

Synthesis and Properties of Thermotropic Compounds with Two Terminal Mesogenic Units and a Central Spacer III. Homologous Series of α, ω -Bis[4-(*p*-nitrobenzoyloxy)phenoxy]alkanes

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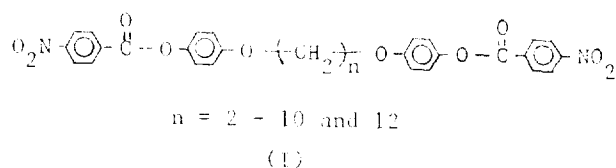
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A series of new liquid crystalline compounds having two identical mesogenic terminal units, the 4-(*p*-nitrobenzoyloxy)phenoxy group, attached to both ends of a central polymethylene spacer of various lengths was prepared. The mesomorphic properties of the compounds were investigated by differential scanning calorimetry (DSC) and by polarizing microscopy. Almost all of the compounds formed monotropic nematic mesophases. The trimethylene spacer compound was found to be non-liquid crystalline, while the one with the hexamethylene central spacer was enantiotropic. A thermodynamic analysis was performed for the phase transitions of the compounds and the results are discussed in relation to their liquid crystal properties.

Introduction

The mesomorphic properties of numerous compounds with a wide variety of structures have been reported since Renitzer's discovery in 1888 of formation of anisotropic melts from cholesterol derivatives¹⁻³. The majority of these compounds, however, consist of a central mesogenic unit with terminal alkyl groups or other substituents attached to it.

Recently we reported the synthesis and thermotropic properties of two different series of compounds which had two identical terminal mesogenic units of an aromatic ester type bracketing a central polymethylene spacer^{4,5}. The mesogenic groups used were *p*-oxybenzoates of *p* substituted phenols. As a part of our continuing efforts to delineate the structure-property relationships of new liquid crystalline compounds, we have synthesized a series of α, ω -bis[4-(*p*-nitrobenzoyloxy)phenoxy]alkanes whose structure is presented below as designated as In, n being the number of methylene units in the spacer.



Since it is rather well known that the nitro group is capable of strongly stabilizing mesophases of the parent compounds, this substituent was chosen for the present series of compounds^{1,4,5}.

Thermotropic properties of the compounds were investigated by observing changes in optical textures on the hot-stage

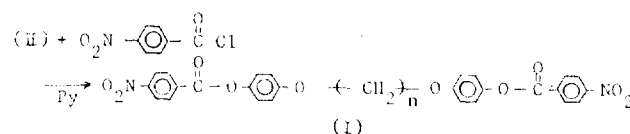
of a polarizing microscope with Nicols crossed and by differential scanning calorimetry.

Experimental

Chemicals and Instruments. All of the chemicals used in this investigation were reagent grade and employed as received, with the exception of several solvents which were dried and distilled by conventional methods before use.

IR and NMR spectra of the compounds were obtained by using a Perkin-Elmer IR Spectrometer 710 B and a Varian Associates EM 360 A, respectively. Thermal analysis of the compounds was performed by Perkin-Elmer DSC-1B or du Pont DSC 910 and on the hot-stage (Mettler FP-2) attached to a polarizing microscope (Leitz, Ortholux.). Elemental analysis of the samples were conducted using a Perkin-Elmer CHN analyzer.

Synthesis of the Compounds. The final compounds were prepared by the following route:



p, p'-Dihydroxy- α, ω -diphenoxyalkanes (II) were synthesized by refluxing an α, ω -dibromoalkane with excess amount of hydroquinone in ethanolic KOH solution, following the literature method⁶. α, ω -Bis[4-(*p*-nitrobenzoyloxy)phenoxy]alkanes (I) were prepared by reacting *p*-nitrobenzoyl chloride (40 m mole) with 10 m mole of II predissolved in 30 ml of dry pyridine. The reaction was conducted at 40°C under a nitrogen atmosphere for 4 to 5 hours.

