

Hydrogen-Bonded Liquid Crystals. Novel Mesogens Incorporating Nonmesogenic Bipyridyl Compounds through Complexation between H-Bond Donor and Acceptor Moieties

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Received February 11, 1993. Revised Manuscript Received May 18, 1993

Mesogenic structures have been built from 2:1 (molar ratio) mixtures of 4-alkoxy- or 4-alkylbenzoic acid (*n*OBA or *n*BA; *n* is the carbon number of the alkyl chain) and 4,4'-bipyridine (BPy) or *trans*-1,2-bis(4-pyridyl)ethylene (BPyE). In these complexes, the benzoic acid derivative functions as an H-bond donor and the bipyridyl compound operates as a bifunctional H-bond acceptor. Well-defined structures of the mesogenic complexes are formed from independent and different molecules. These complexes exhibit stable mesophases that are not observed for each of the single components. For example, a 2:1 (molar ratio) complex prepared from 4-ethoxybenzoic acid (2OBA) and 4,4'-bipyridine (BPy) shows a nematic phase from 150 to 169 °C while both individual compounds are nonmesogenic. The liquid-crystalline phase is induced by the hydrogen bonding. The 2:1 complex of 4-butoxybenzoic acid (4OBA) and *trans*-1,2-bis(4-pyridyl)ethylene (BPyE) exhibits a smectic A phase (146–168 °C) and a nematic phase (168–177 °C). The smectic phase displayed by the complex is not observed for 4OBA and BPyE. The isotropization temperature is increased by the complexation through the H bonds. The effect of the terminal alkyl chain length on thermal properties has been examined for the 2:1 H-bonded complexes of a series of the benzoic acids and the bipyridyl compound. The type of mesophases obtained is affected by the alkyl chain length. Infrared study suggests that the hydrogen bond is an un-ionic type with a double minimum potential energy and its stability is greatly dependent on the order of the molecular complexes. Phase diagrams have been obtained for the binary mixture of H-bond donor and acceptor moieties. The isotropization temperature curves show significant positive deviations because of the intermolecular H-bond interaction.

Introduction

Hydrogen bonding is one of the key interactions for chemical and biological processes in nature. For molecular aggregates, hydrogen bonding plays an important role in the association of molecules. In liquid crystals, mesomorphism results from the proper combination of molecular interactions and the shape of molecules. Dipole-dipole interactions have long been taken into consideration in the design of liquid-crystalline molecules.^{1,2} In contrast, and with few exceptions, intermolecular hydrogen bonds, that are stronger than dipole-dipole interactions had been considered to be deleterious for thermotropic liquid crystallinity in the past because in many cases they cause molecular associations that raise melting temperatures or destroy molecular order of the mesophase.

Aromatic acid derivatives with alkoxy or alkyl terminal groups are known to show mesomorphism due to the

dimerization of their carboxylic acid groups through hydrogen bonding.³ A few monosaccharides⁴⁻⁶ bearing long alkyl chains and some aliphatic compounds⁷⁻⁹ that contain several hydroxyl groups exhibit thermotropic liquid crystallinity. Diisobutylsilanediol exhibits a columnar mesophase.¹⁰ In these cases, the intermolecular hydrogen bonds between hydroxyl groups induce mesomorphism. A series of aromatic-aliphatic polyesteramides shows thermotropic liquid crystallinity through the lateral H-bonded interaction between amide linkages.¹¹ The lateral H-bond interaction is also effective for the molecular arrangement of a smectic C phase for tropone compounds.¹²

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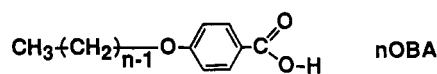
The hydrogen bonding between the amide group of benzene derivatives contributes to the formation of discotic phases.^{13,14} In all of these liquid crystals, intermolecular hydrogen bonds are formed only between identical molecules.

Our strategy¹⁵⁻²³ has been to create a novel class of liquid-crystalline materials using intermolecular hydrogen bonding as a powerful tool to assemble organic molecules. In 1988, we discovered that mesogenic structures could be obtained through intermolecular hydrogen bonds between carboxylic acid and pyridine fragments.^{15,16} For this hydrogen bonding, carboxylic acids operate as H-bond donors and pyridine moieties function as H-bond acceptors. Well-defined structures of liquid-crystalline complexes are formed from independent and different molecules.²⁵ The single hydrogen bond maintains the overall linearity and leads to a mesogenic complex. The mesophases are thermally stable. For example, 1:2 (molar ratio) complexes prepared from isophthalic or terephthalic acid and *trans*-4-alkoxy-4'-stilbazoles exhibit a smectic phase up to 250 °C.¹⁷ A wide variety of mesogenic structures that show stable liquid-crystalline phases have been designed and built through hydrogen bonds.¹⁵⁻²³

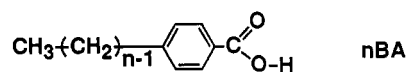
In a preliminary communication,¹⁸ we reported that intermolecular hydrogen bonds between 4-butoxybenzoic acid or 4-butylbenzoic acid and nonmesogenic 4,4'-bipyridine resulted in the formation of a novel mesogenic structure. This mesogenic molecular structure was quite unique because nonmesogenic 4,4'-bipyridine functions as a bidirectional core unit in the hydrogen-bonded mesogen.

