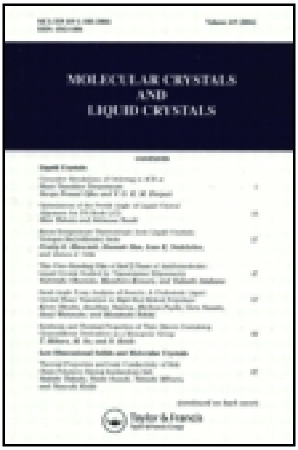

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Mesophases Induced by Hydrogen Bonds between Nonmesogens

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Mesophases Induced by Hydrogen Bonds between Nonmesogens

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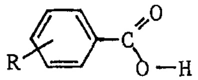
Nematic phases were obtained by mixing 4-methoxy-4′-stilbazole with structural isomers of methyl-, methoxy-, and halo-benzoic acid derivatives, all the components are rod-like nonmesogens. It was shown by NMR, IR, uv-vis and fluorescent spectroscopic studies that the hydrogen bonds played the central role. Enantiotropic with wide temperature ranges were observed for the mixtures of 4-substituted benzoic acids. The stability of induced mesophase decreased for the mixtures of 3- and 2-substitutions.

Keywords: induced mesophases, hydrogen bonds

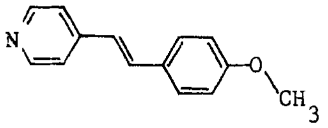
The hydrogen bond interactions are widespread and well studied molecular forces.[1,2,3] Hydrogen bonding occurs in the circumstances where a hydrogen atom covalently bonded to an electronegative atom, such as oxygen or nitrogen, is approached by another electronegative atom, either of the same molecule (intramolecular) or different (intermolecular). The existences of liquid crystal phases due to hydrogen bonds are also well known, e.g., the long alkyl- and alkoxy-benzoic acids. In this case, there are two hydrogen bonds between the carboxylic acid functional groups, and the dimeric structure has been considered as a single component.

Although the hydrogen bonds are the primary interactions rendering these benzoic acid derivatives to be mesogens, they have been overlooked, however, during the past several decades as a useful "bond" in designing new mesogens. It was not until recently that hydrogen bonds were successfully employed for the formation of mesophases. Kato and Fréchet observed the enhancement of mesophase temperature by mixing derivatives of benzoic acid and 4-alkoxy-4′-stilbazole, both components with mesogens.[4] Brienne, et al., reported the observation of mesophases induced by multi-hydrogen-bonds between two different nonmesogens.[5] In both cases cited here, the hydrogen bonds between dissimilar molecules played the central role.

We report here examples that mesophases can be induced by mixing benzoic acid (BA) derivatives (proton donor) and 4-methoxy-4′-stilbazole (MOSB, proton acceptor), all are short rod-like nonmesogens. The occurrence of mesophases depends on the position of substituent of the BA molecule, and wide mesophase temperature ranges were observed in some cases. Various spectroscopic studies indicated the existence of hydrogen bond between the proton donor and proton acceptor. The results presented here are useful for designing new mesogens in the future.



MOSB



R:	H,	CH_3,	OCH_3,	F,	Cl,	Br,	I
Symbol:	BA,	MBA,	MOBA,	FBA,	ClBA,	BrBA,	IBA

EXPERIMENTAL

The MOSB was synthesized according to reference 6, mp. 135.5°C (lit. 135.7°C),[7] elemental results found C: 79.53; H: 6.26; N: 6.67; calcd C: 79.62; H: 6.16; N: 6.64. The hydrochloride salt of MOSB (MOSBHCl) was also synthesized for the purpose of spectroscopic studies. The derivatives of BA employed were structural isomers (4-, 3-, and 2-) of methyl-, methoxy-, fluoro- , chloro-, bromo-, and iodo-BA. All these nonmesogenic proton donors were commercially available and recrystallized wherever necessary.

Mixtures of 1:1 molar ratio were obtained by weighing the components into a small vial and warmed up to isotropic phase for mixing. Mesophase textures were characterized under a polarizing microscope (Nikon, OPTIPHOT-POL) equipped with a home made heating stage. The temperatures and enthalpies of phase transitions were determined with a differential scanning calorimeter (Perkin-Elmer DSC-2). A rate of 10°C/min was used for both heating and cooling runs. The FTIR (BIO-RAD FTS-40) spectra were measured on compressed pellets by grinding these mixtures with KBr. Spectra obtained by using paraffin oil showed the same results. The proton spectra (Bruker WP100SY FTNMR) were recorded with deuterated chloroform as solvent. The electronic absorption spectra, of solutions or thin film coated on quartz disk by evaporation of solvents, were measured with a Hitachi 330 uv-vis-near ir spectrometer. These samples were also used for fluorescence measurements (Jasco FP 770).