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TABLE 1: Yields and Elemental Analysis Data of α, ω -Bis[4-(*p*-nitrobenzoyloxy)phenoxy]alkanes

Compound	Yield wt. %	Elemental Analysis, wt. % ^a		
		C	H	N
I ₂	90	62.01(61.76)	3.73(3.68)	5.11(5.15)
I ₃	90	62.47(62.37)	3.95(3.94)	4.97(5.00)
I ₄	88	63.16(62.94)	4.16(4.20)	4.97(4.90)
I ₅	90	64.05(63.48)	4.39(4.44)	4.76(4.78)
I ₆	84	64.06(64.00)	4.72(4.67)	4.73(4.67)
I ₇	89	65.09(64.05)	4.96(4.89)	4.45(4.56)
I ₈	87	65.22(64.97)	5.37(5.10)	4.29(4.46)
I ₉	87	64.43(65.42)	5.65(5.30)	4.23(4.36)
I ₁₀	82	65.96(65.85)	5.61(5.49)	4.21(4.27)
I ₁₂	85	67.59(66.67)	6.18(5.85)	3.81(4.09)

^a The values shown in the parenthesis indicate theoretical values.

At the end of reaction, the mixture was poured into large volume of distilled water. The precipitates were washed with 0.1*N* aqueous NaOH and then again with distilled water. The crude products of I_n's with even *n*'s were recrystallized from *p*-dioxane, while for those of odd *n*'s *n*-butanol was used. The yields and the results of elemental analysis are tabulated in Table 1. Structures of the compounds were further confirmed by their IR and NMR spectra.

Study of Thermal and Optical Properties of the Compounds. Phase transitions of the compounds were first visually observed both on heating and cooling using an ordinary capillary melting point apparatus. Optical textures of the melts and phase transformations of the compounds were further examined on the hot-stage of a polarizing microscope. Here, a small amount (~ 5mg) of a sample was placed between a microscope slide and a cover slip and secured to the hot-stage.

DSC analysis was performed under a nitrogen atmosphere at the heating and cooling rate of 20°C/min. Thermodynamic parameters for the phase transitions were calculated from the areas of the thermogram peaks. Indium was employed as a standard for calibration.

Results and Discussion

Thermal Properties of the Compounds. All of the compounds, with the exception of I₆, produced clear isotropic liquids upon melting. However, on cooling, these isotropic melts first formed intermediate turbid fluid phases before their transformations into solids. The compound I₃ was not able to produce the intermediate phase, even on cooling. In contrast, the compound I₆ was unique in that it could form the turbid melt reversibly on heating as well as on cooling. Such visual observations were further confirmed by microscope studies and DSC analyses.

The DSC thermograms of I₆ exhibited two endothermic peaks on the heating run and two exothermic peaks on the cooling cycle, leading to the conclusion that this compound is enantiotropic (Figure 1). The peaks appeared at lower temperatures correspond to crystal $\leftrightarrow$ liquid crystal phase interconversions and those at higher temperatures to the phase transitions between liquid crystal and isotropic phases.

The compound I₃, however, both on heating and cooling

of the DSC analysis showed only one transition, direct from solid to isotropic liquid. This indicates that it is not liquid crystalline.

The rest of the compounds revealed only one endothermic peak on heating runs, but two exotherms on cooling cycles (see Figure 2). The first exotherm, appearing at a higher temperature on the cooling thermogram, corresponds to the isotropic melt-to-liquid crystal phase transition ($T_{I \rightarrow LC}$) and the second, at a lower temperature, to the liquid crystal-to-solid ($T_{LC \rightarrow C}$) change.