In the present study, hydrogen-bonded complexes have been prepared from a series of 4-alkoxybenzoic acid (*n*OBA) and 4-alkylbenzoic acids (*n*BA), and nonmesogenic bipyridine compounds, 4,4'-bipyridine (BPy) and *trans*-1,2-bis(4-pyridyl)ethylene (BPyE) through intermolecular hydrogen bonds.²⁶ Thermal properties have

Chart I. H-Bond Donor



1OBA	K	184	I
2OBA	K	196	I
3OBA	K	145	N 154 I
4OBA	K	147	N 160 I
5OBA	K	124	N 151 I
6OBA	K	105	N 153 I
7OBA	K	92	Sc 98 N 146
8OBA	K	101	Sc 108 N 147
10OBA	K	97	Sc 122 N 142



4BA	K	102	N 116 I
5BA	K	88	N 126 I
8BA	K	99	N 112 I

been examined for these complexes. Binary phase diagrams have also been obtained for the mixture of these H-bond donors and acceptors.

Experimental Section

Preparation of Hydrogen-Bonded Complexes.^{15-21,23,24} The requisite amounts of hydrogen bond donor and acceptor molecules are dissolved in dry pyridine. The solvent was removed by slow evaporation. The solid samples were dried at 70 °C in vacuo.

Characterization. DSC measurements were performed on a Mettler DSC 30. The heating rate was 10 °C/min. Samples once heated to 20 °C higher than their melting temperatures were used for the measurement. The onset point of the endotherm in the DSC thermogram was taken as the transition temperature. A polarizing microscope equipped with a Mettler FP82HT hot stage was used for visual observations. X-ray study was performed in the Wilson Synchrotron Laboratory at Cornell University. The details of the measurements were reported in a previous paper.²⁰ FT-IR measurements were performed on a JASCO FT/IR-200 spectrometer equipped with a Mettler FP84 hot stage.

Results and Discussion

Liquid-Crystalline Properties of Hydrogen-Bonded Mesogenic Complexes Incorporating Nonmesogenic 4,4'-Bipyridine (BPy) or *trans*-1,2-Bis(4-pyridyl)ethylene (BPyE).²⁶ The hydrogen-bonded mesogenic structure incorporating the nonmesogenic molecules through the complexation between H-bond donor and acceptor moieties designed for the present study is shown in Figure 1. Benzoic acid derivatives, 4-alkoxybenzoic acid (*n*OBA; $n = 1-8, 10$; n is the carbon number of the alkyl chain) and 4-alkylbenzoic acid (*n*BA; $n = 4, 5, \text{ and } 8$) were used as hydrogen bond donors (Chart I). The thermal properties are given in Chart I. Liquid crystallinities are observed for these benzoic acids except for 1OBA and 2OBA having shorter alkyl chains. Bipyridyl compounds, 4,4'-bipyridine (BPy) and *trans*-1,2-bis(4-pyridyl)ethylene (BPyE) that are capable of recognizing of H-bond donor molecules at each of their pyridyl ends were selected as hydrogen bond acceptors (Chart II). Both bipyridyl compounds are nonmesogenic.

Table I shows the thermal properties of hydrogen-bonded complexes prepared from 2:1 (molar ratio) mixtures of 4-alkoxybenzoic acid (*n*OBA; $n = 1-8, 10$) and 4,4'-bipyridine (BPy). The 2:1 complex will be denoted as (*n*OBA)₂-BPy. The thermal behavior of the complexes

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Chart II. H-Bond Acceptor

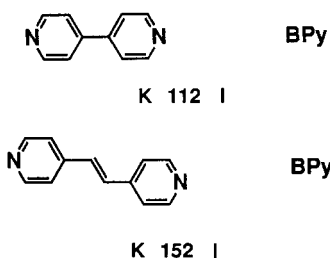
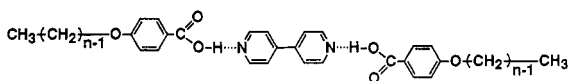


