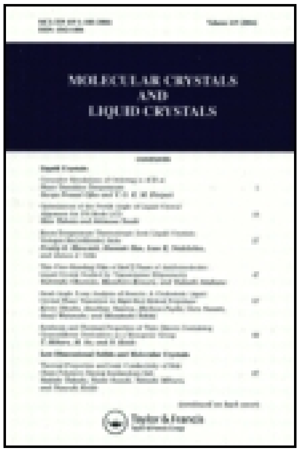

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Liquid Crystalline Properties of Dimesogenic Compounds Consisting of Two Different Azobenzene Types of Mesogens Interlinked Through Central Polymethylene Spacers

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Liquid Crystalline Properties of Dimesogenic Compounds Consisting of Two Different Azobenzene Types of Mesogens Interlinked Through Central Polymethylene Spacers

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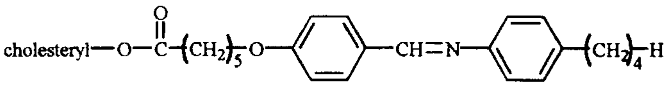
A series of new dimesogenic compounds, S(+)-2-methylbutyl 4-[ω-(4-butylphenylazophenoxy)polymethyleneoxy] phenylazobenzoates, were synthesized and characterized for their liquid crystallinity and thermal transitions. The compounds are consisting of two different azobenzene mesogens interlinked through the central oxypolymethyleneoxy (oxytetramethyleneoxy through oxyoctamethyleneoxy) spacers. One of the two azobenzene mesogenic units carries the S(+)-2-methylbutyl ester tail group and the other the *n*-butyl tail. In other words, one of the mesogenic units is chiral and the other is not. Only the compounds of even-numbered polymethylene spacers form mesophases enantiotropically, whereas those of odd-numbered spacers are monotropic. The compounds of penta- and octamethylene spacers exhibit only the cholesteric phase, while the rest show the S_A phase in addition to the cholesteric phase. A racemic mixture containing hexamethylene spacers forms the S_A and nematic phases enantiotropically. This series reveals a typical odd-even effect in the melting (T_m) and isotropization temperatures (T_i) and also in other themodynamic parameters for phase transitions. Differential scanning calorimetry, wide- and small-angel X-ray diffractometry and opitical microscopy are the principle methods utilized in the characterization of the present series of compounds.

Keywords: Dimesogens; azobenzenes; twin liquid crystals; X-ray diffractometry; differential scanning calorimetry; optical microscopy

INTRODUCTION

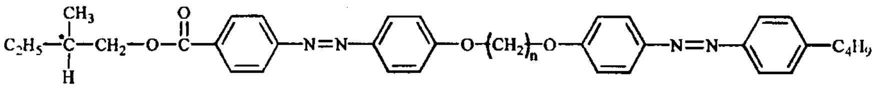
A large number of thermotropic compounds has been synthesized and studied for their phase transitions and molecular organizations in their mesophase in relation to their chemical structures [1–5]. Among them, so-called dimesogenic compounds are now attracting a great deal of interests due to their unique phase transition behavior [6–13]. These compounds consist of two mesogenic units interconnected through a central spacer such as polymethylene, oligo(oxyethylene) and oligosiloxyl groups. When the two mesogenic units are same in their chemical structure, the dimesogenic compounds are often referred to twin or siamese liquid crystals.

Recently, our research has been directing toward the establishment of structure-liquid crystalline property relationship of dimesogenic compounds carrying two dissimilar mesogenic units such as cholesterol moiety and Schiff-base [14, 15] or azobenzene moiety [16]. Surprisingly, it was found that some of the compounds, especially when the spacer is 6-oxyhexanoyl structure, tend to form incommenurate smectic phases in addition to the twisted grain boundary and cholesteric phases before isotropization [14, 15]. A representative example is given below:



This compound exhibits xa rather complicated phase transitions including incommensurate smectic phases. When the imino (—CH=N—) group is replaced with the azo (—N=N—) group, phase transition becomes much simpler [16].

While conducting research on the liquid crystalline properties of the above mentioned compounds, we became interested in the investigation of the liquid crystalline properties of the following series of compounds.



KIV-n (n = 4 ~ 8)

These compounds consist of two azobenzene type mesogenic units interconnected through the central oxypolymethyleneoxy spacers. And only one of the mesogenic units carries a chiral center. The length of the central polymethylene groups was varied from tetramethylene ($n = 4$) to octamethylene

($n = 8$). Although these compounds should be called S(+)-2-methylbutyl 4-[(4-butylphenylazophenoxy)polymethyleneoxy]phenylazobenzoate, for the sake of convenience, they are described as KIV-*n*, where *n* is the number of the methylene groups in the spacer.