RESULTS AND DISCUSSION

The Hydrogen Bond

The characteristic vibrational frequencies for the OH of acid dimers are shown in Figure 1, OH stretching, and Figure 2, OH out-of-plane bending. With the presence of MOSB molecules, a stronger proton acceptor than the acid itself, these two characteristic bands no longer exist. There are two new broad bands of medium strength located at 1950 and 2450 cm^{-1} for all the mixtures. These are the characteristic bands of hydrogen bondings for pyridine and carboxylic acid, as demonstrated by Yoshida and Asai.[8] The carbonyl stretching is shifted slightly to the higher frequencies in the presence of MOSB, as also shown in Figure 1. All the mixtures presented here exhibited the similar properties and only those of MBA and MOBA series are shown for illustration. It is clear from the above results that the two hydrogen bonds between dimeric acid groups are replaced by the acid-pyridine hydrogen bond.

Hydrogen bonds can be studied also by NMR method. The results of 4-MBA/MOSB are shown in Figure 3 for illustration. The proton spectra of pure 4-MBA and its MOSB mixture are shown in Figure 3b and 3a, respectively. It can be seen clearly that the chemical shift of the acidic proton is downfield shifted and the signal is much sharper for the mixture. Furthermore, since the hydrogen bond took place at the lone paired electrons of the nitrogen atom of MOSB, the MOSB molecule should exhibit a charge redistribution. This charge redistribution would affect the chemical shifts of the corresponding protons. As shown in Figure 3d, the chemical shift of protons ortho to the nitrogen atom is downfield shifted by about 0.1 ppm. It is known that the chemical shift of proton involved in hydrogen bond is extremely sensitive to concentration, moisture and solvents used. A more quantitative NMR study for these systems is currently underway.

The involvement of MOSB molecules in hydrogen bond is also evident from the electronic absorption spectra as shown in Figure 4. The quartz coated solid film of MOSB exhibited absorption bands at 245 and 290 nm due to the π-π^* transitions of MOSB. The shoulder located at 365 nm is most probably due to the n-π^* of MOSB. There were discussions in literatures for the hidden n-π^* transitions of MOSB analog molecules.[9] The hydrochloride salt, MOSBHCl, exhibited absorptions at 250 and 370 nm with the absence of 290 nm band. The mixture of 4-MBA/MOSB showed absorption bands at 250 and 300 nm and a shoulder at 370 nm. The relative absorbance is increased for the lower energy bands along with a slight red shift for mixture as compared to those of pure MOSB. The spectra of solutions (in polar or nonpolar solvents) displayed the similar results (not shown here).

The fluorescent spectra of these samples are shown in Figure 5. Upon protonation by HCl, the fluorescence wavelength is red shifted from 415 to 520 nm. The corresponding wavelength for the mixture of 4-MBA/MOSB is located at 450 nm. The fluorescence quantum yield is much higher for MOSBHCl than that of pure MOSB, and the value for 4-MBA/MOSB is in between. A more quantitative study is currently underway. These electronic properties, absorption and emission behaviors, are reasonable and can be accounted for by the consideration of the acidity of proton donors.