Table I. Thermal Properties of Hydrogen-Bonded Complexes (nOBA)₂-BPY from 2:1 (Molar Ratio) Mixture of 4-Alkoxybenzoic Acid (nOBA) and 4,4'-Bipyridine (BPY)

complex	phase transition behavior ^a					
(1OBA) ₂ -BPY			K 153	N 163	I	
			(58.7)	(4.6)		
(2OBA) ₂ -BPY			K 150	N 169	I	
			(50.6)	(8.6)		
(3OBA) ₂ -BPY			K 144	N 157	I	
			(38.4)	(5.9)		
(4OBA) ₂ -BPY	K 130	K 134	S _A 150	N 159	I	
	(10.2)	(24.5)	(3.6)	(6.9)		
(5OBA) ₂ -BPY		K 109	K 118	S _A 155	I	
		(3.9)	(27.8)	(12.9)		
(6OBA) ₂ -BPY	K 102	K 105	S _C 130	S _A 159	I	
	(10.2)	(12.5)	(-) ^b	(15.1)		
(7OBA) ₂ -BPY	K 88	K 96	S _C 129	S _A 159	I	
	(2.8)	(16.5)	(-) ^b	(19.3)		
(8OBA) ₂ -BPY		K 104	S _C 138	S _A 159	I	
		(35.6)	(0.2)	(20.9)		
(10OBA) ₂ -BPY		K 108	S _C 156	S _A 159	I	
		(49.6)	(1.5)	(31.0)		

^a Transition temperatures (°C) and enthalpies of transitions (kJ/mol, in parentheses). ^b The S_C-S_A transition is observed under polarizing microscope. However, it is not apparent in our DSC thermogram.

A



B

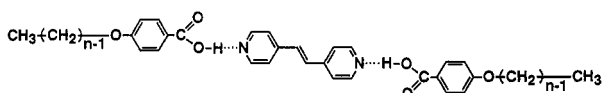


Figure 1. Structure of hydrogen-bonded mesogen formed from 2:1 (molar ratio) mixture of 4-alkoxybenzoic acid (nOBA) and 4,4'-bipyridyl compounds: (A) complex based on 4,4'-bipyridine (BPY); (B) complex based on *trans*-1,2-bis(bipyridyl)ethylene (BPYE).

confirms the selective formation of the hydrogen-bonded mesogen shown in Figure 1A. All complexes behave as the single mesogenic component and show clear phase transitions. The thermal properties are different from those of each H-bond donor and acceptor compounds.

DSC thermogram of 2:1 complex (2OBA)₂-BPY prepared from nonmesogenic components is shown in Figure 2A. The crystalline-isotropic (melting) temperatures of 2OBA and BPY are 196 and 112 °C, respectively, while for the complex, two endothermic peaks are observed at 150 and 169 °C on heating. Observation of these transitions under a microscope shows that the endotherms correspond to crystal-nematic and nematic-isotropic transitions, respectively. It is noteworthy that liquid crystallinity is induced through the intermolecular hydrogen bonds between nonmesogenic components. A schlieren texture

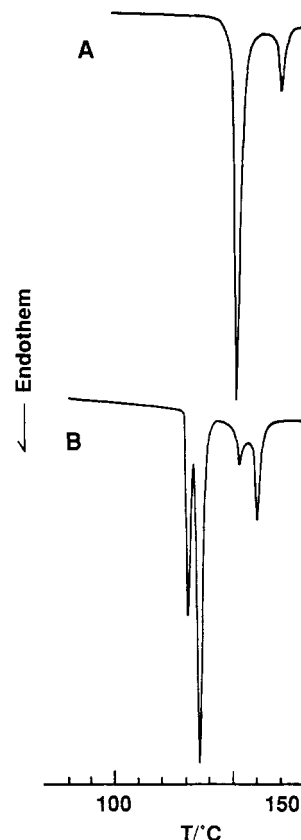


Figure 2. DSC thermograms of hydrogen-bonded complexes on heating: (A) (2OBA)₂-BPY; (B) (4OBA)₂-BPY.

is observed for the mesophase. The isotropization temperature (T_i) of (2OBA)₂-BPY is the highest in the series of (nOBA)₂-BPY. Figure 2B shows the DSC thermogram of (4OBA)₂-BPY. Endothermic peaks of crystal-smectic A, smectic A-nematic, and nematic-isotropic transitions are seen at 134, 150, and 159 °C, respectively. A homogeneous or focal conic texture that is characteristic of the smectic A phase appears below the nematic phase. The peak corresponding to crystal-crystal transition is seen at 130 °C. For (6OBA)₂-BPY, a schlieren texture that is attributable to a smectic C phase is observed from 105 to 130 °C. The transition from a schlieren texture to a homeotropic or focal conic texture is seen visually at 130 °C. However, this transition is not apparent in DSC thermogram. This behavior is typically observed for a smectic C phase.² The peak of S_A-I transition is seen at 159 °C.

For the series of hydrogen-bonded complexes (nOBA)₂-BPY, the type of mesophase is dependent on the alkyl chain length. Figure 3 shows a plot of transition temperatures as a function of the carbon number (n) of the alkyl chain. Nematic phases are seen for the complexes with $n = 1-4$ whereas the complexes with $n = 5-10$ show only smectic phases. The enthalpy changes of N-I transitions for (nOBA)₂-BPY with $n = 1-4$ are between 4.6 and 6.9 kJ/mol. The enthalpy changes of S_A-I for (nOBA)₂-BPY with $n = 5-10$ increase from 12.9 to 31.0 kJ/mol with the increase of the length of the terminal alkyl group. The S_C-S_A enthalpy change also increases and the value becomes 1.5 kJ/mol for (10OBA)₂-BPY.