In this investigation, we paid our attention particularly to the effect of the length of and oddness or evenness in the number of the methylene groups in the spacer on liquid crystalline properties of the present compounds. Thermodynamic parameters for phase transitions were also compared with each other. We also attempted to find similarity or dissimilarity between the liquid crystalline properties of the present series and previously reported compounds that contain the chiral cholesterol moiety instead of the chiral azobenzene moiety. Differential scanning calorimetry (DSC), wide- and small-angle X-ray diffractometry and observation on a hot-stage of a cross-polarizing microscope are the major mothodologies utilized in the studies of thermal transitions and thermotropic behavior of the compounds.

EXPERIMENTAL

Synthesis of the KIV-*n* Compounds

All of the compounds were synthesized following the route shown in Synthetic Scheme I. As a typical example, the synthetic details for KIV-4 are described below. Other compounds were synthesized in the same manner.

S(+)-2-Methylbutyl 4-nitrobenzoate ($\underline{1}$). 4-Nitrobenzoic acid (16.71 g; 0.10 mol) was dissolved in 36 mL of purified thionyl chloride [17] and the mixture was refluxed for 4 h. The excess thionyl chloride was removed by distillation. The obtained acid chloride was dissolved in 100 mL of dry tetrahydrofuran (THF) [18]. A solution of S(+)-2-methyl-l-butanol dissolved in a mixture of 20 mL of dry THF and 24 mL of dry pyridine [19] was added dropwise at 0°C with vigorous stirring to the 4-nitrobenzoyl chloride solution. The mixture was stirred for 12 h at room temperature. The insoluble was removed by filtration. To the filtrate added was 1000 mL of 0.2 M HCl to form a oily layer of the crude product. The oily layer was separated, washed thoroughly with distilled water and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography using silica gel and a mixture of hexane and ethyl acetate ($v/v = 3/1$). The product yield was 85% (20.3 g) and is a liquid at room temperature. Its structure was confirmed by elemental analysis, and ^1H- NMR- and IR-spectroscopy.

Anal.: Cald. for $C_{12}H_{15}NO_4$, C 60.75; H 6.37; N 5.90, Found C 60.88; H 6.57; N 5.94%. ^{1}H-NMR spectrum ($CDCl_3$, δ_{PPM}), 1.0 (*m*, 6H, $—CH_3$), 1.3 (*m*, 1H, $—CH_2—$), 1.55 (*m*, 1H, $—CH_2—$), 1.9 (*m*, 1H, $—\underline{CH}(CH_3)—$), 4.25 (*m*, 2H, $—CH_2O$), 8.3 (*m*, 4H, Ar). IR-spectrum (neat, cm^{-1}), 3004 (aromatic $=C—H$ stretching), 2933 (aliphatic $C—H$ stretching), 1725 ($C{=}O$ stretching), 1530 and 1347 (NO_2 stretching), 1607 (aromatic $C{=}C$ stretching).

S(+)-2-Methylbutyl 4-aminobenzoate (2). Compound 1 (23.7 g; 0.10 mol) was dissolved in a mixture of 300 mL of ethanol and 55 mL of 20% acetic acid. To the solution added was 25 g of iron powder. The mixture was refluxed under nitrogen atmosphere for 4 h. And then 25 mL of 40% aqueous sodium hydroxide solution was added to the reaction mixture. The mixture was filtered through a filter paper. Excess water was added to the filtrate with vigorous stirring. The precipitate was collected and dried. The product was dissolved in ethyl acetate. After removing the insoluble by filtration, ethyl acetate was removed using a rotary evaporator. The solid residue (yield: 74% (15.3 g), mp 50°C) was used in the next synthetic step without any further purification.

Anal.: Calcd. for $C_{12}H_{17}NO_2$, C 69.54; H 8.27; N 6.57, Found C 69.81; H 8.53; N 6.74%. ^{1}H-NMR spectrum ($CDCl_3$, δ_{PPM}), 1.0 (*m*, 6H, $—CH_3$), 1.3 (*m*, 1H, $—CH_2—$), 1.55(*m*, 1H$—CH_2—$), 1.8 (*m*, 1H, $—\underline{CH}(CH_3)—CH_2—$), 4.1 (*m*, 4H, $—CH_2O—NH_2$), 6.65 (*d*, 2H, Ar), 7.85 (*d*, 2H, Ar). IR-spectrum (KBr, cm^{-1}), 3200 ~ 3500 (NH_2 stretching), 3002 (aromatic $=C—H$ stretching), 2948 (aliphatic $C—H$ stretching), 1684 ($C{=}O$ stretching), 1599 (aromatic $C{=}C$ stretching).

