]. A variety of supramolecular liquid-crystalline polymers such as side-chain [9, 40–49], main-chain [11, 50–52], and network [53–55] polymers, and a dye-containing host-guest system [55] were prepared as well as main-chain non-mesomorphic supramolecular polymers [56, 57].

The first side-chain liquid-crystalline polymers were prepared from a polyacrylate having a benzoic acid moiety in the side chain and a stilbazole [9]. The 1:1 mixture of the functionalized polyacrylate and a stilbazole show a particularly stable mesophase due to the 1:1 formation of the supramolecular mesogen. This design has been extended to supramoclecular grafted polymers by Bazuin [45, 46], Ikkala and ten Brinke [49], and Kato [44]. Ikkala and ten Brinke prepared supramolecular block copolymers that form a hierarchical structure through hydrogen bonding [49], which has an impact in the field of block polymers. More recently, Weck has reviewed the development of side-chain functionalized polymers [58].

Supramolecular liquid-crystalline main-chain polymers were first reported by Lehn and coworkers by using triple hydrogen bonds [11]. Griffin used the hydrogen bonding between carboxylic acid and pyridine to prepare such main chain polymeric complexes based on bifunctional hydrogen-bonded molecules [50, 51]. Recently Rowan has used nucleotides as hydrogen-bonded units for supramolecular main-chain polymers [52].

One of the unique properties of the supramolecular liquid-crystalline complexes is that the molecular structures built by non-covalent interactions are dynamic and reversible. The dynamic properties were employed for the formation of liquid-crystalline network polymers [43–56]. Such properties were also used for the preparation of stimuli-responsive supramolecular liquid crystals [59]. Folic acid derivatives change their assembled structures through the change of hydrogen-bonded patterns from ribbons exhibiting a smectic A phase to disks exhibiting a columnar phase. Such a supramolecular process has also been extended for the assembly of other materials such as polymer blends [60–62] and two component gels [63] that show reversible transitions, nanoparticles [64] and thin films obtained by layer-by-layer deposition [65].

The work reported in the 1993 paper was an early example of building functional soft materials using specific molecular interactions. Liquid crystals are promising and unique functional soft materials. The supramolecular and non-covalent approaches to the design of liquid crystals will lead to the formation of a new generation of dynamically functional materials.

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Hydrogen-bonded liquid crystals built from hydrogen-bonding donors and acceptors

Infrared study on the stability of the hydrogen bond between carboxylic acid and pyridyl moieties

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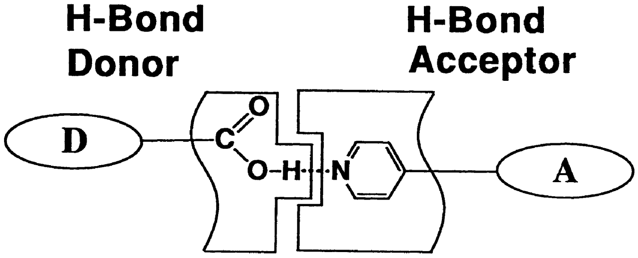
The stability of a hydrogen-bonded complex built through inter-molecular hydrogen bonding between carboxylic acid and pyridine fragments has been examined using infrared spectroscopy. Infrared spectra as a function of temperature have been recorded for the 1:1 complex of 4-hexyloxybenzoic acid and *trans*-4-propoxy-4′-stilbazole from the crystalline state to the isotropic state. A dependence of the stability of the hydrogen bond on molecular orientation is observed clearly in the infrared spectra. The spectra also suggest that the hydrogen bond is an un-ionized type with a double minimum potential energy.

1. Introduction

In 1988, we discovered [1–3] that mesogenic structures could be obtained by self-assembly of pyridine and carboxylic acid fragments through the formation of intermolecular hydrogen bonds. For example, complexation of 4-butoxybenzoic acid 4OBA and *trans*-4-[(ethoxybenzoyl)oxy]-4′-stilbazole 2OPhSz through hydrogen bonding results in the formation of an extended mesogen that exhibits a more stable mesophase than either of the single components [1, 3]. Mesogens with well-defined structures are formed from independent and different molecules. The linear and rigid structure of the complex is achieved through the connecting part of the single hydrogen bond as shown in the scheme.



The concept of building mesogenic structures through the hydrogen bond between the H-bond donor and acceptor moieties has been extended to a variety of mesogenic structures that form a novel family of liquid crystals [1–10]. A non-mesogenic molecule can function as a part of a core unit through the hydrogen bonding [5, 6]. For example, a bifunctional H-bonding acceptor, 4,4′-bipyridine, which is capable of recognizing and binding H-bonding donor molecules at each of its pyridyl ends, forms a mesogen with two benzoic acid molecules. The H-bonded mesogen shows stable mesomorphic behaviour. Hydrogen-bonded polymer systems based on a variety of backbones such as polyacrylates or polysiloxanes exhibit mesogenicity over wide temperature ranges [2, 3, 7–10]. Hydrogen bonding is one of the key interactions used by nature to assemble molecules. This process of molecular self-assembly using the hydrogen bond enables us to design and build new types of functional molecular complexes through non-covalent bonding.