The liquid-crystalline properties of the 2:1 complexes of 4-alkylbenzoic acids (nBA; $n = 4, 5, \text{ and } 8$) and BPY are given in Table II. The significant effects extended by the hydrogen bonds on mesophase stabilization are observed

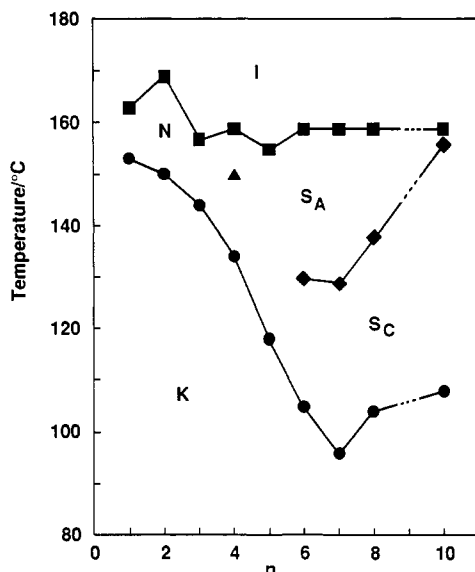


Figure 3. Plot of transition temperatures against the carbon number (n) in the alkyl chain for the series of hydrogen-bonded complex $(n\text{OBA})_2\text{-BPy}$.

Table II. Thermal Properties of Hydrogen-Bonded Complexes $(n\text{BA})_2\text{-BPy}$ from 2:1 (Molar Ratio) Mixture of 4-Alkylbenzoic Acid ($n\text{BA}$) and 4,4'-Bipyridine (BPy)

complex	phase transition behavior ^a						
$(4\text{BA})_2\text{-BPy}$	K	93 (11.4)	K	104 (14.5)	S_A	147 (12.6)	I
$(5\text{BA})_2\text{-BPy}$			K	110 (51.7)	S_A	153 (33.5)	I
$(8\text{BA})_2\text{-BPy}$	K	86 (30.5)	S_C	127 (1.6)	S_A	153 (34.6)	I

^a Transition temperatures ($^{\circ}\text{C}$) and enthalpies of transitions (kJ/mol, in parentheses).

for these complexes. For example, complex $(4\text{BA})_2\text{-BPy}$ exhibits a smectic A phase from 104 to 147 $^{\circ}\text{C}$, whereas 4BA shows a nematic phase between 102 and 116 $^{\circ}\text{C}$ and BPy is nonmesogenic. The isotropization temperature of $(4\text{BA})_2\text{-BPy}$ is 31 $^{\circ}\text{C}$ higher than that of the dimer of 4BA.

trans-1,2-Bis(4-pyridyl)ethylene (BPyE) was used as an H-bond acceptor to build the hydrogen-bonded mesogen shown in Figure 1B.²⁶ The melting temperature ($T_{\text{K-I}}$) is 152 $^{\circ}\text{C}$. The thermal properties of H-bonded complexes $(n\text{OBA})_2\text{-BPyE}$ are listed in Table III. A plot of the transition temperatures as a function of the alkyl chain length is shown in Figure 4. In all cases, the hydrogen-bonded complexes exhibit stable mesophases. The isotropization temperatures for the series of $(n\text{OBA})_2\text{-BPyE}$ are higher than those of the series of $(n\text{OBA})_2\text{-BPy}$. For example, T_i of $(4\text{OBA})_2\text{-BPyE}$ is 177 $^{\circ}\text{C}$ that is 28 $^{\circ}\text{C}$ higher than that of $(4\text{OBA})_2\text{-BPy}$. Melting and smectic-nematic transitions of $(n\text{OBA})_2\text{-BPyE}$ also occur at higher temperatures than those of $(n\text{OBA})_2\text{-BPyE}$ complexes. Complex $(2\text{OBA})_2\text{-BPyE}$ prepared from nonmesogenic components exhibits a nematic phase up to 189 $^{\circ}\text{C}$ which is the highest T_i in this series studied in the present study. This mesophase stabilization can be ascribed to the effect of more planar structure of the bipyridyl component that functions as a bifunctional core unit of the hydrogen-bonded mesogen.