4-[4-S(+)-(2-Methylbutyloxycarbonyl)phenylazo]phenol (3). S(+)-2-Methylbutyl 4-aminobenzoate (20.37 g; 0.10 mol) was dissoved in a mixture of 40 mL of distilled water and 30 mL of concentrated HCl. The mixture was cooled down to 10°C, to which an aqueous solution of sodium nitrite (6.9 g in 16 mL of water) was added dropwise over a period of 15 min, while the temperature of the reaction mixture was maintained at 10 ~ 15°C. To the reaction mixture added was 50 mL of methanol to dissolve some insoluble salt. A phenol solution made of 9.4 g of phenol, 4.0 g of NaOH, 12 g of Na_2CO_3 and 170 mL of distilled water, was added dropwise over the period of 30 min to the diazonium salt solution maintaining the temperature of the mixture at 5°C. The mixture was stirred for 1 more h at 5°C. And then excess distilled water was mixed with the reaction mixture. The precipitate was collected on a filter and the portion soluble in diethyl ether was extracted. The ether solution was dried over anhydrous $MgSO_4$ and ether was removed by distillation. The crude product thus obtained was purified by recrystallization from a mixture of hexane and ethyl acetate ($v/v = 10/1$). The product yield was 59% (18.3 g), mp 123°C.

Anal.: Calcd. for $C_{18}H_{20}N_2O_3$, C 69.22; H 6.45; N 8.96. Found C 68.68; H 6.55; N 8.89%. ^{1}H-NMR spectrum ($CDCl_3$, δ_{PPM}), 1.0 (*m*, 6H, —CH_3), 1.3 (*m*, 1H, —CH_2—), 1.55 (*m*, 1H, —CH_2—), 1.8 (*m*, 1H, —$\underline{CH}(CH_3)$—CH_2—), 4.2 (*m*, 2H, —CH_2O—), 7.0 (*d*, 2H, Ar), 7.9 (*q*, 4H, Ar). IR-spectrum (KBr, cm^{-1}), 3392 (O—H stretching), 3004 (aromatic=C—H stretching), 2962 (aliphatic C—H stretching), 1692 (C=O stretching), 1601 and 1589 (aromatic C=C stretching).

4-(4-Bromobutyloxy)-4′-butylazobenzene ($\underline{5}$). 4-(4-Butylphenylazo)phenol ($\underline{4}$) (5.0 g; 2.0×10^{-2} mol), prepared via the diazo coupling reaction [20] between *n*-butylaniline and phenol, was dissolved in 50 mL of acetone. 1, 4-Dibromobutane (25 g; 0.14 mol) and K_2CO_3 (10.87 g; 7.9×10^{-2} mol) were mixed with the above solution of $\underline{4}$. The mixture was refluxed for 12 h under nitrogen atmosphere. The mixture was filtered through a filter paper and the filtrate was poured into excess ethanol precipitating the product. The product was purified by recrystallization from ethanol. Yield was 44% (3.43 g), mp 64°C.

Anal.: Calcd. for $C_{20}H_{25}N_2OBr$, C 61.70; H 6.47; N 7.19. Found, C 61.74; H 6.66; N 7.60%. ^{1}H-NMR spectrum ($CDCl_3$, δ_{PPM}), 0.9 (*t*, 3H, —CH_3), 1.3 ~ 1.5 (*m*, 2H, —CH_2CH_3), 1.5 ~ 2.2 (*m*, 6H, —CH_2CH_2Ar and —$OCH_2(CH_2)_2CH_2Br$), 2.65 ~ 2.75 (*t*, 2H, —CH_2Ar), 3.5 ~ 3.7 (*t*, 2H, —CH_2Br), 7.0 ~ 8.0 (*m*, 8H, Ar). IR-spectrum (KBr, cm^{-1}), 3002 (aromatic = C—H stretching), 2934 (aliphatic C—H stretching), 1601 and 1589 (aromatic C=C stretching), 1253 (C—O stretching).

S(+)-2-Methylbutyl 4-[4′-{4-(4-butylphenylazophenoxy)butyloxy} phenylazo]benzoate (KIV-4). Compound $\underline{3}$ (2.5 g; 8.0 mmol) and 4.4 g (32 mmol) of K_2CO_3 were stirred in 50 mL of acetone. Compound $\underline{5}$ (2.7 g; 7.0 mmol) was dissolved in the solution and then the mixture was refluxed for 24 h under nitrogen atmosphere. The reaction mixture was poured into excess distilled water. The precipitate was recrystallized from a mixture of methylene chloride and acetone (*v*/*v* = 1/1). The product yield was 3.6 g (82%), mp 137°C.

