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MESOPHASES INDUCED BY HYDROGEN BOND BETWEEN OLIGOETHYLENE GLYCOL SUBSTITUTED BENZOIC ACID AND STILBAZOLE

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Abstract Various oligoethylene glycols were used to replace the alkyl chain of p-alkyloxybenzoic acid and 4-alkyloxy-4'-stilbazole. The compounds obtained were nonmesogenic or monotropic. Mesophases were observed via the formation of hydrogen bond between these proton donors and acceptors , but with narrower mesophase temperature ranges as compared to those of parent mixtures. These effects were attributed to the curving conformation of the ethylene glycol unit as suggested from the results of model calculation.

INTRODUCTION

The p-alkyloxy and p-alkyl benzoic acids were known to exhibit mesophases.[1] The formation of hydrogen bonds between the carboxylic acids was essential and the hydrogen bonded dimer was considered as a single component.The 4-alkyloxy-4'-stilbazole (CnOSB) homologues exhibited smectic B phases for n=5 to 16.[2]

Recently it has been shown that the formation of hydrogen bond between proton donor and acceptor would induce mesophase of various types dependent on the donor and acceptor components employed.[2,3,4] The donors and acceptors could be mesogens or nonmesogens and the hydrogen bonded dimer behaved as a conventional covalently constructed thermotropic mesogen.

The flexible chains were required, in geneal , for constructing a mesogen of either rodlike or disclike. Most frequently, it was the aliphatic hydrocarbons and occasionally the oligoethylene glycols. The situation was quite similar for polymeric liquid crystals of either main chains or side chains, where flexible spacers were needed.[5]

Recently ,polyethylene oxides(PEO)were employed as the matrices for constructing ionic conducting materials, and promising results were observed.[6,7,8] In the present study, the effects on mesophase behaviors by replacing the hydrocarbon chains of mesogens with oligoethylene glycols were examined. Also studied were the mesophases induced by mixing the glycol substituted proton domors and acceptors. The results were discussed on the basis of the conformations of terminal chains obtained by model calculation with a computer program.

EXPERIMENTAL

The preparation of p-alkyloxy benzoic acid (compounds 1~5) and 4-alkyloxy-4'-stilbazole (compounds 9~14) were known in literature.[1,2]

Compound 6 was obtained by deethylation in potassium hydroxide solution and followed by acidification of a product isolated from a refluxed solution of 2-(2-chloroethoxy) ethanol, ethyl 4-hydroxybenzoate and potassium carbonate in acetonitrile. Compounds 7 and 8 were obtained with the same procedures as those of p-alkyloxybenzoic acid except that tosylates of the corresponding oligoethylene glycols were used. These tosylates were obtained by treating the glycols with p-toluene sulfonyl chloride in the presence of triethyl amine in dichloromethane. These tosylates we also converted to arylbromides by reacting with 4-bromophenol in the presence of potassium hydroxide and potassium iodide in ethanol. The arylbromides isolated were coupled to 4-vinylpyridine via Heck reaction to obtain compounds 15 and 16.[2]

The mixtures of proton donor and acceptor in 1 : 1 mole ratio were obtained by weighing the compounds into small vials and heated to isotropic for mixing. The textures of mixtures displayed between microscope slide and coverslip were characterized with an optical polarized microscope (NIKON, OPTIPHOT- POL) equiped with a heating stage (Mettler, FP800 and FP82).The transition enthalpies were measured by a differential scanning calorimeter (Mettler FP800 and FP85) with heating and cooling rates of 5°C/min.

The proton NMR spectra were recorded with a Bruker AC 300 NMR spectrometer.The elemental analysis were carried out with an elemental analyzer Heraeus CHN-O-RAPID. The software of SPARTAN 4.1 MNDO was employed to calculate the optimized geometric structures of the proton donors and acceptors.

RESULTS

The results of elemental analysis and proton NMR spectra of all intermediates and final products were consistent with those desired structures.

The Effect of Glycol Substitution

The phase behaviors of the protron donors employed for the present study were listed in Table I . While the p-alkyloxybenzoic acids were known mesogens,all the oligoethylene glycol substituted benzoic acids were nonmesogens.The mesophase disappeared once an oxygen atom was inserted in the aliphatic chain or a CH_2 unit was replaced by an oxygen atom. The isotropic temperatures were lowered by about 20 ~25 degrees for each oxygen atom inserted.

The phase behaviors of the proton acceptors employed for the present study were listed in Table II .The alkyloxy substituted stilbazoles were known smectic B mesogens. The insertion of oxygen atoms resulted in destabilization of the mesophase. Non-mesogenic behaviors for short chains and monotropic behaviors for long chains were observed. However,the smectic B phase was preserved. The effect upon the temperatures of isotropic to smectic B phase was about 10 degrees lowering for each oxygen atom inserted. However, the changes of crystal to isotropic transition temperatures did not show any regular patterns.

