

# Dimesogenic Compounds Consisting of Two Identical Terminal N-(4-Oxybenzylidene)-4-*n*-butylaniline Units and a Central Polymethylene Spacer

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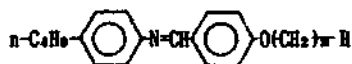
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A series of dimesogenic compounds having two identical, terminal Schiff base type mesogens and a central polymethylene spacer were prepared and their properties were compared with those of the corresponding monomesogenic compounds. The mesomorphic properties of the compounds were studied by differential scanning calorimetry and on a hot-stage of a polarizing microscope. All of the dimesogenic compounds formed mesophases enantiotropically with the exception of pentamethylene-1,5-bis(4-oxybenzylidene 4-*n*-butylaniline). This compound was monotropic and formed only a nematic phase on heating the solid, whereas it formed nematic as well as smectic A phases on cooling the isotropic liquid. Those compounds containing longer (octamethylene and decamethylene) spacers favored the formation of nematic phase whereas those having shorter (dimethylene and tetramethylene) spacers formed smectic phases. In general, the variety of mesophase forms exhibited by the dimesogenic compounds was significantly less than that shown by the corresponding monomesogenic compounds.

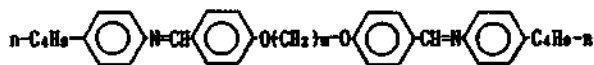
## Introduction

Synthesis and properties of low molecular weight, liquid crystalline monomesogenic compounds have been reported intensively for the past 30 year.<sup>1-7</sup> In addition, the structure-property relationships of thermotropic compounds consisting of terminal mesogenic units and central spacers, *i.e.*, dimesogenic compounds, are recently attracting a great deal of interest.<sup>12,8-26</sup> This type of compounds not only has interesting mesomorphic properties but also can be taken as simple low molecular weight models for the main-chain thermotropic polymers having alternating sequence of the similar mesogenic units and spacers.<sup>27-30</sup> While trying to establish the structure-property relationship of the dimesogenic compounds, we become interested in the liquid crystalline behavior of dimesogenic compounds having two identical terminal Schiff base type mesogens interconnected through a central, polymethylene spacer. Especially their thermal behavior and the nature of the mesophases that they form were of our interest.

In the present investigation, we tried to compare the mesomorphic properties of the two different series of compounds, Series I and II, shown below:



Series I:  $n = 1-7$  and  $10$  (I-n)



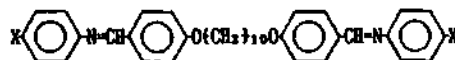
Series II:  $n = 2, 4, 5, 8$  and  $10$  (II-n)

Most of the Series I compounds are known and only I-6 and I-10 were prepared anew. The compound I-6 was reported earlier by Smith *et al.*,<sup>7</sup> but we found that the reported transition temperatures revealed some discrepancy when compared with those of our data.<sup>23</sup> In connection with the

present investigation earlier we studied the mesomorphic properties of the following two series of the compounds:<sup>10</sup>



$n = 2-10$



X = H, CH<sub>3</sub>, OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>, Br, CN, NO<sub>2</sub>, and  $\text{CH}_3\text{CO}$   
 $\text{O}$

All of the compounds of the first series and most of the second series exhibited the formation of nematic phase only. Moreover, the odd-even dependence of transition temperatures and thermodynamic parameters for phase transitions were observed in the first series.

## Experimental Section

**Chemicals and Instruments.** All of the chemicals used in this investigation were of reagent grade and employed as received, with the exception of several solvents which were purified before use by the literature methods.<sup>31</sup>

The IR and NMR spectra of the compounds were obtained on a Perkin-Elmer IR Spectrometer 710B and on a Varian Associates EM 360A, respectively. Elemental analyses of the samples were conducted using a Perkin-Elmer CHN analyzer by the Analytical Department of the Korea Research Institute of Chemical Technology. Thermal behavior of the compounds was studied under a N<sub>2</sub> atmosphere on a duPont DSC 910 with a heating or cooling rate of 10°C/min. Indium was employed as a reference for temperature calibration and estimation of thermodynamic parameters for the phase transitions. The optical textures of the melts were examined on a cross-polarizing microscope (Leitz, Ortholux) equipped with

a Mettler hot stage FP-2. Magnification was 150X.