Significant thermal stability is observed for the hydrogen-bonded mesogenic complex obtained from the carboxylic acid and the pyridyl group. For example, the mesophase of a 1:1 complex of 4OBA and 2OPhSz is stable up to 238°C [1]. The 1:2 complex from isophthalic or terephthalic acid and *trans*-4-octyloxy-4′-stilbazole exhibits a smectic phase up to 250°C [6]. Molecular ordering of the mesomorphic state may contribute to the stabilization of the hydrogen bonding of the molecular complex.

The objective of the present study is to examine the stability of the hydrogen-bonded mesogenic complex

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within various phases by infrared spectroscopy. Infrared spectroscopy provides useful information on hydrogen bonding. The mesogenic 1:1 complex from 4-hexyloxybenzoic acid 6OBA and *trans*-4-propoxy-4′-stilbazole 3OSz has been examined by infrared spectroscopy from the crystalline state to the isotropic state. A hydrogen-bonded dimer of 4-hexyloxybenzoic acid, $(6OBA)_2$ which is a conventional liquid crystalline compound has also been studied by infrared spectroscopy to compare its spectral features with those of the 1:1 complex from 6OBA and 3OSz.

2. Experimental

2.1. *Preparation of the hydrogen-bonded complex*

The preparation and characterization of *trans*-4-propoxy-4′-stilbazole 3OSz, that functions as a H-bond acceptor have been reported elsewhere [10, 11].

The hydrogen-bonded complex was prepared by an evaporation technique from pyridine solution containing an equimolar amount of H-bonding donor and acceptor moieties followed by drying *in vacuo* at 60°C.

2.2. *Characterization*

DSC measurements were conducted on a Mettler DSC30. A heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$ was used to determine phase transition temperatures. Onset points of the endothermic peaks were taken as the transition temperatures. A polarizing microscope (Olympus BH 2) equipped with a Mettler FP 82 HT hot stage was used for visual observation. Once melted samples were used for the measurements.

2.3. *FT–IR measurements*

Infrared spectra at various temperatures were obtained by using a JASCO Micro FT/IR-200 spectrometer equipped with a Mettler FP 84 hot stage at a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$ from 70 to 168°C. The resolution was $4\,\mathrm{cm^{-1}}$. The sample sandwiched by two KBr crystal plates was pressed to prepare the disk for the measurement. The thickness of the KBr disk was less than 1 mm. Samples heated to 20°C higher than the melting point and then cooled to room temperature were used for the measurements.

3. Results and discussion

The hydrogen-bonded 1:1 complex prepared from an equimolar mixture of 4-hexyloxybenzoic acid 6OBA and *trans*-4-propoxy-4′-stilbazole 3OSz was examined by infrared spectroscopy at various temperatures. The equimolar complex of 6OBAand 3OSz will be denoted as 6OBA–3OSz. The structure of complex 6OBA–3OSz is shown in figure 1. In this structure, 6OBA acting as the H-bond donor and 3OSz functioning as the H-bond acceptor form a well-defined structure of the mesogen through the single hydrogen bond. Table 1 summarizes the transition temperatures of 6OBA–3OSz and each of the H-bond donor and acceptor moieties. The complex, 6OBA–3OSz, behaves as a single component and shows clear phase transitions and homogeneous mesophases. After the sharp melting transition at 102°C, a smectic phase is observed in contrast to $(6OBA)_2$ which exhibits only a nematic phase, and 3OSz, which is non-mesogenic. A homeotropic and focal-conic for texture characteristic of a smectic A phase is observed under

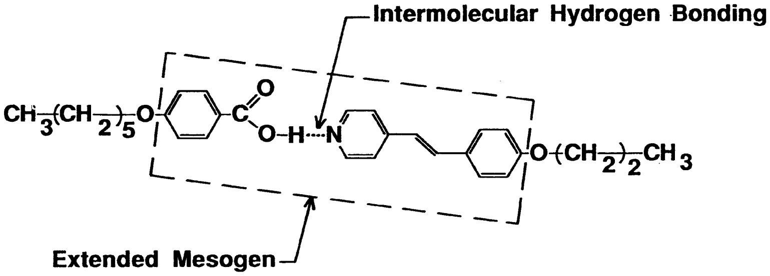

Figure 1. The structure of the hydrogen-bonded mesogenic complex of 6OBA and 3OSz.

