Thermotropic Compounds with Two Terminal Mesogenic Units

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Synthesis and Properties of Thermotropic Compounds with Two Terminal Mesogenic Units and a Central Spacer (II). Homologous Series of α,ω-Bis(4-p-substituted phenoxycarbonyl)phenoxyalkanes

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Two series of thermotropic compounds were prepared and their thermal and liquid crystal properties were examined by differential scanning calorimetry and on the hot-stage of a cross-polarizing microscope. The first series of the compounds has two terminal mesogenic units based on unsubstituted and substituted p-(phenoxycarbonyl) phenyl ethers bracketing a central decamethylene spacer, and the second has 4-(p-phenylphenoxycarbonyl) phenyl ether moiety as the two terminal mesogenic units and central polymethylene spacers of varying lengths. A thermodynamic analysis of the phase transitions was made and explained in relation to structures and thermotropic behavior of the compounds.

Introduction

Recently we reported on the thermotropic behavior of several different series of polyesters which contained mesogenic units of dyad or triad aromatic esters interconnected through flexible spacers such as polymethylene or polyoxyethylene or disiloxyl groups.[1-5] While those investigations were being conducted, it became of interest to us to compare the structure-property relationships of the polymers with those of low molecular liquid crystal compounds containing two terminal mesogenic units on either side of a central flexible spacer.
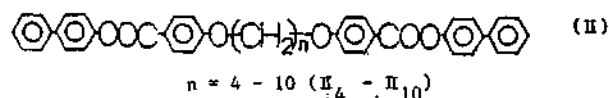
Although numerous studies on the structure-liquid crystal property relationships of a wide variety of compounds have been reported[6] since Reinitzer's first observation was made on

the thermal transitions of cholesteryl esters[7], there exist very few reports describing the thermotropic behavior of compounds which have two terminal mesogenic units bracketing central flexible spacers. Most of earlier reports discussed the liquid crystal properties of the compounds consisting of central mesogenic groups with terminal alkyl or other substituents.

We have prepared two different series of compounds, I and II shown below, and their thermal transitions and thermotropic behavior were studied by differential scanning calorimetry (DSC) and on the hot-stage of a polarizing microscope. The thermal and liquid crystal properties of the compounds of series I were briefly described ealier by us[8]. The structures and designation of the compounds discussed in this paper are as follows:
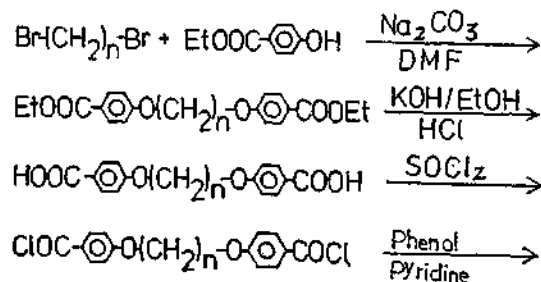
X-$\bigcirc$-OOC-$\bigcirc$-O$(CH_2)_n$-O-$\bigcirc$-COO-$\bigcirc$-X   (I)
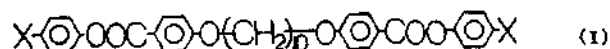
X = H(I_a), CH_3(I_b), Cl(I_c), NO_2(I_d), CHO(I_e), CN(I_f)

and $\bigcirc$ (I_g).

$\bigcirc\bigcirc$-OOC-$\bigcirc$-O$(CH_2)_n$-O-$\bigcirc$-COO-$\bigcirc\bigcirc$ (II)

n = 4 - 10 (II_4 - II_{10})

A compound having the 2-naphthol moiety(I_h) in place of the *p*-substituted phenol units of the series I was also included in this study.