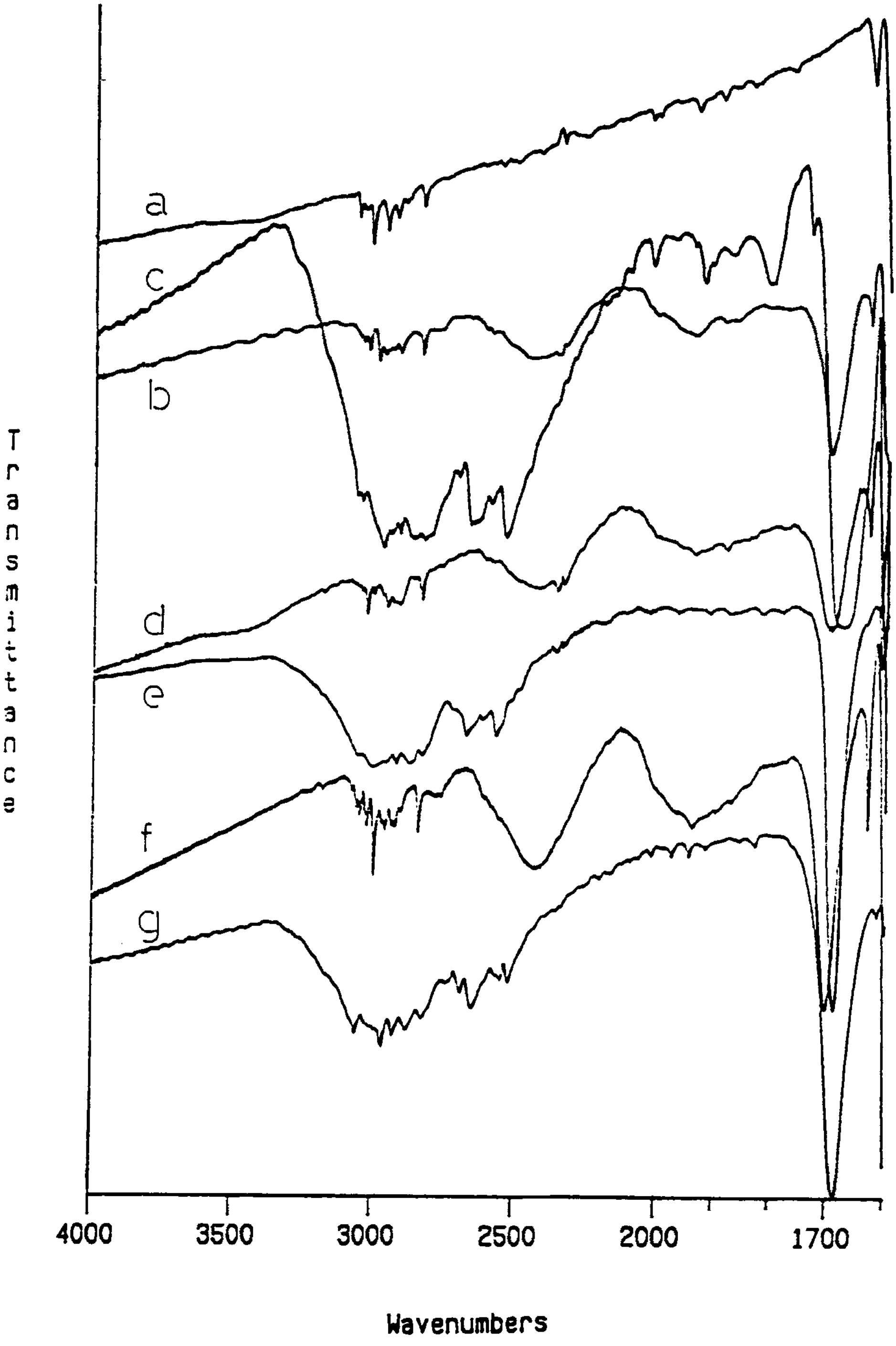


FIGURE 1 The FTIR spectra (1600–4000 cm^{-1}) for a, MOSB; b, 4-MBA/MOSB; c, 4-MBA; d, 3-MBA/MOSB; e, 3-MBA; f, 2-MBA/MOSB; g, 2-MBA.