X-ray diffraction studies have been done for complexes $(4\text{OBA})_2\text{-BPyE}$ and $(6\text{OBA})_2\text{-BPyE}$ in the smectic A phase. The layer spacings for $(4\text{OBA})_2\text{-BPyE}$ and $(6\text{OBA})_2\text{-BPyE}$ are 36 \AA (157 $^{\circ}\text{C}$) and 40 \AA (165 $^{\circ}\text{C}$), respectively. The

Table III. Thermal Properties of Hydrogen-Bonded Complexes $(n\text{OBA})_2\text{-BPyE}$ from 2:1 (Molar Ratio) Mixture of 4-Alkoxybenzoic acid ($n\text{OBA}$) and *trans*-1,2-Bis(4-pyridyl)ethylene (BPyE)

complex	phase transition behavior ^a								
$(1\text{OBA})_2\text{-BPyE}$			K	166 (54.9)	N	185 (2.7)	I		
$(2\text{OBA})_2\text{-BPyE}$			K	160 (63.0)	N	189 (6.5)	I		
$(3\text{OBA})_2\text{-BPyE}$		K	128 (11.5)	K	152 (36.6)	N	177 (4.9)	I	
$(4\text{OBA})_2\text{-BPyE}$		K	146 (59.0)	S_A	168 (2.1)	N	178 (6.9)	I	
$(5\text{OBA})_2\text{-BPyE}$	K	114 (22.1)	K	129 (23.6)	S_A	173 (-) ^b	N	174 (14.8) ^b	I
$(6\text{OBA})_2\text{-BPyE}$			K	140 (44.7)	S_A	177 (17.8)	I		
$(7\text{OBA})_2\text{-BPyE}$			K	144 (40.2)	S_A	177 (19.4)	I		
$(8\text{OBA})_2\text{-BPyE}$			K	144 (40.6)	S_A	178 (21.6)	I		
$(10\text{OBA})_2\text{-BPyE}$		K	127 (36.2)	S_C	154 (1.2)	S_A	177 (26.2)	I	

^a Transition temperatures ($^{\circ}\text{C}$) and enthalpies of transitions (kJ/mol, in parentheses). ^b The S_A -N transition is overlapped with the isotropization peak.

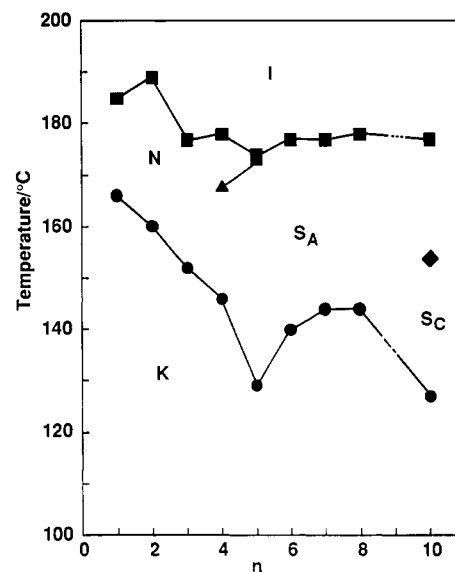


Figure 4. Plot of transition temperatures against the carbon number (n) in the alkyl chain for the series of hydrogen-bonded complex $(n\text{OBA})_2\text{-BPyE}$.

lengths of the fully stretched conformations of the complexes with $n = 4$ and 6 estimated by molecular modeling are 38 and 42 \AA . These data further support the formation of 2:1 hydrogen-bonded complexes having overall linear structure.

The mesomorphic behavior of $(n\text{BA})_2\text{-BPyE}$ ($n = 4, 5$, and 8) is given in Table IV. These complexes also behave as stable mesogenic components. For example, $(5\text{BA})_2\text{-BPyE}$ shows a smectic A phase from 110 to 153 $^{\circ}\text{C}$ (Figure 5), while for the 5BA dimer the mesophase is stable up to 127 $^{\circ}\text{C}$. The isotropization temperature is increased significantly by the complexation.

These results indicate that the liquid-crystalline complex with well-defined structure shown in Figure 1 is obtained through the specific noncovalent interaction between different nonmesogenic components.

Infrared Study of the Hydrogen-Bonded Complexes. Figure 6 shows the infrared spectrum of hydrogen-

Table IV. Thermal Properties of Hydrogen-Bonded Complexes (nBA)₂-BPy from 2:1 (Molar Ratio) Mixture of a 4-Alkylbenzoic Acid and *trans*-1,2-Bis(4-pyridyl)ethylene (BPyE)

complex	phase transition behavior ^a						
(4BA) ₂ -BPyE	K	116 (28.1)	S _A	155 (2.9)	N	163 (5.6)	I
(5BA) ₂ -BPyE			K	132 (33.7)	S _A	167 (12.5)	I
(8BA) ₂ -BPyE	K	130 (30.8)	S _C	140 (-) ^b	S _A	170 (20.7)	I

^a Transition temperatures (°C) and enthalpies of transitions (kJ/mol, in parentheses). ^b The S_C-S_A transition is observed under polarizing microscope. However, it is not apparent in our DSC thermogram.