Table 1. Transition temperatures of the H-bonded complex 6OBA–3OSz and H-bonding donor and acceptor molecules on heating.

	Phase transition behaviour						
$(6OBA)_2$	C	106°C	N	153°C	I		
6OBA–3OSz	C	102°C	S_A	130°C	N	155°C	I
3OSz	C	110°C	I				

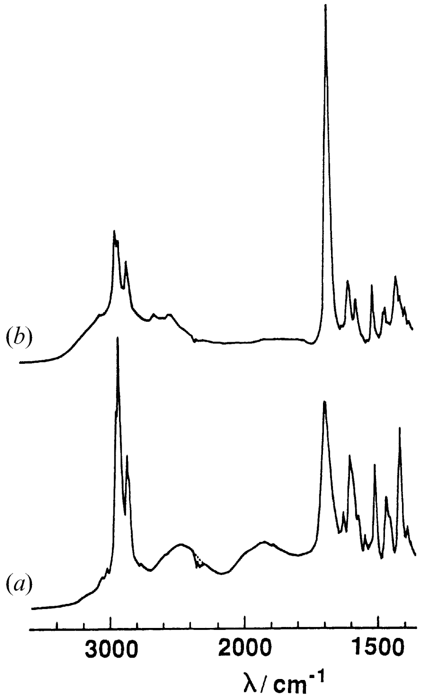

Figure 2. Infrared spectra of 6OBA–3OSz (*a*) and $(6OBA)_2$ (*b*) in the range of 1400–3400 cm^{-1}.

microscopic observation. The nematic–isotropic transition is clearly seen at 155°C. These results confirm the formation of the complex shown in figure 1.

Infrared spectra of 6OBA–3OSz and $(6OBA)_2$ in the range of 1500–3400 cm^{-1} at room temperature are shown in figures 2 (*a*) and (*b*), respectively. The O–H bands at 2500 and 1920 cm^{-1} indicative of strong hydrogen bonding between the carboxylic acid and the pyridyl unit [1–10, 12–14] are observed in figure 2 (*a*). The broad O–H band centred at 3000 cm^{-1} is seen in the spectrum of $(6OBA)_2$ (see figure 2 (*b*)). The bands at 2560 and 2670 cm^{-1} for $(6OBA)_2$ are considered to be Fermi resonances [15, 16]. The carbonyl band at 1682 cm^{-1} due to the dimer formation of the carboxylic acids (see figure 2 (*b*)) is replaced by the C=O band at 1697 cm^{-1} when 6OBA–3OSz is formed (see figure 2 (*a*)). The 1697 cm^{-1} band is attributable to the 'free' carbonyl group due to the formation of the H-bonded complex between the O–H group of the carboxylic acid and the pyridyl group. It should be noted that the intensity of the C=O bands increases after the samples are melted.

Infrared spectra have been recorded for the complex of 6OBA–3OSz while increasing the temperature from the crystalline phase to the isotropic phase to examine the stability of the hydrogen bond of the mesogenic complex. Figure 3 shows the infrared spectra of 6OBA–3OSz in the range of 1500–1800 cm^{-1} from 70 to 168°C.

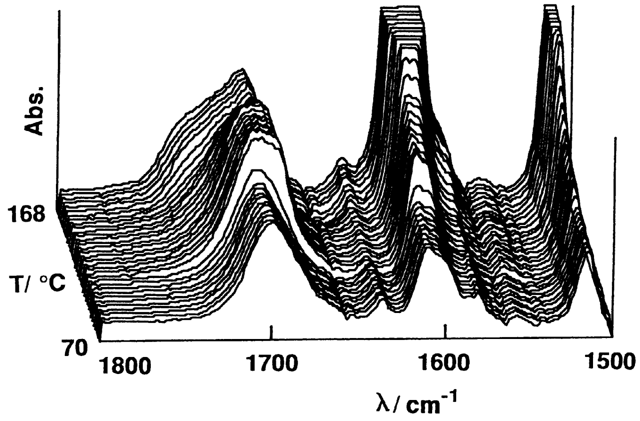

Figure 3. Infrared spectra of 6OBA–3OSz in the range of 1500–1800 cm^{-1} from 70 to 168°C.

The carbonyl band of 6OBA–3OSz shows significant changes at the melting and isotropization transitions. In particular, the carbonyl band becomes broader with a shift to higher frequencies once the isotropization temperature at 155°C is reached. Curve fitting has been conducted at 92°C (crystalline), 140°C (nematic), and 165°C (isotropic). The results are shown in figure 4 and table 2. In the crystalline state, the carbonyl band is separated into two bands at 1693 and 1705 cm^{-1}, suggesting the existence of two states of the carbonyl group involving the hydrogen bond between the carboxylic acid and pyridyl group. In the nematic state, the fraction of the area of the 1705 cm^{-1} band increases.