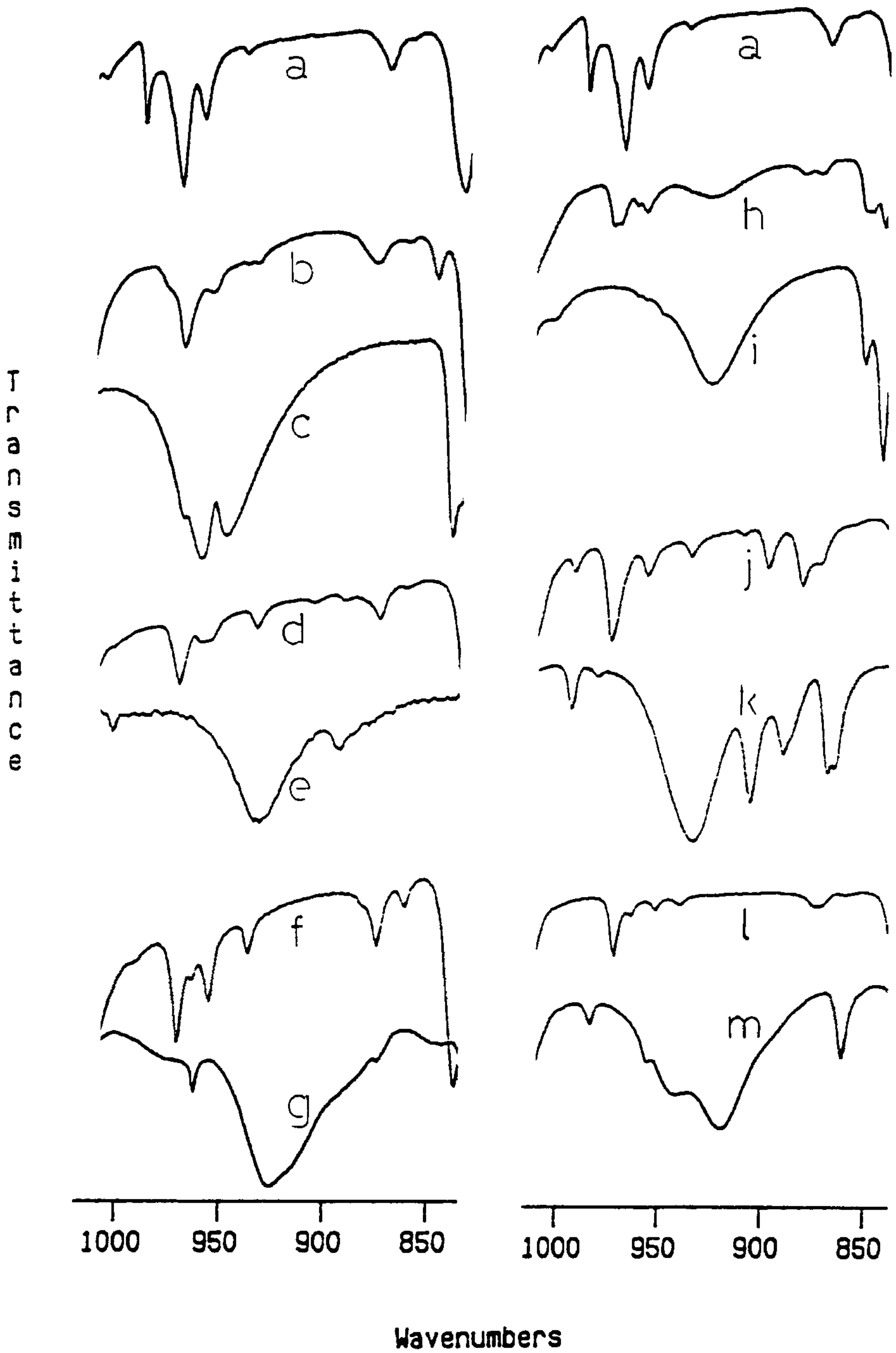


FIGURE 2 The FTIR spectra (850–1000 cm^{-1}) for a, MOSB; b, 4-MBA/MOSB; c, 4-MBA; d, 3-MBA/MOSB; e, 3-MBA; f, 2-MBA/MOSB; g, 2-MBA; h, 4-MOBA/MOSB; i, 4-MOBA; j, 3-MOBA/MOSB; k, 3-MOBA; l, 2-MOBA/MOSB; m, 2-MOBA.