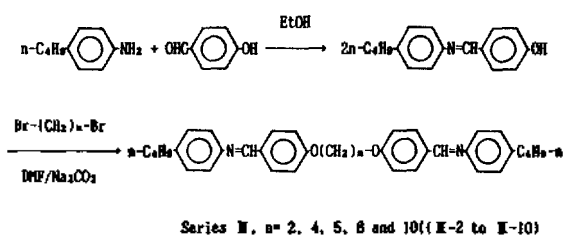
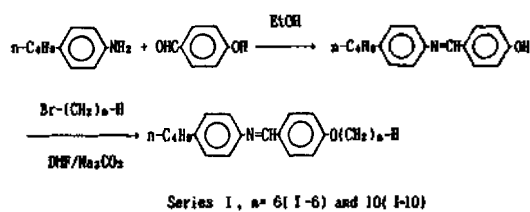
**Synthesis of I-10.** 4-Hydroxybenzaldehyde (24.4 g; 0.20 mole) and 4-*n*-butylaniline (29.8 g; 0.20 mole) were placed in a three-necked, round-bottomed flask equipped with a stirrer and a water-cooled condenser. Absolute ethanol (200 ml) was mixed with the reactants in the flask. The reaction mixture was refluxed for two hours. Afterwards, the solution was chilled in an ice-water bath and the precipitate formed was collected on a filter. After being dried, the crude product of *N*-(4-hydroxybenzylidene)-4-*n*-butylaniline was recrystallized from absolute ethanol. The yield was 92% (46.6 g); mp. 173-174°C.

A portion of *N*-(4-hydroxybenzylidene)-4-*n*-butylaniline thus obtained (3.80 g; 0.015 mole) and 0.848 g (8.0 mmole) of anhydrous sodium carbonate were dissolved in 20 ml of DMF. To this solution was added 3.32 g (0.015 mole) of 1-bromodecane. The mixture was stirred vigorously at 135°C for 24 hours. The reaction mixture was then poured into a large excess aqueous 0.5 M sodium carbonate solution. The precipitate was thoroughly washed with water. The product, *N*-(4-*n*-decyloxybenzylidene)-4-*n*-butylaniline, was recrystallized from petroleum ether. The yield was 63% (3.71 g); mp. 48-49°C. Anal. Calcd: C, 82.44; H, 9.92; N, 3.56%. Found: C, 82.54; H, 9.92; N, 3.60%. The structure was confirmed by its IR and NMR spectra.

**Synthesis of Series II Compounds.** *N*-(4-Hydroxybenzylidene)-4-*n*-butylaniline (5.06 g; 0.020 mole) and 1.06 g (0.010 mole) of anhydrous sodium carbonate were dissolved in 20 ml of DMF. To this solution was added 0.010 mole of  $\alpha, \omega$ -dibromoalkanes. The reaction mixture was stirred vigorously at 135°C for 4 hours. The reaction mixture was then poured into a large excess aqueous 0.5 M sodium carbonate solution. The precipitate was thoroughly washed with water. The product, polymethylene- $\alpha, \omega$ -bis(4-oxybenzylidene)-4-*n*-butylaniline, was recrystallized from *n*-butanol. The product yields and the results of elemental analyses of Series II compounds are tabulated in Table 1. The structures were confirmed by their IR and NMR spectra.

## Results and Discussion

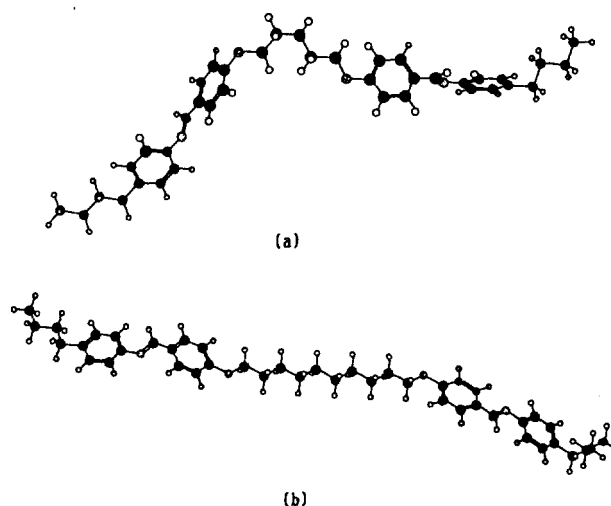
As described in Experimental Section, the synthesis of the Series I and II compounds is rather straightforward and each reaction step is of relatively well known type. The synthetic schemes are as follow:



**Table 1.** The Yields and Results of Elemental Analysis of Series II Compounds

n	Yield, %	Elemental analysis, wt.% <sup>a</sup>		
		C	H	N
2	78	81.20(81.35)	7.52(7.59)	5.26(5.46)
4	82	81.43(81.44)	7.86(7.93)	5.00(5.07)
5	75	81.53(81.55)	8.01(8.03)	4.88(4.91)
8	83	81.82(81.90)	8.44(8.54)	4.55(4.56)
10	80	81.99(82.02)	8.70(8.74)	4.35(4.38)

<sup>a</sup>The values in the parentheses are the calculated ones for the molecular formulas.



**Figure 1.** Molecular structures of (a) II-5 and (b) II-10.

Their yields and results of elemental analyses are given in Table 1. The yields reported in Table 1 are for the final steps and they are in the range of 75-85% after recrystallization. The results of the compounds' elemental analyses are in good agreement with calculated values. The structures of the compounds were further confirmed by IR and NMR spectra. Purity of the compounds was checked by TLC.

Figure 1 compares the molecular structures of II-5 and II-10. They are of minimum conformation energies drawn by a Macintosh SE using Chem. Draw 3D. These molecular structures reveal a few interesting features. First of all, the two phenylene rings linked through imino group are not exactly coplanar and twisted to each other. The compound II-10 is not exactly of linear rigid rodlike structure, but close to it. On the contrary, the II-5 compound having pentamethylene spacer has a bent molecular shape mainly due to the odd number of methylene units in the central part. And the dihedral angle between the adjacent phenylene rings appear larger in II-5 than in II-10.

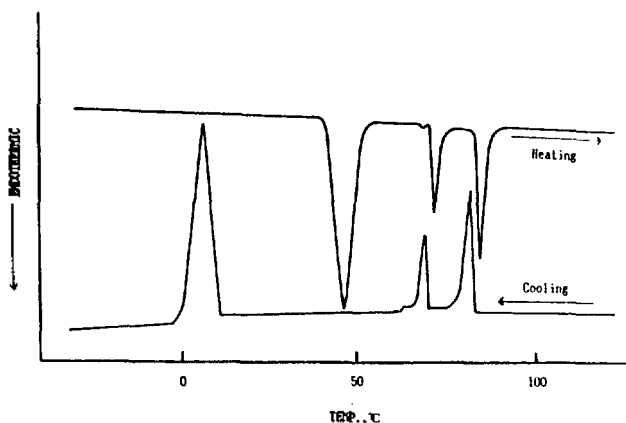
Table 2 summarizes the mesomorphic properties of the Series I compounds. Only the data for I-6<sup>23</sup> and I-10 are our experimental results and others are quoted from the reference.<sup>7</sup> When the terminal alkoxy group is methoxy or ethoxy group, the compound is able to form only a nematic phase. The compound with *n*-propoxy terminal, however, forms a *S<sub>B</sub>* phase monotropically in addition to the nematic phase. The compounds with *n*-butoxy and *n*-pentoxy groups form

**Table 2.** Transition Temperatures and Liquid Crystal Phases of Series I Compounds<sup>a</sup>

$$n\text{-C}_4\text{H}_9\text{-C}_6\text{H}_4\text{-N=CH-C}_6\text{H}_4\text{-O(CH}_2)_n\text{H}$$