Experimental

Synthesis of Compounds. The compounds were prepared following the route shown schematically below:

Br$(CH_2)_n$Br + EtOOC-$\bigcirc$-OH $\xrightarrow{\dfrac{Na_2CO_3}{DMF}}$

EtOOC-$\bigcirc$-O$(CH_2)_n$-O-$\bigcirc$-COOEt $\xrightarrow{\dfrac{KOH/EtOH}{HCl}}$

HOOC-$\bigcirc$-O$(CH_2)_n$-O-$\bigcirc$-COOH $\xrightarrow{SOCl_2}$

ClOC-$\bigcirc$-O$(CH_2)_n$-O-$\bigcirc$-COCl $\xrightarrow{\dfrac{Phenol}{Pyridine}}$

PRODUCTS

Because the literature procedures were employed for the synthesis of 4,4'-dichloroformyl-α,ω-diphenoxyalkanes[15], only the synthetic method used for the last step is described. 4,4'-Dichloroformyl-α,ω-diphenoxyalkane (0.012 mole) was dissolved in 30 ml of dry pyridine to which was added 0.024 moles of the appropriate phenol. The reaction mixture was stirred under a nitrogen atmosphere for 2 hours at room temperature and then at 70°C for 1 hour. At the end of the reaction the mixture was poured into cold water with vigorous stirring. The precipitate was filtered and dried in air. The crude

TABLE 1: Yields and Elemental Analysis of Series (I) Compounds

Compounds	X	Yield, wt. %	Elemental analysis, wt. %[a]			
			C	H	N	Cl
I_a	H	93	76.24 (76.32)	6.77 (6.71)	—	—
I_b	CH_3	94	76.73 (76.76)	6.91 (7.07)	—	—
I_c	Cl	91	68.0 (67.92)	5.56 (5.66)	—	11.08 (11.16)
I_d	NO_2		66.06 (65.85)	5.45 (5.48)	4.30 (4.26)	—
I_e	CHO	87	73.44 (73.31)	6.17 (6.10)	—	—
I_f	CN	82	73.95 (74.03)	5.73 (5.84)	4.51 (4.55)	—
I_g	C_6H_5	95	79.05 (78.80)	6.44 (6.46)	—	—
I_h	Naph[b]	95	79.05 (78.80)	6.84 (6.86)	—	—

[a] Values in parenthesis are of calculated ones. [b] 2-Naphthyl derivative

product was recrystallized from a solution in a toluene/ethanol mixture. The yields and results of the elemental analysis are tabulated in Table 1 and 2.

The structures of the compounds were further confirmed by IR (Perkin Elmer Infrared Spectrometer 710 B) and NMR (Varian Associates EM 360 A) spectra.

Thermal Behavior and Optical Textures of the Compounds. Thermal transitions and thermodynamic analysis of the compounds were performed under a nitrogen atmosphere by DSC (Perkin Elmer DSC-2 or DuPont 910). Heating and cooling rates were maintained constant at 20 °C/min. throughout the present investigation. Indium was used as a standard.

### TABLE 2: Yields and Elemental Analysis of Series II Compounds

Compounds	n	Yield, wt. %	Elemental Analysis, wt. %[a]	
			C	H
II_4	4	95	78.95(79.48)	5.26(5.36)
II_5	5	94	79.11(79.61)	5.46(5.40)
II_6	6	95	79.43(79.73)	5.64(5.59)
II_7	7	96	79.32(79.86)	5.88(5.96)
II_8	8	96	80.05(79.98)	5.90(6.13)
II_9	9	93	80.04(80.09)	6.18(6.29)
II_{10}	10	95	79.05(80.22)	6.44(6.41)

[a] Values in parenthesis are of calculated ones.

The optical textures and the thermal transitions of the compounds were also examined on the hot-stage (Mettler FP-52) attached to a polarizing microscope (Leitz Ortholux).