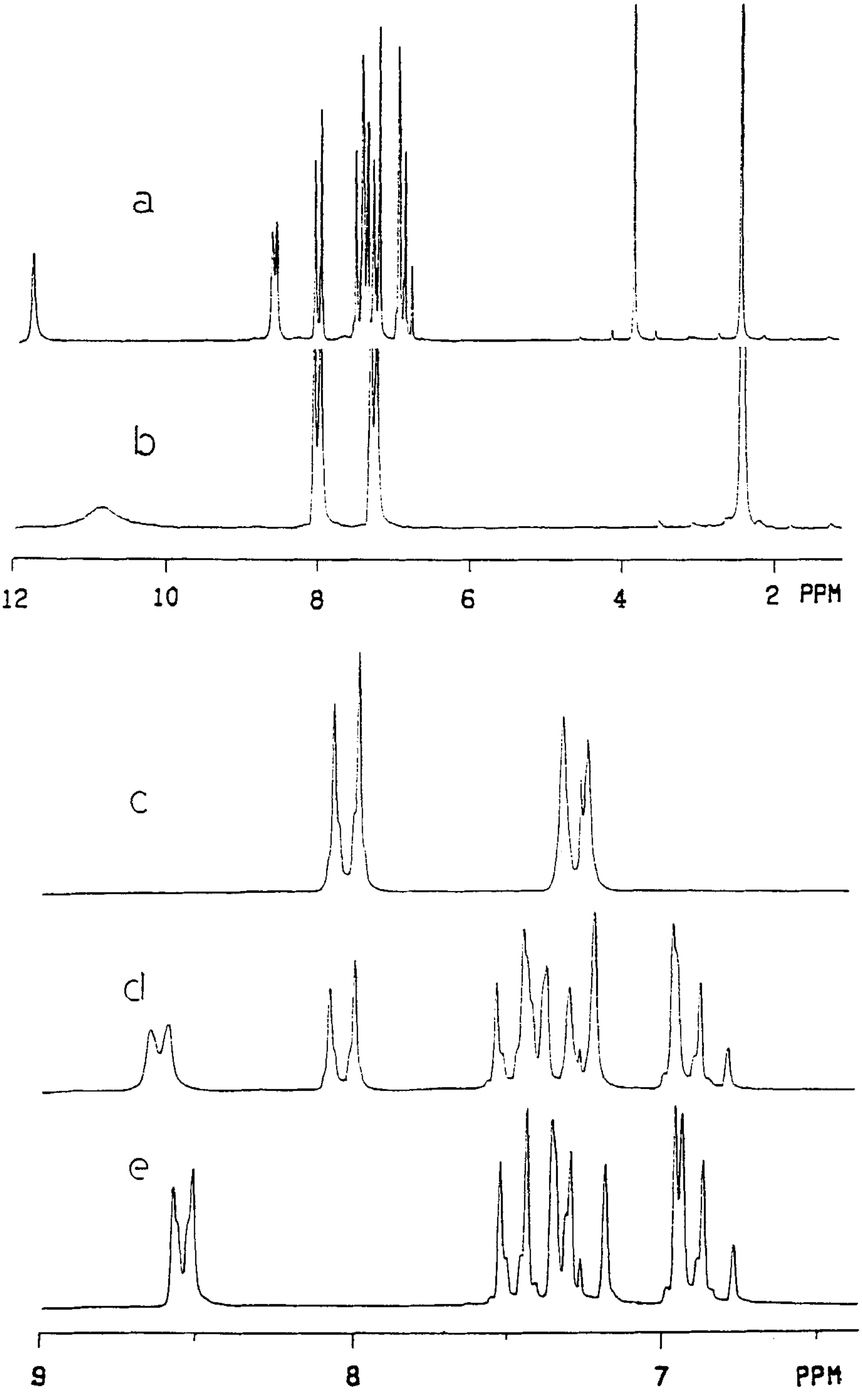


FIGURE 3 The proton spectra of 4-MBA/MOSB, a and d; 4-MBA, b and c; and MOSB, e. In $CDCl_3$.

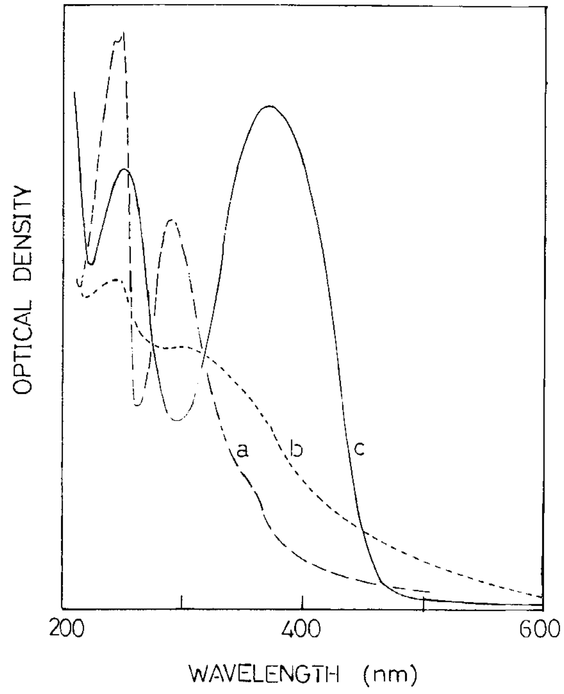


FIGURE 4 The electronic absorption spectra of a, MOSB; b, 4-MBA/MOSB; and c, MOSBHCl.