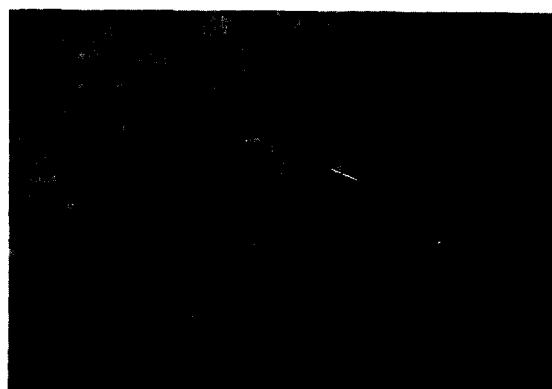
Compound	Transition temperatures, °C					
	<i>n</i>	<i>S<sub>B</sub></i> <sup>b</sup>	<i>S<sub>C</sub></i> <sup>b</sup>	<i>S<sub>A</sub></i> <sup>b</sup>	<i>N</i> <sup>b</sup>	<i>I</i> <sup>b</sup>
1					20.9	45.9
2					35.3	79.0
3		(23.3)			41.1	55.7
4		41.0		45.2	45.7	74.7
5		12.0		52.1	52.4	69.0
6		35.0 <sup>d</sup>	59.9 <sup>d</sup>	59.9 <sup>d</sup>	69.0 <sup>d</sup>	77.7 <sup>d</sup>
7		32.2	63.3	64.8	74.1	76.2
10		48.0 <sup>e</sup>	70.3 <sup>e</sup>	73.0 <sup>e</sup>		85.8 <sup>e</sup>

<sup>a</sup>Values from Ref. 7. <sup>b</sup>*S<sub>B</sub>*; smectic B, *S<sub>C</sub>*; smectic C, *S<sub>A</sub>*; smectic A, *N*; nematic, *I*; isotropic. <sup>c</sup>The value in parenthesis denotes monotropic transition. <sup>d</sup>Values from Ref. 23. <sup>e</sup>Values from the present investigation.

**Figure 2.** DSC thermograms of Series I Compound with *n* = 10. The heating and cooling rates were 10°C/min.

*S<sub>B</sub>*, *S<sub>A</sub>* and *N* phases before isotropization, while those having the longer *n*-hexyloxy and *n*-heptyloxy terminals form the *S<sub>C</sub>* phase additionally. The transition temperatures<sup>23</sup> of I-6 given in Table 2 are higher than those reported earlier by others<sup>7</sup>, although the types of mesophases it formed are the same as reported. Purity of the newly prepared sample may be higher causing higher transition temperatures. In contrast, the compound having *n*-decyloxy substituent does not form a nematic phase and exhibits direct phase transition from *S<sub>A</sub>* to isotropic phase enantiotropically (See Figure 2 and 3).

Such an observation for this monomesogenic series leads us to the conclusion that, as the length of the terminal alkoxy substituent increases, these compounds tend to form higher number of different smectic phases in addition to the nematic phase and that, when the alkoxy group becomes even longer, the compounds are not able to form nematic phase, but form only smectic phases. This can be explained on the basis of the increased lateral intermolecular attraction by added methylene unit.<sup>32</sup> Another point is that the very common odd-even effect is observed for nematic-isotropic phase



(a)



(b)



(c)

**Figure 3.** Photomicrographs taken for I-10. (a) at 58°C; (b) at 71°C, and (c) at 80°C (Magnification 150×).

transitions in the plot of *N-I* transition temperatures *vs.* chain length, although this plot is not given in the present paper. Other transitions, however, do not show any odd-even alternation and simply tend to increase smoothly with length of the alkoxy group. For example, *S<sub>A</sub>-N* transition temperatures increase smoothly as the alkoxy chain is extended.