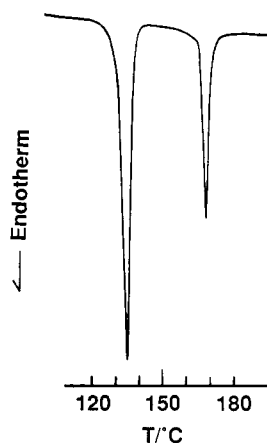


Figure 5. DSC thermogram of hydrogen-bonded complex (5BA)₂-BPyE on heating.

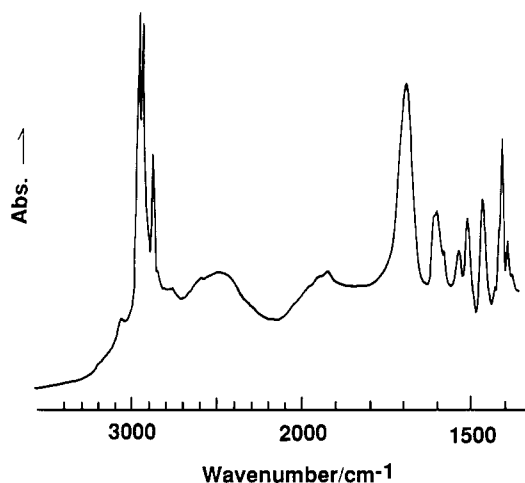


Figure 6. Infrared spectrum of hydrogen-bonded complex (4OBA)₂-BPy in the crystalline state at 100 °C.

bonded complex (4OBA)₂-BPy in the crystalline state at 100 °C. The O-H bands at 2500 and 1920 cm⁻¹ indicative of strong hydrogen bonding²⁷⁻²⁹ are seen in the spectrum. For a phenol-pyridine complex that forms a weaker hydrogen bond,²⁸ the O-H band appears at about 3000 cm⁻¹. The carbonyl band centered at 1696 cm⁻¹ is ascribed to the free carbonyl group of the complex from the carboxylic acid and the pyridyl group, while the band at 1681 cm⁻¹ due to the dimer formation of the carboxylic

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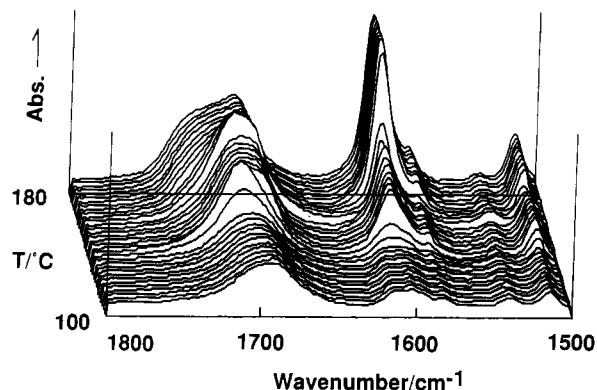


Figure 7. Infrared spectra of (4OBA)₂-BPy in the range 1500-1800 cm⁻¹ from 100 to 180 °C.

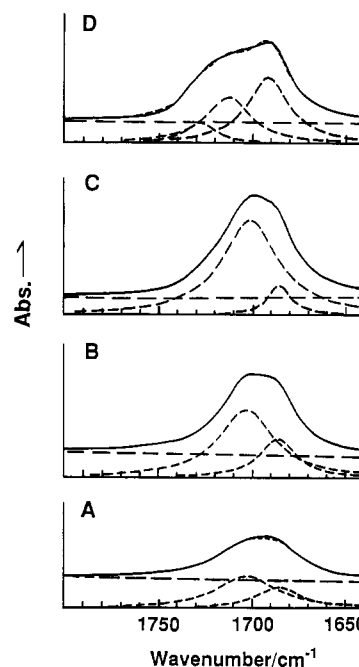


Figure 8. Curve fitting results of the carbonyl bands of (4OBA)₂-BPy at 120 (A), 140 (B), 154 (C), and 175 °C (D).

acid is observed for the single component of 4OBA.

Infrared spectra for complex (4OBA)₂-BPy have been recorded while increasing the temperature from the crystalline state to the isotropic phase at a heating rate of 10 °C/min. Figure 7 presents the infrared spectra in the range 1500-1800 cm⁻¹ from 100 to 180 °C. The sudden changes of the carbonyl band are observed at the phase transition temperatures. In particular, the band abruptly becomes broader with a shift to higher wavenumbers once the temperature reaches the isotropization temperature at 159 °C. Curve fitting has been performed for the carbonyl band at 120 (crystalline), 140 (smectic A), 154 (nematic), and 175 °C (isotropic). The results are shown in Figure 8 and Table V. In the crystalline state (Figure 8A), the C=O band is separated into two bands at 1686 and 1703 cm⁻¹. The proportion of the band at 1703 cm⁻¹ increases in the liquid-crystalline phase. It was reported that the hydrogen bond between pyridine and a benzoic acid with pK_a ~ 4 is non-ionic but shows a double minimum potential.²⁷ The two carbonyl bands observed in the present study can be ascribed to the double minimum potential state of the hydrogen bond. The two separated C=O bands of the H-bonded complex shift to higher wavenumbers after isotropization and the carbonyl band