Results and Discussion

Properties of the Compounds of Series I. This series of
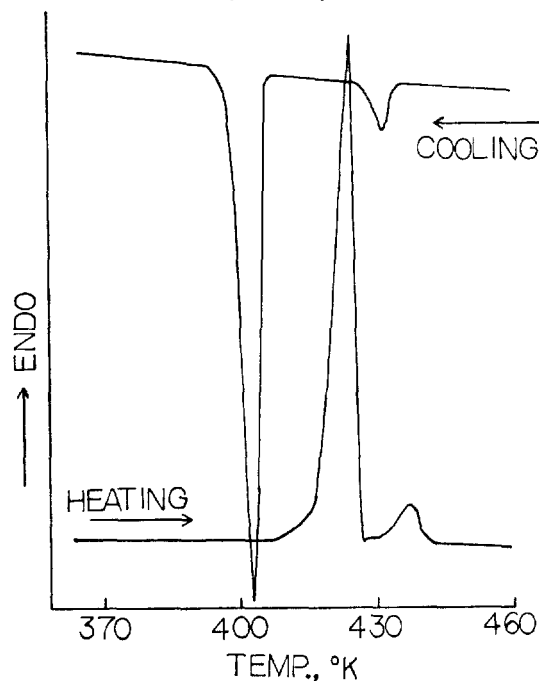
Figure 1. DSC thermogram of compound I_e at heating and cooling rate of 20 °C/min.
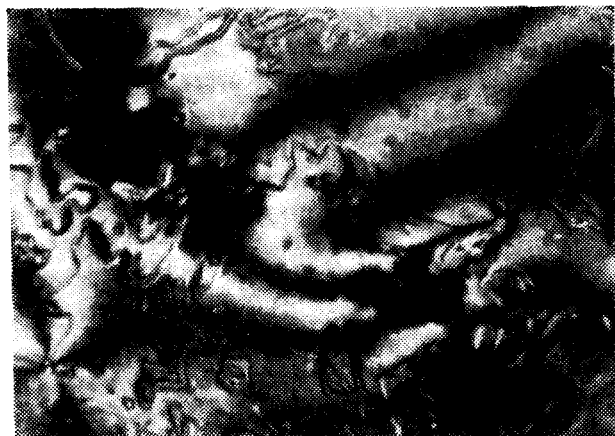
Figure 2. Photomicrograph of compound I_e taken at 150 °C. (magnification of 360x)

compounds had different substituents at the para-position of the terminal phenolic rings of the mesogenic unit, as shown above. The flexible spacer was the same decamethylene group for all of the compounds. The influence of terminal substituents on liquid crystal behavior has been systematically evaluated for a great many series of compounds[6], but very few studies describing the structure-property relationship for the type of compounds studied here have been reported in detail.

When observed on a Fisher–Johns melting point apparatus, all of the compounds, except the 2-naphthol derivative (I_h), developed turbid intermediate melts upon melting and then formed clear isotropic melts on further heating. This process was reversible when the clear melts were cooled below the transition temperatures. The DSC thermograms of those compounds contained two sharp endotherms in the heating cycle and two exotherms on cooling, see Figure 1.

Those transitions could also be clearly observed on the hot-stage of a polarizing microscope. These compounds exhibited an intense birefringence upon melting and became isotropic at the temperature corresponding to that of the second endotherm on the DSC thermograms of the heating cycle. This transition process was observed to be reversible. The optical textures observed for all of the compounds were those typical for a nematic mesophase, see Figure 2.

All of the observations made so far indicate that the first transition in the heating cycle of the DSC thermograms corresponded to solid–to–mesophase transformation, the melting point (T_m), and the second to mesophase–to–isotropic melt conversion, the clearing point (T_i), and that all of the compounds formed enantiotropic liquid crystal phases with the exception of the compound(I_h) whose thermal behavior will be discussed later. Another interesting observation was that the degree of supercooling for transition from the isotropic melt to the mesophase was far less than that for the transition from the mesophase to the crystalline solid state. This comparison, in turn, suggests that much less reorganization in molecular orientation is required for the transformation from the isotropic phase into liquid crystal phase than for the liquid crystal-to-solid crystal transition. The same phenomenon has often been observed for liquid crystalline polymers[2,3]. These conclusions agree clearly with the thermodynamic analysis of these transitions to be discussed below.

TABLE 3: Thermodynamical Data for the Phase Transition of the Series I Compounds

Compounds	T_m, °C	T_i, °C	ΔT, °C	ΔH_m kcal/mole	ΔS_m e. u.	ΔH_i kcal/mole	ΔS_i e. u.	$(\Delta H_i/\Delta H_m)\times 100$ %
I_a	121.5	127.5	6	16.0	40.6	1.40	3.5	8.8
I_b	137	146	9	14.6	35.6	1.44	3.4	9.9
I_c	146	156	10	12.8	30.5	1.16	2.7	9.0
I_d	144	160	16	11.5	27.6	1.02	2.3	8.8
I_e	150.5	162.5	12	17.0	40.1	1.15	2.6	6.5
I_f	158	181	23	11.6	26.9	1.28	2.8	10.9
I_g	183	212	29	24.3	31.4	1.06	2.2	7.4
I_h*	166	—	—	18.0	41.2	—	—	—
	(127)	(148)	(21)	(17.6)	(44.0)	(0.27)	(0.64)	(1.5)

Values in parenthesis are from the cooling thermogram of DSC analysis.