In the Series II compounds the structure of the two terminal mesogenic unit was fixed and the length of the central polymethylene spacer was varied. Figure 4 shows DSC thermograms of the Series II compounds obtained on heating as well as on cooling. The compounds II-2, II-8 and II-10 exhibit two sharp endothermic peaks on heating and the corresponding two exotherms on cooling. In contrast, II-4

**Table 3.** Thermodynamical Data for the Phase Transitions of the Series II Compounds

$n\text{-C}_6\text{H}_5\text{-}\langle\bigcirc\rangle\text{-N=CH-}\langle\bigcirc\rangle\text{-O(CH}_2\text{)}_n\text{-O-}\langle\bigcirc\rangle\text{-CH=N-}\langle\bigcirc\rangle\text{-C}_6\text{H}_5\text{-}n$							
$n$	$T_m$ °C	$T_i$ °C	$\Delta H_m$ , kJ/mole	$\Delta H_i$ , kJ/mole	$\Delta H_i/\Delta H_m$ , %	L.C. Phases	
2	205	237	32.1	4.4	14	$S_A$	
4	146 <sup>a</sup> , 151 <sup>b</sup>	213	43.1 <sup>a</sup> , 3.2 <sup>b</sup>	5.8	13	$S_C^c$ , $S_A^b$	
5	116	127	20.2	1.3	6.4	$N$	
	88 <sup>c</sup> , 112 <sup>c</sup>	124 <sup>c</sup>				$S_A^c$ , $N^c$	
8	136	162	36.6	5.3	15	$N$	
10	134	148	48.9	7.2	15	$N$	

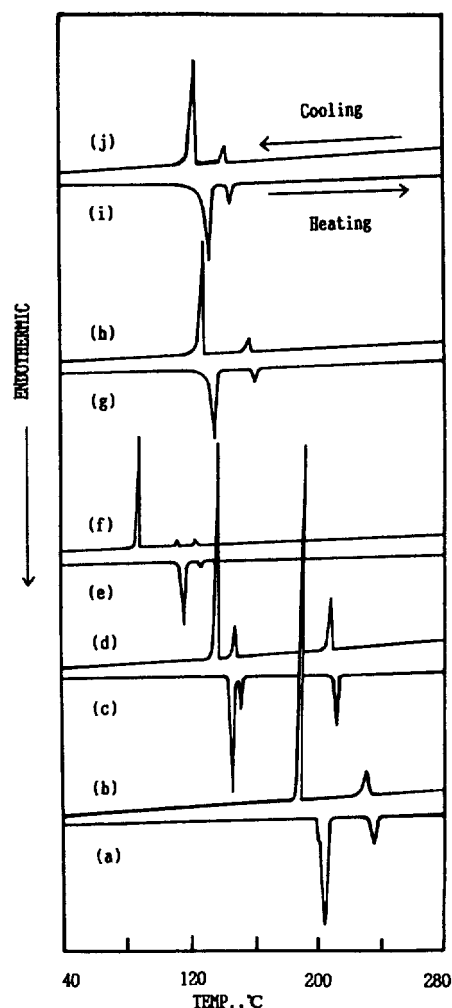
<sup>a</sup> Crystal-Smectic  $C(K-S_C)$  transition. <sup>b</sup> Smectic  $C$ -Smectic  $A(S_C-S_A)$  transition. <sup>c</sup> Values obtained from the cooling cycle of DSC analysis.

exhibits three transition peaks reversibly. The compound II-5 is unique in that it shows two endothermic peaks on heating, but three exothermic peaks on cooling.

According to the optical textures of the melts observed on a polarizing microscope, II-2 formed enantiotropically  $S_A$  mesophase, whereas the two compounds having long polymethylene spacers, II-8 and II-10, formed nematic phase. For II-4, the lowest temperature peak in the DSC thermogram (Figure 4c, d) corresponds to the crystal-smectic  $C(K-S_C)$  transition, the middle peak is for the smectic  $C$ -smectic  $A(S_C-S_A)$  transition and the highest temperature one corresponds to isotropization, i.e., smectic  $A$ -isotropic phase ( $S_A-I$ ) transition. In other words, II-4 formed  $S_C$  as well as  $S_A$  phase enantiotropically.

The compound II-5 has a polymethylene spacer with odd number of methylene groups and is the only one monotropic compound among those described in this article. This compound exhibited  $K-N$  and  $N-I$  transitions on heating. But, it showed the formation of nematic and  $S_A$  phases on cooling before crystallization, see Table 3 and Figure 5d and 5e. On cooling it went through  $I-N$ ,  $N-S_A$  and  $S_A-K$  transition at 124, 112 and 88°C, respectively (Figure 4f).

