Thermotropic Compounds having Two Terminal Mesogenic Units and Central Spacers. Part 7. Homologous α,ω-Bis-[*p*-(4-alkoxyphenoxycarbonyl)phenoxy]-alkanes

Jung-Il Jin,* Heung-Tak Oh, and Joo-Hoon Park
Department of Chemistry, College of Sciences, Korea University, 1-Anam Dong, Seoul 132, Korea

A homologous series of α,ω-bis-[*p*-(4-alkoxyphenoxycarbonyl)phenoxy]alkanes was prepared; their thermal and liquid crystalline properties were studied by differential scanning calorimetry and on the hot-stage of a polarizing microscope. The nature of the liquid crystalline phase of the compounds depended greatly on the length of the central polymethylene spacer and on the terminal alkoxy groups. The 'odd–even' effect of the terminal alkoxy groups was observed neither for the melting nor for the clearing transition temperatures of the compounds. However, the changes in enthalpy and entropy for the isotropic transitions showed a zig-zag dependence on the number of methylene units in the alkoxy groups. Values for 'even' members were consistently higher than those for 'odd' ones, regardless of whether the central polymethylene spacer was odd-numbered or even-numbered.

Structure–property relationships of thermotropic compounds (**1**) consisting of terminal mesogenic units and central spacers are attracting a great deal of interest.[1–5] This type of compound not only has interesting mesomorphic properties but also can be taken as simple low molecular weight models for main-chain thermotropic polymers having alternating sequences of similar mesogenic units and spacers.[4,6] They can duplicate or simulate especially well the dependence of the thermal transitions of the polymers on the length of the polymethylene spacers.

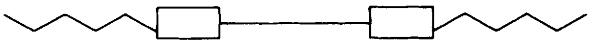
It also has been claimed that compounds of type (**2**), which have two alkyl 'wings' attached to the mesogenic units of structure (**1**), can be regarded as low molecular weight model compounds for polymers of structural type (**3**).[7] Partly as a continuation of our efforts to clarify the structure–property relationships of liquid crystalline compounds, and partly in order to ascertain whether compounds of structure (**2**) can indeed be taken as models for polymers of structure (**3**), we have prepared the series of compounds (**4**), and have compared their thermal behaviour with that of the polymers (**5**). The nature of the mesophases formed by compounds (**4**) was also compared with that of the polymers (**5**).

Results and Discussion

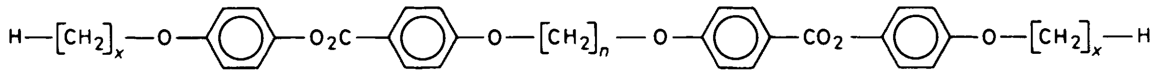
Synthesis of Compounds (**4**).—As described in the Experimental section, the synthesis of the compounds (**4**) is straightforward.[8] The yields given (Tables 1—3) are those for the final steps, and are reasonably high. I.r. and n.m.r. spectra were consistent with the given structures. Purity of the compounds was checked by t.l.c.

Thermal Behaviour.—All the compounds exhibited two endothermic and two exothermic peaks, respectively, in the heating and cooling cycles of the DSC analysis (Figure 1). This observation, together with the results of microscopic studies (see later), confirmed that the first peak on the heating runs corresponded to the melting transition (T_m) and the second to the transition (T_i) from mesophase to isotropic phase. Reversible phase transitions reveal that the compounds are enantiotropic. As one can see from the Figure, a substantial degree of supercooling was observed for the mesophase-to-solid transition; the degree of supercooling was much less for the transition from isotropic melt to mesophase. A similar phenomenon has been consistently observed for other liquid

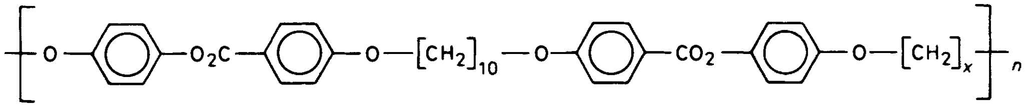

(1)


(2)


(3)


(4)

n = 5, 6 or 10
x = 1—7


(5)

x = 2—10

Table 1. Yields and elemental analyses of the compounds (**4**) with pentamethylene spacers (x = 1—7)

		Found (%) (Required)	
	Yield (%)	C	H
$x = 1$	96	71.3	5.8
($C_{33}H_{32}O_8$)		(71.2)	(5.8)
$x = 2$	98	72.1	6.2
($C_{35}H_{36}O_8$)		(71.9)	(6.2)
$x = 3$	92	72.4	6.4
($C_{37}H_{40}O_8$)		(72.5)	(6.5)
$x = 4$	90	73.0	6.8
($C_{39}H_{44}O_8$)		(73.1)	(6.9)
$x = 5$	93	73.2	7.2
($C_{41}H_{48}O_8$)		(73.6)	(7.3)
$x = 6$	93	74.3	7.4
($C_{43}H_{52}O_8$)		(74.1)	(7.5)
$x = 7$	91	74.7	7.9
($C_{45}H_{56}O_8$)		(74.5)	(7.8)

Table 2. Yields and elemental analyses of the compounds (**4**) with hexamethylene spacers (x = 1—7)