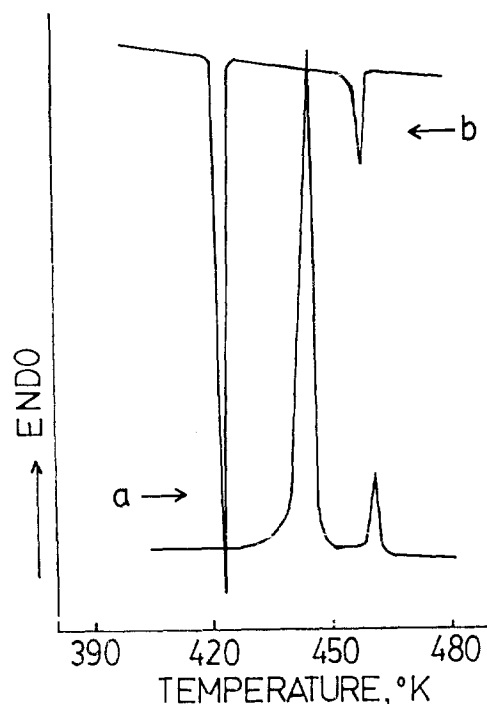


Figure 1. DSC thermogram of 1, 6-bis [4-(*p*-nitrobenzoyloxy)-phenoxy]hexane, I₆ (a-heating curve; b-cooling curve).

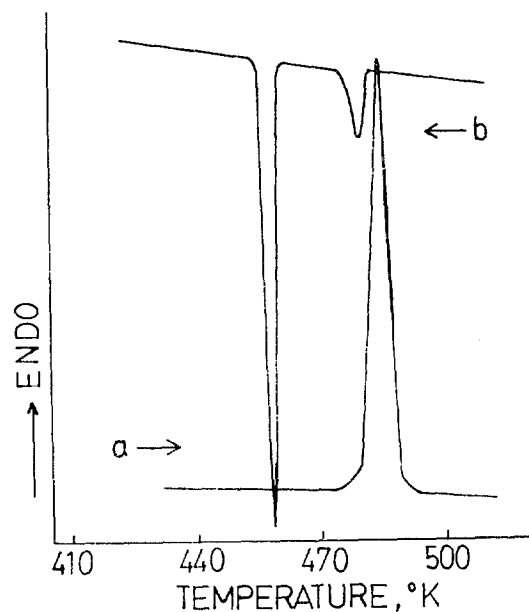


Figure 2. DSC thermogram of 1, 4-bis [4-(*p*-nitrobenzoyloxy)phenoxy] butane, I₄ (a-heating curve; b-cooling curve).

It is very well documented that a prerequisite for the ability to form a liquid crystal phase is a rigid, rod-like structure^{1,2}. The structure of **I**₃ apparently is not in line with this requirement. This molecule seems to adopt a bent shape due to its relatively short central spacer and its odd number of methylene units. This can be easily visualized by considering the O-C-C and C-C-C bond angles of the spacer and the preferred anti conformation about the C-C bonds. Aharoni recently reported a similar phenomenon in the thermotropic behavior of the compounds which consisted of two identical, terminal, Schiff base-type mesogenic units attached to a central methylene or ethylene unit⁷. The compound with a methylene linkage did not form a liquid crystal phase, while the one with an ethylene spacer was able to form a nematic mesophase.

When the spacer becomes relatively long, the mesogenic units apparently attain a sufficient degree of freedom to orient themselves in the melt in an organized manner, regardless of whether the polymethylene spacer is even or odd numbered. It is also possible that as the length of the spacer increases, the degree of bending in molecules having odd-numbered polymethylene spacer becomes insignificant in comparison with the total length of molecules.

The enantiotropic nature of **I**₆ and monotropic character of the rest of the compounds are related to their thermodynamic properties at their respective phase transitions. This will be discussed later.