Anal.: Calcd. for $C_{38}H_{44}N_4O_4$, C 75.33; H 7.14; N 9.02. Found, C 73.11; H 7.19; N 9.00%. ^{1}H-NMR spectrum ($CDCl_3$, δ_{PPM}), 0.9 ~ 1.1 (*m*, 9H, —CH_3), 1.2 ~ 2.0 (*m*, 8H, —CH_2—), 2.65 ~ 2.75 (*t*, 2H, —CH_2Ar), 4.1 (*m*, 6H, —OCH_2), 7.0 ~ 8.2 (*m*, 16, Ar). IR-spectrum (KBr, cm^{-1}), 3005 (aromatic=C—H stretching), 2936 (aliphatic C—H stretching), 1709 (C=O stretching), 1599 (aromatic C=C stretching), 1253 (C—O stretching).

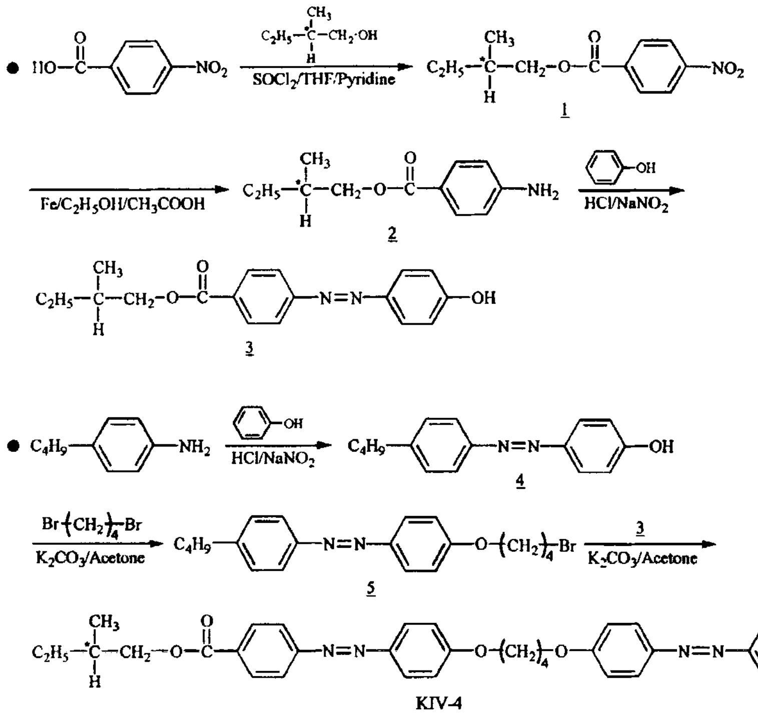
Thermal and Liquid Crystalline Properties

The thermal properties of the compounds were studied under a nitrogen atmosphere by differential scanning calorimetry (Perkin Elmer DSC 7) at the heating and cooling rate of 5°C/min. Indium was employed as a reference for the calibration of temperature and estimation of transition enthalpies. The endo- or exothermic peak maxima or minima are taken as transition temperatures. The optical textures of melts were observed on a hot-stage (Mettler FP-82) with a central control system (Mettler FP-90) attached to a polarizing microscope equipped with an Olympus PM-6 camera. Magnification was 200. X-ray diffractograms were obtained on a Rigaku Denki instrument using a Ni-filtered CuK$_\alpha$ radiation (0.1542 nm). The sample holder was heated with two cartridge heaters and temperature was monitored by a thermocouple.

RESULTS AND DISCUSSION

Synthesis of Compounds

All of the compounds were synthesized following the steps shown in Scheme I as given below:



SCHEME I

TABLE I Phase Transitions of 4-(4-Bromoalkoxy)-4'-butylazobenzene

		Transition Temperature, °C		
n	*K*	S_A	*N*	*I*
4		64.3	66.7	77.0
5		61.7	69.1	72.0
6		65.0	71.3	76.4
7		61.0	68.9	78.0
8		62.0	74.5	

Description of a representative synthetic procedure is given only for KIV-4 as an example. S(+)-2-Methylbutyl 4-nitrobenzoate (1), prepared from 4-nitrobenzoic acid and S(+)-2-methylbutanol, was reduced to the corresponding amino compound 2 by using Fe—CH_3COOH. Diazo coupling of 2 with phenol produced 4-[4-S(+)-(2-methylbutoxycarbonyl) phenylazo]phenol (3). The structure of 3 could be confirmed by elemental and spectroscopic analyses.