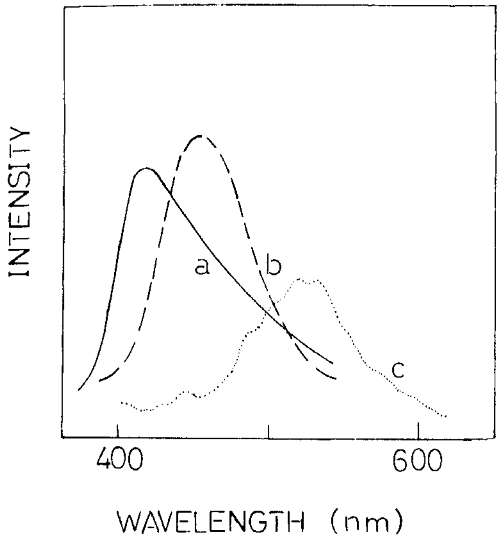


FIGURE 5 The fluorescence spectra of a, MOSB (ex. 290 nm); b, 4-MBA/MOSB (ex. 300 nm) and c, MOSBHCl (ex. 370 nm).

From these spectroscopic studies, it is clear that MOSB is hydrogen bonded with the acidic proton via the lone paired electrons of the nitrogen atom.

The Mesophase

The mesophases observed for the mixtures presented here displayed textures similar to those of typical rod-like nematic (N) phase sandwiched between microscopic slide and cover slip. The phases and corresponding transition temperatures are listed in Table I. Also listed are the melting points of pure acids, the temperature ranges of nematic phase measured on heating and cooling runs and the enthalpies of transitions from isotropic to nematic phase for the mixtures.

TABLE I

The mesophase, transition temperature, temperature range, and enthalpy of isotropic to nematic phase observed for the mixtures of 4-methoxy-4′-stilbazole and structural isomers of methyl-, methoxy-, and halo-benzoic acid (BA) derivatives

Acids	mp(°C)[a]	Phase and Transition Temperatures (°C)	Temperature Range (°C)[b]	Enthalpy, (kJ/mol mix)
BA	123.5	$\mathrm{C} \xrightarrow{110} \mathrm{Iso}$ $\mathrm{C} \xleftarrow[77]{} \mathrm{N} \xleftarrow[104.5]{} \mathrm{Iso}$	$\frac{0}{27.5}$	1.03
4-MBA	182	$\mathrm{C} \underset{76.5}{\overset{124}{\rightleftharpoons}} \mathrm{N} \underset{145.5}{\overset{158}{\rightleftharpoons}} \mathrm{Iso}$	$\frac{34}{69}$	4.51
3-MBA	112	$\mathrm{C} \xrightarrow{77} \mathrm{Iso}$ $\mathrm{C} \xleftarrow[24]{} \mathrm{N} \xleftarrow[57.5]{} \mathrm{Iso}$	$\frac{0}{33.5}$	1.28
2-MBA	107	$\mathrm{C} \xrightarrow{68} \mathrm{Iso}$ $\mathrm{C} \xleftarrow[< \mathrm{RT}]{} \mathrm{N} \xleftarrow[62.5]{} \mathrm{Iso}$	$\frac{0}{>25}$	1.01
4-MOBA	185	$\mathrm{C} \underset{112}{\overset{148.5}{\rightleftharpoons}} \mathrm{N} \underset{162.5}{\overset{166}{\rightleftharpoons}} \mathrm{Iso}$	$\frac{17.5}{50.5}$	4.28
3-MOBA	110	$\mathrm{C} \xrightarrow{} \mathrm{Iso}$ $\mathrm{C} \xleftarrow[< \mathrm{RT}]{} \mathrm{N} \xleftarrow[52]{} \mathrm{Iso}$	—	—
2-MOBA	101	$\mathrm{C} \rightleftharpoons \mathrm{Iso}$	—	—
4-FBA	185	$\mathrm{C} \underset{106}{\overset{119.5}{\rightleftharpoons}} \mathrm{N} \underset{149}{\overset{152.5}{\rightleftharpoons}} \mathrm{Iso}$	$\frac{33}{43}$	3.30
3-FBA	124	$\mathrm{C} \underset{78}{\overset{93}{\rightleftharpoons}} \mathrm{N} \underset{104.5}{\overset{107.5}{\rightleftharpoons}} \mathrm{Iso}$	$\frac{14.5}{26.5}$	0.77
2-FBA	126.5	$\mathrm{C} \underset{36.5}{\overset{65.5}{\rightleftharpoons}} \mathrm{N} \underset{81}{\overset{84.5}{\rightleftharpoons}} \mathrm{Iso}$	$\frac{19}{44.5}$	0.67