Table 3 summarizes the results of the thermodynamic analysis of the phase transition obtained from the DSC thermograms. In general, as seen in Table 3, the melting and clearing temperatures increased in a more or less parallel fashion for the series of substituents, and the ability of the substituents to stabilize the mesophase followed the following order:

$$H < CH_3 < Cl < CHO < NO_2 < CN < C_6H_5$$
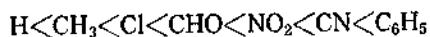
This order is in good agreement with the results for other types of liquid crystal compounds[6]. Either enhanced polarizability or increased polarity or lengthening of the rigid–rodlike structure by a substituent or a combination thereof are the most important factors in stabilization of the nematic phase.

In contrast to the compounds described above, 2–naphthyl ester (I_h) was found to be a monotropic liquid crystalline compound. As seen in Figure 3, this compound showed only one endotherm on heating but two exothermic peaks on cooling. The polarizing microscope studies revealed that this compound was directly transformed into the isotropic melt from the solid crystal on heating, while, on cooling, nematic liquid crystal phase was formed before the transition to solid state from isotropic melt. Therefore, the compound is concluded to be monotropic.

The thermodynamic data for the phase transitions of all of the compounds, summarized in Table 3, show that the heats of transition for the nematic–to–isotropic phase change, ΔH_i, of the compounds are much lower than those for the melting transition, ΔH_m. The values of ΔH_i range from about 7 to 11 % of those of ΔH_m. The magnitude of ΔS_i are about 10 % of those of ΔS_m for the corresponding compounds.
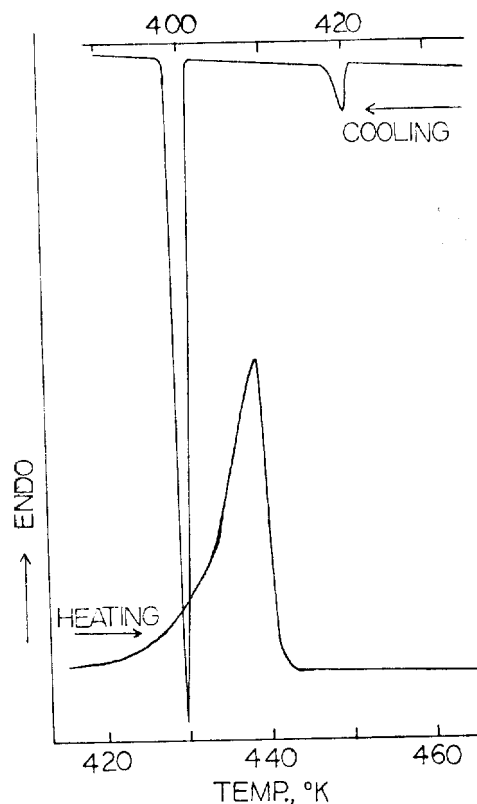
This result strongly implies that, as suggested above from the observations on the supercooling phenomenon of the phase transitions, the nematic phase is thermodynamically much closer to the isotropic state than to the solid crystal state. Recently, Yu confirmed this supposition by studying the equilibrium and dynamic order parameters of nematic liquid crystals[9].

For many nematic compounds it has been reported that ΔH_i is only 3–5 % of ΔH_m in magnitude[10], which is about one-half of that observed for the present compounds. Certainly it is to be expected that two mesogenic unit present in same molecule should increase the values of ΔH_i.

It is also interesting that the 2–naphthyl compound (I_h) was monotropic while the phenyl ester (I_g) was enantiotropic. According to the data given in Table 3, the 2–naphthyl compound had a considerably higher ΔH_m than that of the phenyl compound, 18 vs. 14 kcal/mole, which can account for the observation of a direct transition from the crystal to the isotropic phase.