The most striking contrast between Series I and II lies in the more or less reverse order of the types of mesophases formed as the length of alkoxy terminal groups of Series I and the length of the central spacer in Series II increase. As shown in Table 2, Series I compounds have a tendency to form nematic phase only, nematic and smectic phases, and then smectic phases only as the length of alkoxy terminals gets longer. The Series II compounds, however, form only smectic phases when  $n=2$  or 4, smectic and nematic phases when  $n=5$ , and only nematic phase when  $n=8$  or 10. None of Series II members formed the  $S_B$  phase. Such a contrasting behavior between the two series can be explained on the basis of the assumption that, when a polymethylene spacer is flanked by the two mesogenic structure as in Series II, the increase in the lateral intermolecular attraction by added methylene unit in the central spacer is less than in the structures like Series I. Instead, the increased freedom by the increased length of the central spacer makes it easier for the mesogenic units to form less ordered

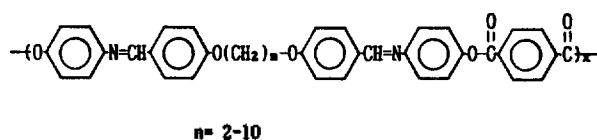


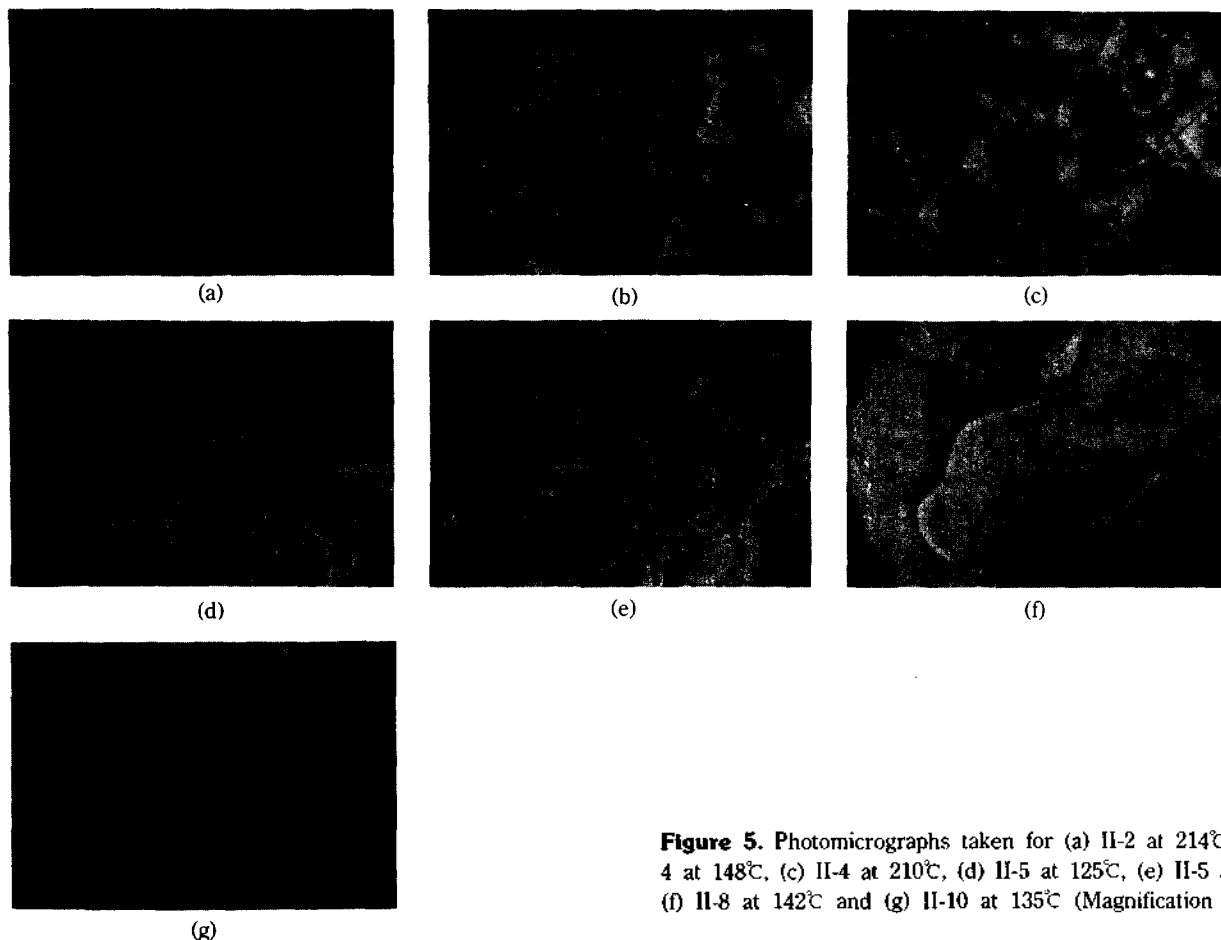
**Figure 4.** Heating and cooling DSC thermograms of II-2 (a, b), II-4 (c, d), II-5 (e, f), II-8 (g, h), and II-10 (i, j).