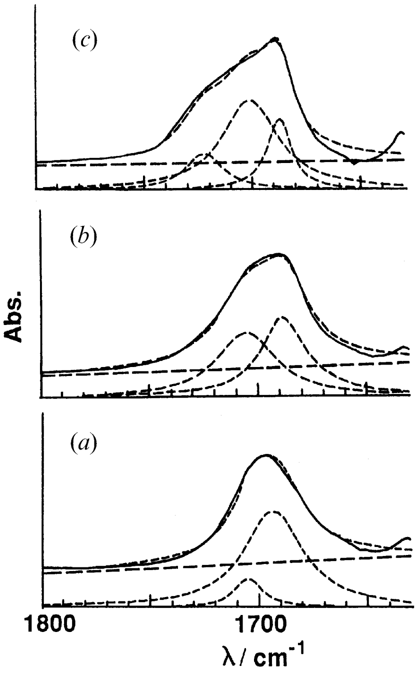

Figure 4. Curve fitting results of the carbonyl bands of 6OBA–3OSz at 92°C (*a*), 140°C (*b*), and 165°C (*c*).

Table 2. Curve fitting results of the carbonyl peak of 6OBA–3OSz for various phases.

	C=O bands of 6OBA–3OSz		C=O band of monomeric 6OBA	
	λ/cm^{-1}	Fraction of area	λ/cm^{-1}	Fraction of area
Crystalline (92°C)	1705	0.13	—	—
	1693	0.87		
Nematic (140°C)	1705	0.50	—	—
	1687	0.50		
Isotropic (162°C)	1702	0.59	1723	0.18
	1687	0.23		

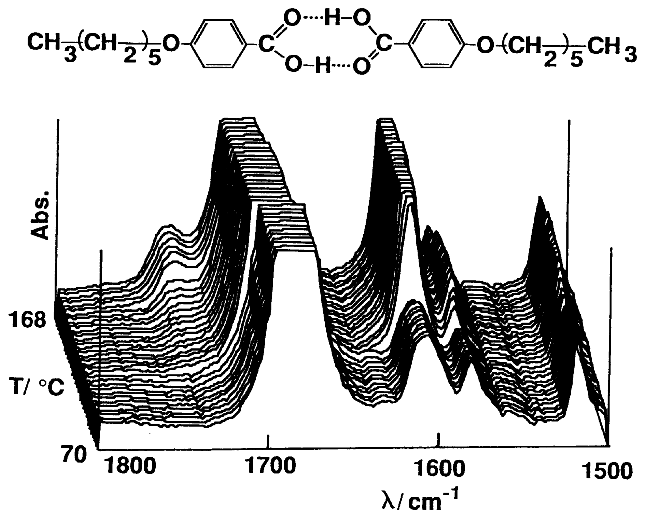

Figure 5. Infrared spectra of $(6OBA)_2$ in the range of 1500–1800 cm^{-1} from 70 to 168°C.

It was reported that for a 1:1 complex of pyridine with a benzoic acid with pKa~4, the hydrogen bond is an un-ionized type which has double minimum energy potential [13]. The present results may show that an un-ionized hydrogen bond with double minimum potential is formed between 6OBA and 3OSz. In the isotropic state (see figure 4 (*c*)), the carbonyl absorption is separated into three bands. The bands at 1687 and 1703 cm^{-1} are due to the hydrogen-bonded complex of 6OBA–3OSz. The band at 1722 cm^{-1} indicates the existence of monomeric 6OBA. The C=O band of monomeric carboxylic acid is observed at a higher frequency than those of hydrogen-bonded carboxylic acids [15, 16]. These results show that the stability of the hydrogen bond decreases greatly once the temperature reaches the isotropization temperature, while the amount of free 6OBA increases.

Infrared spectra have also been recorded for the dimer of 4-hexyloxybenzoic acid, $(6OBA)_2$ on heating, as shown in figure 5. A significant effect of molecular ordering on the stability of the H-bond is also observed for the dimer of the benzoic acid. The carbonyl band at 1630 cm^{-1} due to monomeric 6OBA appears after the crystal–nematic transition at 106°C, whereas no peak due to monomeric 6OBA is observed for 6OBA–3OSz after the crystal–mesophase transition occurs (see figure 4 (*c*)). This difference suggests that the double H-bond between two benzoic acid moieties is weaker than the single H-bond between the carboxylic acid and pyridine fragments disussed earlier in this study. The abrupt increase in the intensity of the C=O band at 1630 cm^{-1} is observed at the nematic–isotropic transition at 153°C, showing the stability of the hydrogen bonds decreases significantly in the disordered phase.

The present results may provide useful information to design functional molecular complexes through intermolecular hydrogen bonding. Further infrared studies on a variety of H-bonded mesogenic complexes are now in progress.

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