TABLE I (*continued*)

4-ClBA	243	$\mathrm{C} \underset{124}{\overset{141}{\rightleftharpoons}} \mathrm{N} \underset{164.5}{\overset{168}{\rightleftharpoons}} \mathrm{Iso}$	$\frac{27}{40.5}$	3.79
3-ClBA	158	$\mathrm{C} \xrightarrow{98} \mathrm{Iso}$ $\mathrm{C} \xleftarrow[73]{} \mathrm{N} \xleftarrow[76.5]{} \mathrm{Iso}$	$\frac{0}{3.5}$	0.74
2-ClBA	142	$\mathrm{C} \xrightarrow{103.5} \mathrm{Iso}$ $\mathrm{C} \xleftarrow{} \mathrm{N} \xleftarrow[55.5]{} \mathrm{Iso}$	—	—
4-BrBA	254.5	$\mathrm{C} \underset{140.5}{\overset{159}{\rightleftharpoons}} \mathrm{N} \underset{166}{\overset{169.5}{\rightleftharpoons}} \mathrm{Iso}$	$\frac{10.5}{25.5}$	4.90
3-BrBA	155	$\mathrm{C} \xrightarrow{} \mathrm{Iso}$ $\mathrm{C} \xleftarrow[67]{} \mathrm{N} \xleftarrow[69]{} \mathrm{Iso}$	—	—
2-BrBA	150	$\mathrm{C} \underset{73}{\overset{98}{\rightleftharpoons}} \mathrm{Iso}$	—	—
4-IBA	270	$\mathrm{C} \xrightarrow{178} \mathrm{Iso}$ $\mathrm{C} \xleftarrow[148]{} \mathrm{N} \xleftarrow[155]{} \mathrm{Iso}$	$\frac{0}{7}$	1.88

[a] From CRC Handbook of Chemistry and Physics, 57th, 1976, ed. R. C. Weast.
[b] Heating/Cooling Ranges.

As can be seen from Table I, all the mixtures of 4-isomers showed enantiotropic nematic phase except that of 4-IBA. The mixture of BA also gave nematic phase but monotropic. The enantiotropic behavior became monotropic and then non-mesophasic when the site of substituent was changed from 4 to 3 and then 2. This trend is more evident for bulkier substituents and in accord with the typical rod-like thermotropic mesogens. The enthalpy values for isotropic to nematic transition correlated to this behavior very well. The enthalpy values for mixtures of 4-isomer are comparable to one another and are three to four times the corresponding values for mixtures of 3- and 2-isomers. These enthalpy values indicate that the orderness of the hydrogen-bonded dimers of 3- and 2- substituted BA/MOSB is smaller than that of 4-isomer/MOSB. And a substitution at the 2 position resulted in a greater hindrance in molecular packing, since the dipole moment persists regardless the site of the substitution. These results indicate that the geometric factor is very important, if not more than the dipole-dipole interactions, regarding to the arrangements of molecules in the mesophase.

It is interesting to see that BA molecule without any substituent also induces nematic phase although monotropic. A substitution at the 4 position of BA is helpful in the enhancement of molecular ordering. This is also observed in the enthalpy values of isotropic to nematic transition. The monotropic behavior of 4-IBA mixture is most probably due to the high melting of 4-IBA and the large radius of the iodine atom. All the three FBA mixtures gave enantiotropic nematic.

This is important since in some cases where mesophase consisting of molecules with dipole moment pointing in the lateral directions are needed.

It is known that the hydrogen bonds are temperature dependent molecular interactions. Although, it is shown here that hydrogen bonds existed in the solid and solution phases, they are expected to persisting in the mesophases. The presented results show that hydrogen bond is a useful chemical "bond" in the design of new mesogens.

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