4-(4-Bromobutoxy)-4'-butylazobenzene (5) was prepared by reacting 4-(4-butylphenylazo)phenol (4) at the refluxing temperature with large exess 1,4-dibromobutane in acetone in the presence of potassium carbonate. Compound 5 was found to be thermotropic and formed the smectic A and nematic phases before isotropization. Its phase transition is as follows:

$$\text{Crystal} \xrightarrow{64.3\ ^\circ\text{C}} S_A \xrightarrow{66.7\ ^\circ\text{C}} \text{N} \xrightarrow{77.0\ ^\circ\text{C}} \text{isotropic liquid}$$

Thermotropic properties of other intemediates 5 with longer spacers are summarized in Table I. Only the compound with the octamethylene spacer did not form nematic phase, whereas all others formed the smectic A as well as nematic phases before isotropization.

Compounds 3 and 5 were condensed in acetone to produce the final compound, KIV-4. The base utilized in this reaction was K_2CO_3. Structure of all of the final compounds were confirmed by elemental and spectroscopic analyses as described in Experimental.

Liquid Crystalline Properties

Liquid crystalline behavior of the present series of compounds were studied by DSC analysis and wide- and small-angle X-ray diffractometry. Changes in optical textures also were observed on a polarizing microscope equipped with a hot-stage.

Table II summarizes the phase transition temperatures of the compounds. The most striking feature of the phase transition behavior of the present of compounds lies in the fact that KIV-5 and KIV-7, both of which have an odd number of methylene units in the spacer, are monotropic, whereas all of the even-numbered compounds are enantiotropic. This phenomenon can be ascribed to the relatively higher heat of melting, i. e., the ΔH_m values, of the odd-numbered members when compared with those of the even-numbered ones (see Tab. III). It is rather well established that the compounds having high ΔH_m values tend to be monotropic or non-liquid crystalline [9, 21–23], because too much of thermal energy has to be applied in order to destroy crystal lattices, which, in turn, leads to direct transformation of crystalline solids into isotropic liquids. KIV-7 of the heptamethylene spacer monotropically forms the S_A and cholesteric phases, but KIV-5 of the shorter spacer forms only the cholesteric phase. The next interesting point to be noted is that KIV-8 with the longest central spacer forms only the cholesteric phase while KIV-4, KIV-6 and KIV-7 form the S_A phase in addition to the cholesteric phase. This indicates that longer spacers hinder the formation of layered mesophases probably due to their conformational flexibility. The KIV-6r compound was synthesized using a racemic mixture of the chiral mesogenic unit. This compound formed the S_A and N phases as expected.

TABLE II Phase Transition Temperatures of KIV-*n* Series

		Transition Temperature, °C		
n	*K*	S_A	N^*	*I*
KIV-4		137.9	196.6	200.9
		(122.9)[a]	(195.5)	(199.6)
KIV-5		123.8		
		(113.3)		(121.2)
KIV-6		130.7	150.3	172.3
		(120.7)	(149.5)	(171.0)
KIV-6r[b]		131.5	151.5	172.9
		(120.7)	(150.1)	(171.0)
KIV-7		125.8		
		(99.0)	(100.5)	(118.3)
KIV-8		129.2		152.2
		(114.8)		(150.4)

[a] The values in the parenthesis were obtained from the cooling DSC curve.

[b] Racemic mixture.

TABLE III Thermodynamic Parameters for Phase Transitions

	ΔH_m	$\Delta H_{S\text{-}N^*}$	$\Delta H^2_{N^*\text{-}I}$	ΔS_i	$\Delta H_{N^*\text{-}I}/\Delta H_m$
Compound	*KJ/mol*	*KJ/mol*	*KJ/mol*	*J/mol·K*	%
KIV-4	38.1	2.2	4.4	9.3	12
	(35.6)[b]	(2.0)	(4.3)	(9.1)	12
KIV-5	46.2				
	(39.5)		(1.0)	(2.5)	2.5
KIV-6	44.6	0.4	4.6	10.3	10
	(42.1)	(0.4)	(4.4)	(9.9)	11
KIV-6r[c]	43.6	0.2	4.9	11.0	11
	(42.1)	(0.2)	(4.7)	(10.6)	11
KIV-7	66.8				
	(51.9)		(1.1)	(2.8)	2.1
KIV-8	53.1		4.8	11.3	9.0
	(47.9)		(4.4)	(10.4)	9.2

[a] $\Delta H_{N^*\text{-}I}$ has been simplified to ΔH_i in the text. The subscript letter i in ΔH_i describes isotropization.

[b] The values in the parenthesis were obtained from the cooling DSC curve.

[c] Racemic mixture.

The phase transition behavior of the KIV-*n* series is in a great contrast to that of the intermediates, 5, 4-(ω-bromopolymethyleneoxy)-4-butylazobenzenes as shown in Table I. These intermediates all reveal the formation of the S_A and N phases regardless of the length of and oddness or evenness in the number of the methylene groups in the ω-bromoalkoxy tails with the exception of 5 with $n = 8$ that forms only the S_A phase. The presence of the chiral mesogenic structure in the KIV-*n* compounds certainly leads to the formation of the cholesteric phase.