Optical Textures of the Liquid Crystalline Phases. The compounds **I**₄ through **I**₁₀ above their melting points show optical textures characteristic of the nematic mesophase when observed through a polarizing microscope, see Figure 3. The singular points associated with 1 as well as 1/2 can clearly be observed in the Schlieren texture⁸. The dodecamethylene spacer compound, **I**₁₂, however, forms a smectic mesophase, see Figure 4. This Schlieren texture exhibits only the singular points associated with 1 having four brushes⁸. It often has been observed that, when the alkyl group attached to a mesogenic group becomes significantly long, the compound or the linear polymer tends to form a smectic phase^{1,2}. It is believed that the long and flexible spacer allows the mesogenic units to form an ordered structure with lamellar layer, giving rise to the smectic mesophase.

Thermodynamics of Phase Transitions. The melting transition temperatures, T_m , of the compounds, as measured by DSC analysis, decrease regularly in a zig-zag fashion as the length of the spacer, n , increases (see Figure 5). As is commonly observed, the compounds with an even number of methylene units show consistently higher melting points than those with odd number n 's.

Since all of the compounds, with the exception of **I**₃ and **I**₆, were monotropic, a thermodynamic study of the phase transitions was conducted using the DSC cooling thermograms. The temperatures of the transition from the isotropic phase to the mesophase, $T_{I \rightarrow LC}$, also show a regular trend with a zig-zag decrease as n increases as seen in Figure 6. The transition temperatures from the mesophase to solid, $T_{LC \rightarrow C}$, however, decreases in an irregular manner, probably due to

the rather unpredictable degree of supercooling. It was repeatedly observed in earlier studies that, for enantiotropic liquid crystals, supercooling for isotropic melt-to-mesophase transition was much less in degree than that for the transition from



Figure 3. Photomicrograph of **I**₇ taken at 125°C. The sample was cooled down from 150°C at the rate of 3°C/min (original magnification; 150X).



Figure 4. Photomicrograph of **I**₁₂ taken at 130°C. The sample was cooled down from 150°C at the rate of 3°C/min (original magnification; 150X).

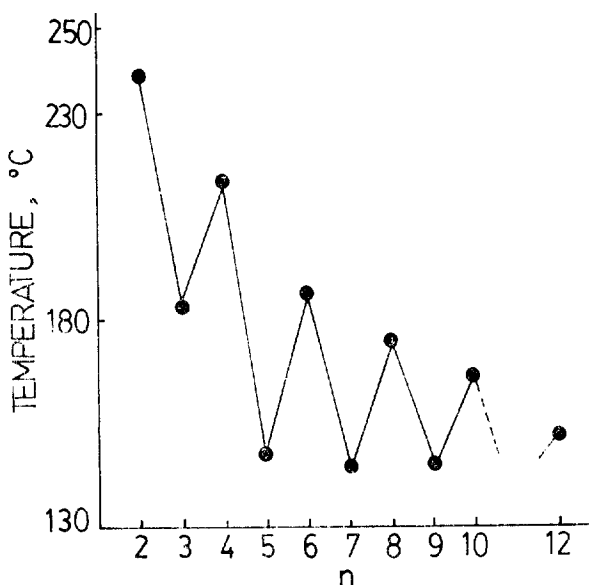


Figure 5. The dependence of transition points T_m on the length of the flexible spacer n in compounds **I** _{n} .

TABLE 2: Thermodynamic Data for the Isotropic $\rightarrow$ Mesophase Transition of α,ω -Bis[4-(*p*-nitrobenzoyloxy)phenoxy]alkanes^a

n	T_m , °C	$T_{I \rightarrow LC}$, °C	$T_{LC \rightarrow C}$, °C	ΔH_i kcal/mole	ΔH_c kcal/mole	ΔS_i e.u.	ΔS_c e.u.	$\frac{\Delta H_i}{\Delta H_c} \times 100$ %
2	239	215	208	0.8	11.0	1.6	22.9	7.7
3	186.6	—	142.5	—	18.8	—	—	—
4	213	207	185	1.2	13.3	2.5	29.1	9.0
5	147.5	131	122.3	0.3	12.3	0.8	31.2	2.4
6	171 ^b 186.5	182	147.5	1.1	9.5	2.5	22.7	11.5
7	144.5	135	117.2	0.5	15.8	1.2	40.6	3.2
8	175	162	148	1.0	10.9	2.4	26.1	9.2
9	145	131.5	117.5	0.7	14.5	1.7	40.3	4.8
10	166.5	153	148	1.2	14.0	2.8	31.5	8.6
12	152	134.5	127.5	1.6	13.7	3.9	38.2	11.6