The Hydrogen Bonded Complexes

For mixtures consisted of alkyloxy substituted proton donors and acceptors (TableIII), enantiotropic nematic and smectic A phases for the shorter chain members and enantiotropic smectics A 、 C and X1(monotropic for 2/12 mixture) for the longer chain members were observerd.The smectic B phase of the proton acceptors no longer existed. The mesophases exhibited wider temperature ranges and with higher isotropic transition temperatures.

When the acceptors were replaced with the oligoethylene glycol derivatives, enantiotropic nematic and smectic A were observed .The mesophase temperature ranges were narrower and isotropic temperatures were lower as compared to those of alkyloxy substituted counter parts.

For mixtures consisted of glycol substituted proton donor and alkyloxy stilbazoles (5/9~12),the phase behaviors were similar to those of mixtures contained component 2 as the proton donor(2/9~12).Enantiotropic nematic and smectics A and C were observed. However,the isotropic temperatures were lower by about ten degrees .When both donors and acceptors contained the oligoethylene glycol as terminal group , the mesophases were severely suppressed (5/13~16):short temperature ranges for the short chain members and nonmesophases for long chain members.

Among the donor and acceptor components employed, components 6 and 14 were distinct in that they consisted of a hydroxyl group at the end of the terminal chain.The mixtures contained component 6 as the proton donor exhibited lower isotropic temperatures (TableIII). However, the mesophase temperature ranges were slightly wider than those of mixtures contained component 5 as the proton donor.

DISCUSSION

The replacement of the alkyl chain of p-alkyloxybenzoic acid and 4-alkyloxy-4'-stilbazole by oligoethylene glycol unit resulted in destabilization of mesophases,either in pure components or the hydrogen bonded mixtures.This effect was apparently due to the replacement of the terminal chains,since the rigid cores were the same.A model calculation of the conformations of these molecules was carried out with the SPARTAN 4.1 MNDO program.Examples were shown in Figure 1 for illustration. The conformation having the minimun energy for the alkyl chain was an all trans and rather straight structure,and that of the oligoethylene glycol was a curved structure. Due to the curved conformation of the terminal chain,the mesophases would be preserved less likely.

TABLE I The phase behaviors of alkyloxy and oligoethylene glycol of p-substituted derivatives of benzoic acid. Temperature in °C.

compounds	R =	compounds	R =
1	$-C_5H_{11}$ C 124 N 151 I	5	$-C_2H_4OC_2H_5$ C 134~136 I
2	$-C_6H_{13}$ C 105 N 153 I	6	$-C_2H_4OC_2H_4OH$ C 123.5~124.7 I
3	$-C_8H_{17}$ C 101 S_c 108 N 147 I	7	$-C_2H_4OC_2H_4OC_2H_5$ C 105~106.3 I
4	$-C_{10}H_{21}$ C 97 S_c 122 N 142 I	8	$-C_2H_4OC_2H_4OC_2H_4OCH_3$ C 75.5~77 I

TABLE II The phase behaviors of alkyloxy and oligoethylene glycol of p-substituted derivatives of stilbazole. Temperature in °C

compounds	R =	compounds	R =
9	$-C_5H_{11}$ C 86.3 I (83.2 S_B 85)	13	$-C_2H_4OC_2H_5$ C 90.2 I
10	$-C_6H_{13}$ C 68.1 S_B 87.4 I	14	$-C_2H_4OC_2H_4OH$ C 118.7 I
11	$-C_8H_{17}$ C 74.5 S_B 88.6 I	15	$-C_2H_4OC_2H_4OC_2H_5$ C 84.4 I (58.9 S_B 62.5)
12	$-C_{10}H_{21}$ C 81.6 S_B 85.6 I	16	$-C_2H_4OC_2H_4OC_2H_4OCH_3$ C 89-91.5 I (r.t S_B 51.6)

TABLE III The phase behaviors of mixtures of proton donor and acceptor in 1:1 mole ratio . Temperature in °C and transition enthalpy (in parentheses) in kJ/mole. [a]:included in the ΔH of isotropization.