Table V. Curve-Fitting Results of the Carbonyl Peak of (4OBA)₂-BPy in Various Phases

	C=O bands of (4OBA) ₂ -BPy		C=O band of monomeric 4OBA	
	ν (cm ⁻¹)	fraction of area	ν (cm ⁻¹)	fraction of area
crystalline (120 °C)	1703	0.68		
	1686	0.32		
smectic (140 °C)	1703	0.72		
	1686	0.28		
nematic (154 °C)	1702	0.87		
	1686	0.13		
isotropic (175 °C)	1713	0.38	1728	0.11
	1691	0.51		

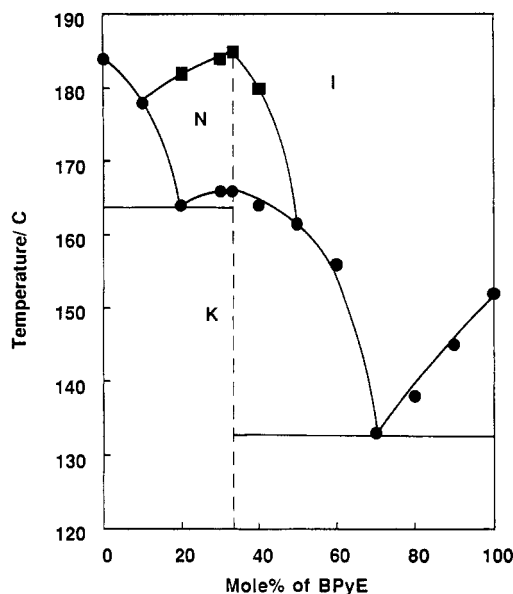


Figure 9. Binary phase diagram for 1OBA and BPyE.

of the monomeric 4OBA is seen at 1728 cm⁻¹ in the isotropic state. These results suggest that the stability of the hydrogen-bonded complex suddenly decreases once the complex becomes an isotropic disordered state. The stability of the hydrogen bond is not simply a function of temperature, and it is greatly dependent on the state of molecular ordering. The dependence of the hydrogen bond on the phase behavior was also observed for a 1:1 mesogenic complex of a stilbazole and 6OBA.²³

Binary Phase Diagram for Hydrogen-Bond Donors and Acceptors. The phase behaviors of the binary mixtures of H-bond donor and acceptor have been examined for mixtures of *n*OBA and BPyE. These mixtures are obtained by the evaporation method from a pyridine solution.^{15-21,23,24}

Figure 9 shows the binary phase diagram for 1OBA and BPyE on heating. Both components of the H-bond donor and acceptor moieties are nonmesogenic. A nematic phase is induced for the mixture containing between 10 and 50 mol % of BPyE. This effect can be ascribed to the hydrogen bonding interaction between two components. The maximum isotropization temperature is observed at the point where 33 mol % of BPyE is used in the mixture. This corresponds to an equimolar amount of H-bond donor and acceptor fragments and therefore the mesogenic complex is formed quantitatively.

The binary diagram of 4OBA and BPyE presented in Figure 10 is also very unusual because of the strong non-covalent interaction. The significant effect of the mixing on mesophase stabilization is observed in the diagram.

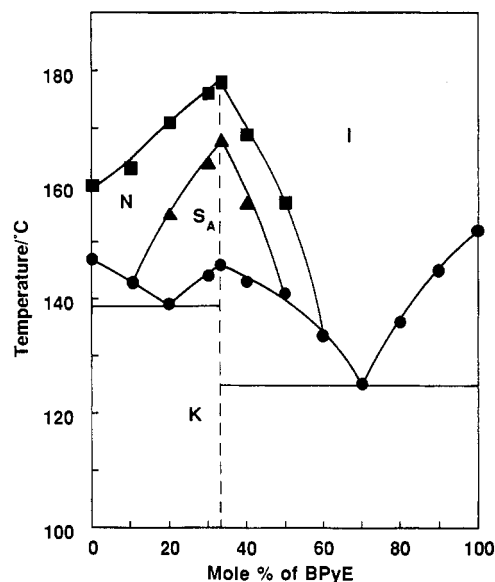


Figure 10. Binary phase diagram for 4OBA and BPyE.