Mainily the fan or focal conic textures (Fig. 1) and oily-streak textures (Fig. 2) were observed for the S_A and N* phases, respectively. The spacings estimated for the S_A phases from the X-ray diffraction peaks (Figs. 3 and 4) in the small-angle region were in general slightly greater than those calculated for the molecular length using CS CHEM 3D assuming fully extended zig-zag trans conformations for the central polymethylene spacers. The X-ray diffractograms of the cholesteric phases of the compounds that form the S_A phase as well show very broad and weak small angle diffractions whose peak maxima are very close to the ones observed for the S_A phases as one can see from Figure 3. This must be due to the remnant S_A-like molecular order remaining in the cholesteric phase. But KIV-8 that forms only the cholesteric phase does not show this phenomena (refer to Fig. 4).

Figure 5 represents the dependence of the crystalline melting points, T_m, and the isotropization temperatures, T_i, of the present compounds on the

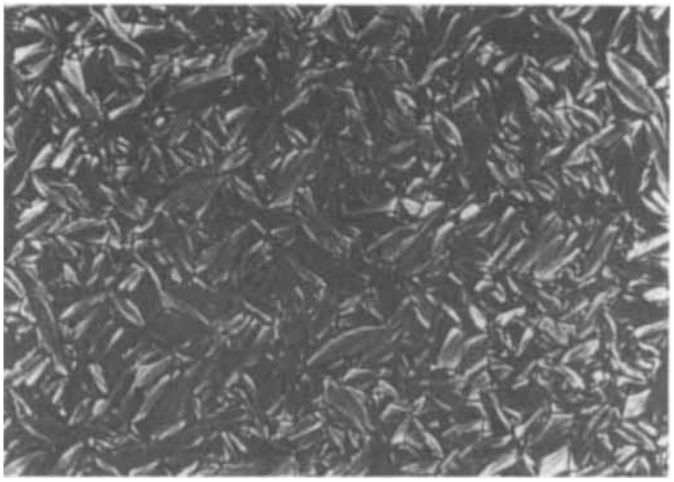


FIGURE 1 Optical photomicrograph of the S_A texture of KIV-4 (180°C) (magnification 200x).

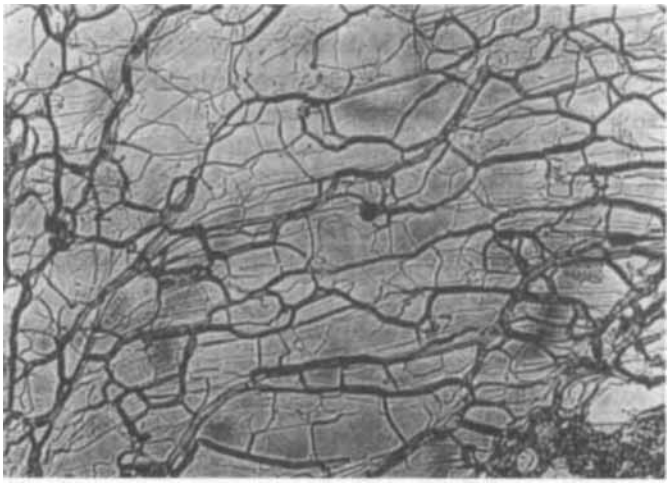


FIGURE 2 Optical photomicrograph of the N* texture of KIV-6 (153°C) (magnification 200x).

length and the oddness or evenness of the spacers. A couple of interesting trends can be found: first, the T_m and T_i values reveal a typical odd-even effect [11, 12, 24, 25] with those for even members being higher than those for odd members. Similar phenomena have repeatedly observed for other series of dimesogenic compounds [6, 7, 9]. Secondly, the amplitude in the