	mp	c		S_m		S_c		S_A		N		I
2/ 9	105.5	*					99.6 [15.94]	*	145.7 [a]	*	150.8 [7.48]	*
2/10	94.0	*			86 [8.85]	*	99.0 [0.69]	*	149.9 [a]	*	153.3 [7.75]	*
2/11	62.4	*	36.8 [12.74]	S_{X1}	72.1 [3.97]	*	111.4 [2.04]	*			154.2 [10.46]	*
2/12	64.5	*	41.9 [23.59]	S_{X1}	56 [1.73]	*	115.9 [2.95]	*			155.1 [13.02]	*
2/13	106.8	*					102.8 [32.26]	*	123.7 [a]	*	133.7 [8.74]	*
2/14	73.1	*	49.7 [11.15]	S_B			86.0 [1.20]	*	118.7 [0.95]	*	129.7 [1.88]	*
2/15	96.8	*					94.5 [13.80]	*	108.3 [a]	*	110.5 [4.50]	*
2/16	78.9	*	75.6 [6.49]	S_E			81.5 [3.63]	*	86.6 [a]	*	95.3 [4.26]	*
5/ 9	107.9	*					103.3 [19.56]	*	131.2 [1.83]	*	139.3 [2.05]	*
5/10	96.6	*			92.1 [9.77]	*	103.4 [2.27]	*	136.4	*	139.4 [7.07]	*
5/11	79.5	*			74.5 [6.59]	*	112.8 [3.25]	*			140.8 [10.17]	*
5/12	67.6	*	54.7 [2.65]	S_E	65.5 [1.43]	*	117.2 [3.56]	*			141.8 [12.03]	*
5/13	110.3	*							107.6 [20.60]	*	118.1 [1.44]	*
5/14	105.0	*					91.5 [27.08]	*	107.2 [1.01]	*	119.8 [1.72]	*
5/15	96.7	*									94.4 [24.16]	*
5/16	86.7	*									84.3 [20.07]	*
6/ 9	96.5	*					95.3 [1.72]	*	118.5 [1.33]	*	135.3 [1.92]	*
6/10	71.7	*	48.4 [1.63]	S_{X2}			91.2 [1.54]	*	116.7 [1.76]	*	129.1 [2.75]	*
6/11	66.1	*	53.7 [2.23]	S_{X2}			105.1 [2.85]	*	125.6 [a]	*	129.8 [14.40]	*
6/12	64.2	*	47.5 [2.05]	S_{X2}			107.7 [3.46]	*			128.0 [8.50]	*
6/13	105.9	*							94.7 [26.19]	*	117.4 [1.22]	*
6/14	106.2	*					99.2 [17.48]	*	109.9 [1.04]	*	123.6 [1.36]	*
6/15	81.4	*							77.3 [a]	*	80.4 [19.24]	*
6/16	79.8	*							76.1 [a]	*	82.0 [18.49]	*

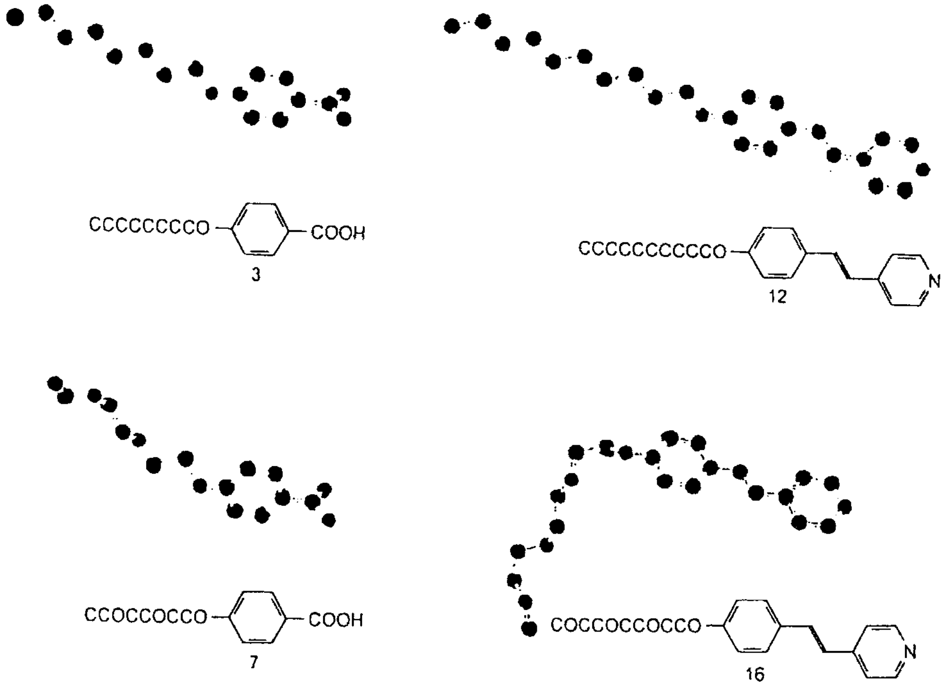

Figure 1 The minimum energy conformations of proton donors and acceptors calculated by SPARTAN 4.1 MNDO.

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