^a All of the $T_{I \rightarrow LC}$, $T_{LC \rightarrow C}$ and corresponding thermodynamic quantities, with the exception of T_m 's, were obtained from the cooling thermograms on DSC. ^b Crystallization temperature from DSC cooling runs.

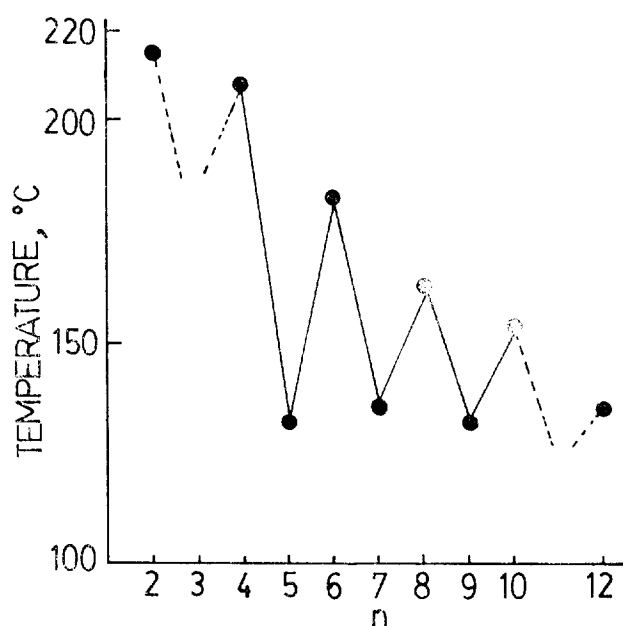


Figure 6. The dependence of transition points $T_{I \rightarrow LC}$ on the length of the flexible spacer n in compounds I_n .

the mesophase to crystal^{5,9}.

Thermodynamic parameters for phase transitions are listed in Table 2. The heat of crystallization, ΔH_c , for the compound I_3 was significantly higher than those for the other members of the series. This means that the reverse process, melting, requires the highest amount of thermal energy. This, in addition to the possible geometric reason discussed above, could explain why this compound is not liquid crystalline. In comparison, the heat of melting of I_6 is much lower than those of the others. Even though the reason for this low ΔH_c is not yet clear, the enantiotropic nature of the compound may be ascribed to the low transition energy.

Table 2 also shows that the values of the enthalpy change ΔH_i , between the liquid crystal and the isotropic phases of the compounds ranged from about 3 to 12 % of heat of melting, ΔH_c , which is about twice the corresponding values (usually 1 to 5 %) of similar compounds having only one

mesogenic unit¹⁰. The values of ΔH_i for the compounds with odd n 's were much lower than those with even n 's. A similar phenomenon was observed by us earlier for α , ω -bis-[4-(*p*-substituted phenoxy)carbonyl]phenoxy]alkanes⁵.

As observed in previous investigations on the thermotropic compounds with similar structural features and polyesters having alternating sequence of mesogenic groups and flexible spacers, the values of the change in entropy, between the mesomorphic and isotropic states, ΔS_i , of the compounds with even n 's were consistently higher than those with odd n 's. This could be taken as an indication that the mesophases originating from compounds having the polymethylene spacers with even n 's are more highly ordered than those with odd n 's⁵. Further study of the molecular organization of the compounds in the liquid crystalline phase are necessary to explain this phenomenon on a molecular scale. It is also worthwhile to point out the fact that ΔS_i for the compound I_{12} was significantly higher than those of the other compounds. This can be readily understood by the observation that the compound I_{12} formed a smectic mesophase, while the others formed nematic phases. The smectic phase is of a higher degree of order than the nematic state. Similar differences between the two phases have been observed for many other liquid crystalline compounds¹⁰.