Properties of the Compounds of Series II. For the compounds of series II, the structure of the mesogenic unit was fixed, the 4–phenylphenoxycarbonylphenyl ether group, while the length of polymethylene spacer was varied. Because the study on the compounds of the previous series revealed that the phenyl substituent most effectively stabilized the mesophase, this substituent was selected for the second series. The thermal behaviors of these compounds were basically the same as for the previous series when examined either visually or by DSC (Figures 4 and 5) or on a polarizing microscope.

As shown in Figure 4, however, a double melting transition

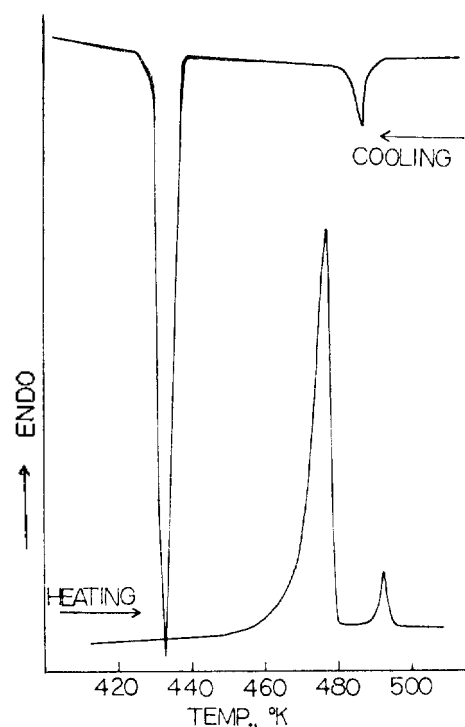**Figure 3.** DSC thermogram of compound I_h at heating and cooling rate of 20 °C/min.
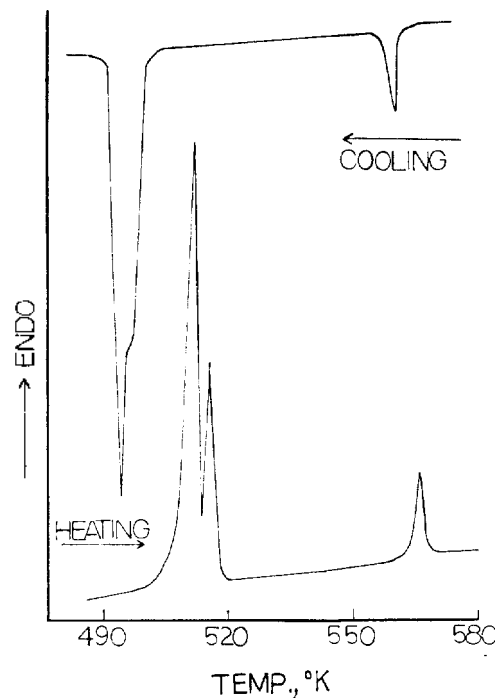
Figure 4. DSC thermogram of compound II_4 at heating and cooling rates of 20 °C/min.

Figure 5. DSC thermogram of compound II_7 at heating and cooling rate of 20 °C/min.

Figure 6. Photomicrograph of compound II_5 taken at 233 °C (magnification of 150x).

was observed in the heating cycle of compound II_4. The endothermic peak at the lower temperature was larger than the one at the higher temperature. In the cooling thermogram a weak shoulder also appeared on the high temperature side of the crystallization exotherm. This behavior was reproducibly observed in repeated heating and cooling cycles. It is not known if the double melting transition is caused by the exis-

TABLE 4: Thermodynamical Data for the Phase Transitions of the Series II Compounds

Compounds	T_m	T_i, °C	ΔT, °C	ΔH_m kcal/mole	ΔS_m e. u.	ΔH_i kcal/mole	ΔS_i kcal/mole	$(\Delta H_i/\Delta H_m) \times 100$ %
II_4	243	293	50	16.2	31.2	1.74	3.1	11
II_5	228	236	8	16.7	33.4	0.91	1.8	5.5
II_6	241	266	25	15.2	29.6	2.05	3.8	13
II_7	203	219	15	9.6	20.2	0.94	1.9	9.8
II_8	219	240	21	15.8	32.0	1.70	3.3	10
II_9	171	228	47	13.8	31.0	1.06	2.2	11
II_{10}	183	212	29	14.3	31.4	1.06	2.2	7.4