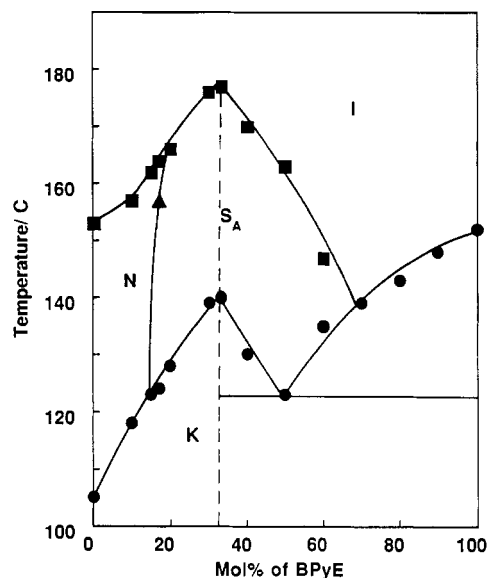


Figure 11. Binary phase diagram for 6OBA and BPyE.

The smectic A phase that does not appear for either of the single components is seen in the range of about 20–40 mol % of BPyE. The S_A-N and N-I transition curves show a large positive deviation. This remarkable stabilization is of a magnitude not observed for conventional binary mixtures. The highest clearing temperatures are observed at the point where equimolar amount of donor and acceptor moieties (33.3 mol % of BPyE) are present.

Figure 11 illustrates the phase diagram for 6OBA and BPyE. Extended mesophases are also observed for these mixtures. A nematic phase is seen for the mixture containing up to 20 mol % of BPyE. The mixtures with 20–60 mol % of BPyE exhibit only smectic A phases, while 6OBA shows only a nematic phase and BPyE is nonmesogenic.

Conclusion

Novel H-bonded mesogenic structures are formed through the formation of bidirectional H-bonded complexes. The mesogen reported herein is quite unique because nonmesogenic compounds act as the core units of the mesogens that are formed by self-assembly through

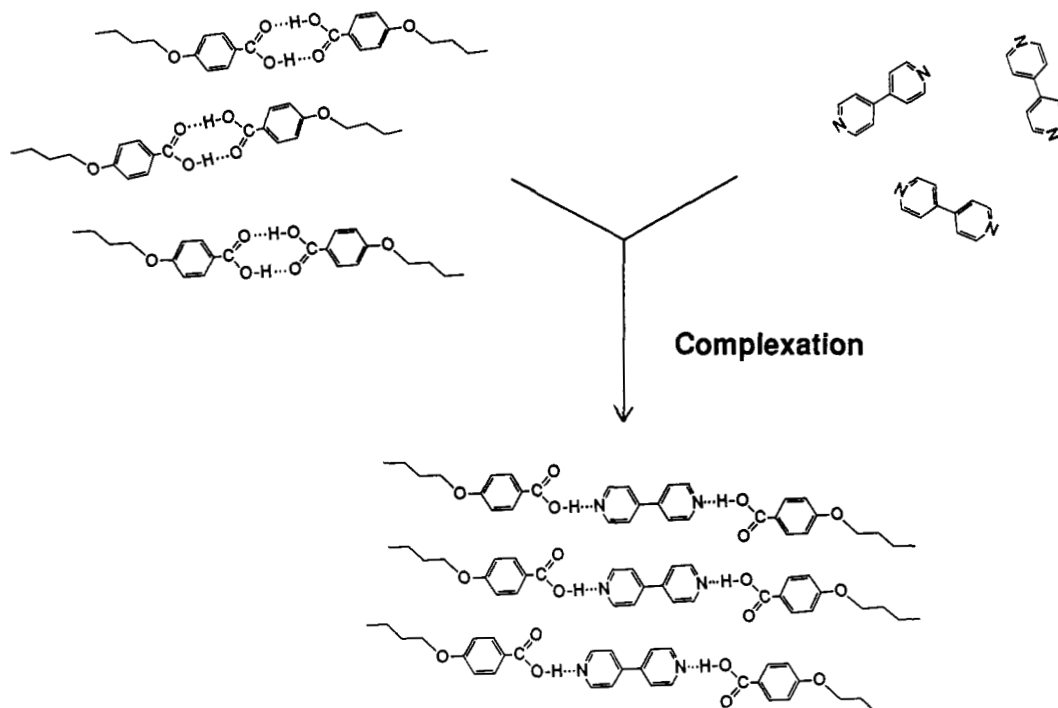


Figure 12. Schematic illustration of molecular self-assembly of the mesogenic hydrogen-bonded complex through selective recognition between H-bond donor and acceptor moieties.

specific intermolecular interactions. This finding may open a new avenue for the design of liquid-crystalline materials. A schematic illustration that represents the molecular self-assembly¹⁵⁻²³ through the hydrogen bonding is illustrated in Figure 12. This type of molecular association of H-bond donor and acceptor moieties is a new class of molecular recognition using selective intermolecular interactions.

Acknowledgment. Financial support by the Ogasawara Foundation for the Promotion of Science & Engineering and by the Cornell Material Science Center under a grant from the National Science Foundation (NSF-DMR 9121654) is acknowledged. The authors also thank Dr. Uday Kumar and Dr. Kazuchika Ohta for helpful discussion.