Conclusions

The following conclusions can be drawn from the present investigation:

- (1) The compounds described in this work were monotropic with the exception of I_3 and I_6 . I_3 was not liquid crystalline, while I_6 was enantiotropic.
- (2) All of the liquid crystalline compounds formed nematic mesophases. The only exception was the compound I_{12} which appeared to have produced a smectic phase.
- (3) The transition temperatures of $T_{I \rightarrow LC}$ and $T_{LC \rightarrow C}$ of the compounds decreased in a zig-zag fashion as the number of methylene units in the polymethylene spacer increased. The values for the compounds with even n 's were consistently higher than those with odd n 's.

- (4) The values of the enthalpy change ratios of isotropization to melting, $\Delta H_i/\Delta H_c$, were about twice those of compounds having only one mesogenic unit.
- (5) Judging by the ΔS_i values, the compounds with even n 's seemed to form more highly ordered liquid crystal phases than those with odd n 's.

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Homogeneous Catalysis (VI). Hydride Route with Chloro Ligand Dissociation for the Hydrogenation of Acrylonitrile with *trans*-Chlorocarbonylbis(triphenylphosphine)iridium(I)

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The reaction of $\text{IrClH}_2(\text{CO})(\text{Ph}_3\text{P})_2$ (Ph_3P =triphenylphosphine) with acrylonitrile (AN) produces a stoichiometric amount of propionitrile (PN) at 100°C under nitrogen, which suggests that the catalytic hydrogenation of AN to PN with $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ proceeds through the hydride route where the formation of the dihydrido complex, $\text{IrClH}_2(\text{CO})(\text{Ph}_3\text{P})_2$ is the initial step. The rate of the hydrogenation of AN to PN with $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ is decreased by the presence of excess Cl^- in the reaction system, which suggests that Cl^- is the dissociating ligand in the catalytic cycle. It has been also found that the rate of the hydrogenation increases with increase both in hydrogen pressure and in concentration of free Ph_3P , and with decrease in AN concentration in the reaction system.

Introduction and Objectives

Wilkinson's catalyst, $\text{RhCl}(\text{Ph}_3\text{P})_3$ is a very active catalyst for hydrogenation of various olefins even at room temperature,¹⁻⁷ while the iridium analog, $\text{IrCl}(\text{Ph}_3\text{P})_3$ catalyzes only certain terminal olefins with very slow rates.⁸ It is well known that the high catalytic activity of $\text{RhCl}(\text{Ph}_3\text{P})_3$ results in part from the significant dissociation of a Ph_3P from $\text{RhCl}(\text{Ph}_3\text{P})_3$ in solution,¹⁻⁷ whereas the dissociation of a Ph_3P from $\text{IrCl}(\text{Ph}_3\text{P})_3$ is so small that the concentration of the catalytically active species, $\text{IrCl}(\text{Ph}_3\text{P})_2$ is very low.⁸ On the other hand,

the rhodium carbonyl complex, $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$ is practically inactive for the hydrogenation of olefins at room temperature, but catalyzes the hydrogenation of various olefins at above 80°C.¹⁰⁻¹² It is already known that $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$ dissociates CO (but not Ph_3P) at elevated temperature.¹³ We also found that the dissociation of CO from $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$ initiates the catalytic hydrogenation of AN to PN at above 80°C.¹² Consequently, we have become interested in the nature of the dissociating ligand in the catalytic cycle for the hydrogenation of AN with the iridium analog, $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ (**1**) (which is known not to dissociate any ligand