tence of polymorphic crystal states or possibly an indication of a crystal-to-crystal transition. The existence of two separate and distinct solid phase was reported by Chow and Martire for p-azoxyanisole[10]. All of the compounds of series, except the above discussed compound, showed only one melting transition, see Figure 5. All of the compounds formed enantiotropic nematic mesophases (Figure 6). The thermodynamic data for the phase transition were tablated in Table 4. The melting, T_m, as well as the isotropic transition temperatures, T_i, of the compounds in this series decreased in a zigzag fashion, see Figure 7, as the length of spacer, n, increased. Both T_m and T_i for the compounds with an even number of methylene units were higher than those with odd n. Similar trends were reported for many other series of low molecular liquid crystal compounds[6] and also for polymers[3], which have mesogenic units and polymethylene spacers in the main chain.

The ΔH_i values of the compounds ranged from about 6 to 13% of ΔH_m in magnitude, which is again very high compared with the corresponding values of similar compounds having only one mesogenic unit[11]. Another interesting point observ-

ed is that the values of ΔH_i for the compounds with an even number of methylene units were generally significantly higher than those for the odd-numbered compounds.

The values of ΔS_i of this series were plotted against the number of methylene unit in the spacer in Figure 8. In general the ΔS_i for the compounds with even-numbered spacer are higher than those with odd-numbered ones. Also, a slight increase in ΔS_i with n is observed. Although similar trends have been reported for many other series of compounds[12-14], the physical significance of such comparisons is not yet clear. It appears that the mesophases of the compounds with spacers of even-numbered methylene units are generally of a higher degree of order than those with odd-numbered ones.

Conclusion

From this study the following conclusions can be drawn:

(1) All of the compounds reported in this paper, having are terminal mesogenic units and central flexible spacers, two enantiotropically thermotropic with the exception of the compound I_b, the 2-naphthyl ester. Only nematic optical textures were observed for the compounds.
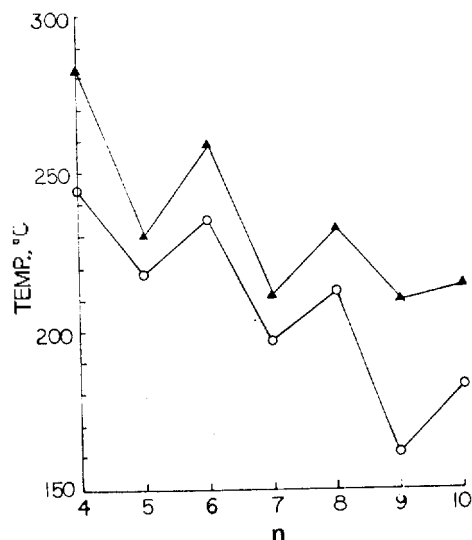
Figure 7. Dependence of $T_m(\bigcirc)$ and $T_i(\blacktriangle)$ of the compounds II on the length, n, of po'ymethylene spacer.
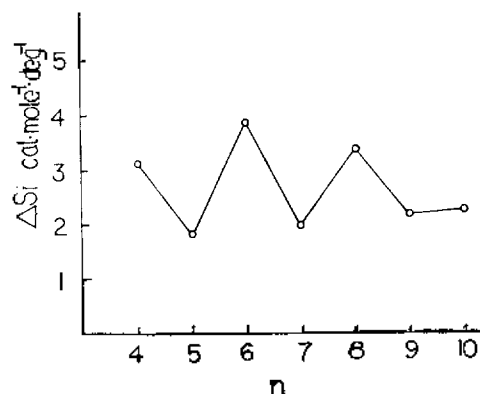

Figure 8. Dependence of ΔS_i on the length of flexible spacer.

(2) The ability of the substituents to statbilize he mesophase was in the following order:

$$H < CH_3 < Cl < CHO < NO_2 < CN < C_6H_5$$

(3) The melting and clearing transition temperatures, T_m

and T_i, of the compounds of Series II decreased with central spacer length and the decrease showed an even–odd relationship.

(4) The entropy change in clearing, ΔS_i, of the compounds of Series II also showed a zig-zag, even–odd effect.

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