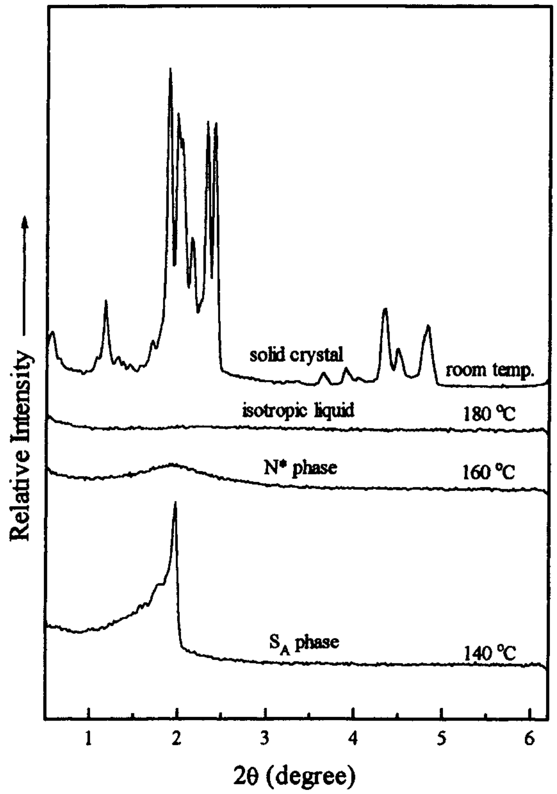


FIGURE 3 X-ray diffractograms of KIV-6.

alternation both in T_m and T_i values appear to diminish as the length of the spacers increases [9]. At the same time, the alternating amplitudes in T_i values is consistently much greater than those in T_m values. The transition temperatures of the racemic KIV-6r compound are practically same as those for KIV-6.

The thermodynamic parameters for phase transitions of the present series are summarized in Table III. As already referred to above, the melting enthalpies of KIV-5 and KIV-7 are significantly greater than others. This was described to be responsible for their being monotropic. In general, the magnitude of ΔH_m values of the present series are much greater than those of other monomesogenic compounds [23]. This must be due to the presence of two mesogenic units in the present compounds, which lead to a higher crystal lattice force and also due to their increased molar mass. The entropy

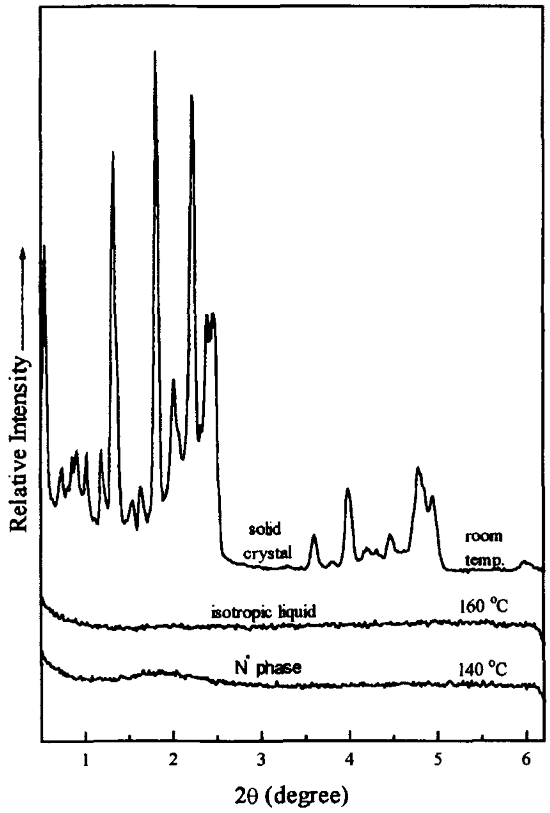


FIGURE 4 X-ray diffractograms of KIV-8.

changes, i.e. the ΔS_i values, for due to their increased molar mass. The entropy changes, i.e. the ΔS_i values, for isotropization transitions are consistently higher for the compounds having the even numbered spacers than those for odd-numbered members. This can be taken as a suggestion that the cholesteric phases of the formers are of a greater molecular order than the latters. Lastly, the magnitude of heat of isotropization, ΔH_i ($1.0 \sim 5.0$ KJ/mol) is about $2 \sim 10\%$ of ΔH_m($36 \sim 67$ kJ/mol); this is unusually high when compared with the cases for monomesogenic compounds, for which the ΔH_i value is usually in the range of $1 \sim 5\%$ of ΔH_m values [23]. Probably, the presence of two mesogenic units in the present compounds requires higher thermal energy to destroy liquid crystalline order, which, in turn, gives rise to much higher T_i values than the monomesogenic compounds (refer to Tab. I). This observation appears to be general of