molecular organization. A combined effect of the two phenomena favors the formation of the nematic phase by the Series II compounds, when their spacers are long enough.

Another contrast between Series I and II is that the mesophase forms exhibited by the Series II compounds are much less in variety. With the exception of II-4, they formed only one mesophase on heating. As mentioned in Introduction we<sup>10</sup> earlier observed that the ethoxy terminal containing compounds only formed the nematic phase when the number of methylene groups in the central spacer was varied from 2 to 10. The present compounds having  $n$ -butyl terminals, however, are capable of the formation of smectic phases as well, when their central spacers are relatively short. Certainly, the longer alkyl terminals appear to favor the formation of smectic phases even for the series II type compounds.

It is also very interesting to recall our earlier observation that the following series polymers formed only nematic phase:<sup>29</sup>





**Figure 5.** Photomicrographs taken for (a) II-2 at 214°C, (b) II-4 at 148°C, (c) II-4 at 210°C, (d) II-5 at 125°C, (e) II-5 at 108°C, (f) II-8 at 142°C and (g) II-10 at 135°C (Magnification 150×).

When the chains contain a large number of mesogenic units interconnected by polymethylene spacers, the types of mesophase that can be formed by the polymers appear to become fewer. This can be ascribed to the limited freedom for the mesogenic units to form a variety of ordered structures in mesophase. This reduced motional freedom for mesogenic units arises from the fact that they are tied on both ends in the chains to which they belong. This is in a great comparison with the fact that the Series II compounds form a smectic or nematic phase(s) depending on the length of the central spacer.

Table 3 shows the values of heat of melting ( $\Delta H_m$ ) and isotropization ( $\Delta H_i$ ) and they range from about 20 to 49 kJ/mole and from 1.3 to 7.2 kJ/mole, respectively. The magnitude of  $\Delta H_i$  values is about 7-15% of those of  $\Delta H_m$ . This percentage values are much greater than those (about 3-5%) observed for the monomesogenic compounds.<sup>33</sup> In fact, the values of  $\Delta H_m$  and  $\Delta H_i$  for the dimesogenic compounds are much higher when compared to those of monomesogenic compounds. The presence of two mesogenic units in the dimesogenic compounds certainly causes stronger intermolecular attraction. The similar phenomenon was repeatedly observed by us earlier for other series of dimesogenic compounds.<sup>8-11,13</sup>

### Conclusion

Following conclusions are drawn from the present investi-

gation:

1. A new series of dimesogenic compounds having two identical, terminal Schiff base type mesogenic units and a central polymethylene spacers could be synthesized.

2. All of the newly prepared dimesogenic compounds are thermotropic. And the compounds having shorter spacer tend to form smectic phases, whereas those having longer spacers tend to form nematic phase.

3. The variety of mesophase forms shown by the dimesogenic compounds is less than that shown by the monomesogenic compounds. The fact that the two mesogenic units are tied to each other through the spacer appears to reduce the freedom for the molecules to form ordered molecular organization in melts.

4. The relative magnitude of isotropization enthalpy changes in relation to melting enthalpy changes is much higher for the dimesogenic compounds than for the monomesogenic compounds.

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