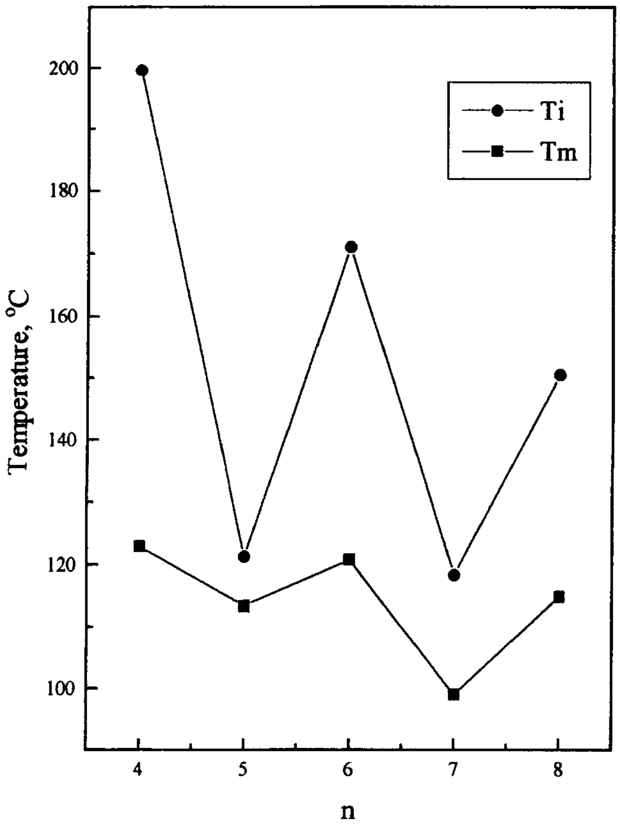


FIGURE 5 Dependence of T_m and T_i of KIV-*n* series on the length, *n*, polymethylene spacer.

dimesogenic LC compounds as was described for other series [7, 9, 21, 22]. The particularly low ΔH_i values for the monotropic compositions (KIV-5 and KIV-7) indicate that thermal stability of their cholesteric phases is rather poor.

Figure 6 represents the dependence of enthalpy (ΔH_i) and entropy (ΔS_i) changes for isotropization on the number of the methylene units in the spacers. For the sake of consistency, the values obtained from the cooling DSC thermograms were taken for this comparison. For the both thermodynamic parameters, a perfect odd-even effect is observed. The value for the members of even-numbered spacers are much higher than those for the odd-numbered members. Therefore, we believe that the odd-even effect is applicable even to a series of dimesogenic compounds where the structures of the two mesogenic units are not the same. Once again, the molecular

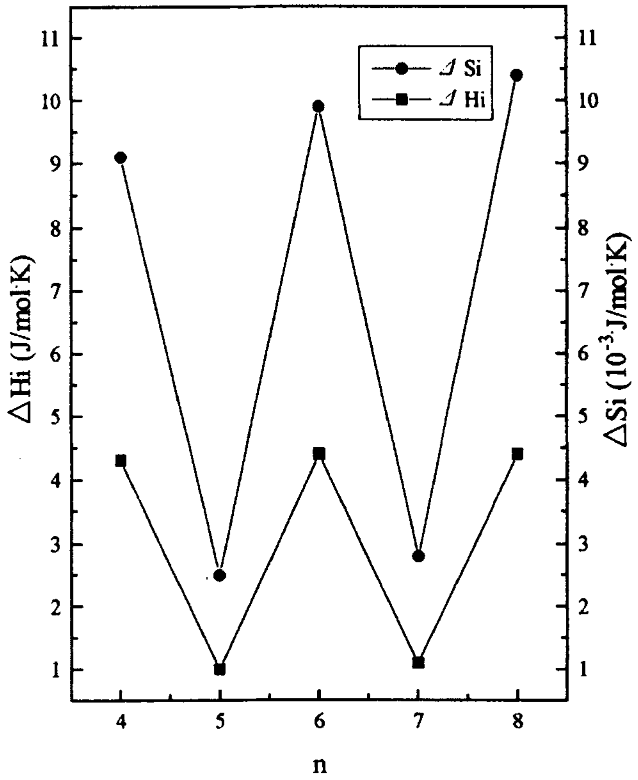


FIGURE 6 Dependence of ΔH_i and ΔS_i of KIV-*n* series on the length, *n*, polymethylene spacer.

order in the cholesteric phase of the even-numbered members is judged to be significantly higher than that of the odd-numbered members.

CONCLUSION

Liquid crystalline properties of S(+)-2-methylbutyl 4-[ω-(4-butylphenylazophenoxy)polymethyleneoxy]phenylazobenzoate are strongly dependent on the length of and oddness or evenness in the number of the methylene units in the central polymethylene spacer. The even members are enantiotropically thermotropic, whereas the odd members are monotropic, which is ascribed to higher heat of melting transitions for the latters. KIV-4, KIV-6, and KIV-7 form the S_A and N* phases and the rest only the N* phase. These compounds exhibit a clear odd-even effect in T_m as well as in T_i values with the values for the even members being higher than those for the odd ones. The phase behavior of the present compounds are much different from those of the monomesogenic components and also from those containing cholesterol unit [14, 15] in place of the present chiral mesogenic unit. This implies that molecular ordering of the dimesogenic compounds should be analyzed more in detail in future works. It certainly is not a simple combination of the molecular ordering of each monomesogenic components.

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