		Found (%) (Required)	
	Yield (%)	C	H
$x = 1$	94	71.4	6.1
($C_{34}H_{34}O_8$)		(71.6)	(6.0)
$x = 2$	88	72.5	6.5
($C_{36}H_{38}O_8$)		(72.2)	(6.4)
$x = 3$	93	72.8	6.9
($C_{38}H_{42}O_8$)		(72.8)	(6.8)
$x = 4$	88	73.1	7.2
($C_{40}H_{46}O_8$)		(73.4)	(7.1)
$x = 5$	86	73.7	7.4
($C_{42}H_{50}O_8$)		(73.9)	(7.4)
$x = 6$	85	74.4	7.7
($C_{44}H_{54}O_8$)		(74.3)	(7.7)
$x = 7$	94	74.7	7.8
($C_{46}H_{58}O_8$)		(74.8)	(8.0)

Table 3. Yields and elemental analyses of the compounds (**4**) with decamethylene spacers (x = 1—7)

		Found (%) (Required)	
	Yield (%)	C	H
$x = 1$	92	72.3	6.8
($C_{38}H_{42}O_8$)		(72.8)	(6.7)
$x = 2$	90	72.9	7.0
($C_{40}H_{46}O_8$)		(73.4)	(7.1)
$x = 3$	87	73.3	7.3
($C_{42}H_{50}O_8$)		(73.9)	(7.4)
$x = 4$	97	73.9	7.6
($C_{44}H_{54}O_8$)		(74.3)	(7.7)
$x = 5$	94	74.0	7.8
($C_{46}H_{58}O_8$)		(74.8)	(7.9)
$x = 6$	85	74.7	8.1
($C_{48}H_{52}O_8$)		(75.2)	(8.2)
$x = 7$	92	75.1	8.3
($C_{50}H_{66}O_8$)		(75.5)	(8.4)

Table 4. Transition temperatures of compounds (**4**)[a]

	$n = 5$		$n = 6$		$n = 10$	
x	T_m/°C	T_i/°C	T_m/°C	T_i/°C	T_m/°C	T_i/°C
1	145	160.5	172	202	127.5	158.5
2	165.5	176	199.5	207.5	154.5	178
3	154.5	187.5	173	187.5	130.5	160
4	131	154.5	166	184	128.5	166
5	129	142	142	174	119.5	149
6	128	144.5	131.5	174.5	117.5	147
7	129.5	143.5	131.5	176	120	149.5

[a] All the data were obtained from the second DSC heating run of the samples. The positions of peak maxima were taken as transition temperatures.

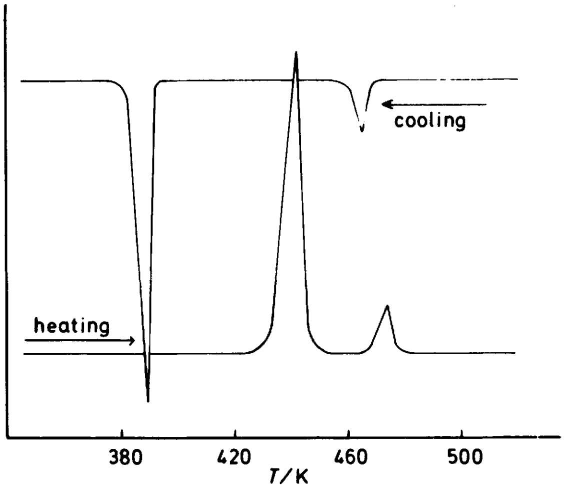


Figure 1. DSC thermogram of compound (**4**) with n = 6, x = 1

crystalline compounds and polymers.[1,9] The difference in supercooling can be taken as an indication that much more molecular reorganization is needed for crystallization than for the isotropic-to-mesophase transition. The temperatures for melting (T_m) and isotropic transitions (T_i) are shown in Table 4. The compounds with decamethylene spacers (n = 10) are of particular interest, because the length of their central spacer is the same as that of the polymers (**5**).

Figure 2 shows a comparison of the transition temperatures of these compounds (n = 10) with those of the polymers (**5**). The thermal behaviour is quite different. The transition temperatures (T_m as well as T_i) of compounds (**4**) change irregularly as x is increased. Although T_i of compounds (**4**) with short alkoxy groups seems to show some degree of zig-zag decrease with x, the 'odd–even' effect is not obvious. However, the polymers (**5**) exhibit a regular zig-zag decrease in T_m as well as in T_i.[6] The transition temperatures of the polymers with even numbers of methylene units in the spacer are consistently higher than those with odd numbers. Therefore, it can be concluded that compounds (**4**) [which can be depicted as (**2**)] do not simulate the thermal behaviour of the polymers (**5**) [represented by structure (**3**)].

A similar, irregular dependence of transition temperatures on the length of alkoxy groups was also observed for compounds (**4**) with the shorter central pentamethylene or hexamethylene spacers (see Figure 3). It appears that, at least for the present compounds (**4**), the 'odd–even' effect does not exist for transition temperatures.

Thermodynamics of Phase Transitions of Compounds (**4**).—The thermodynamic parameters for the phase transitions of compounds (**4**) are presented in Table 5. For all three series, no

Table 5. Thermodynamic parameters for the phase transitions of compounds (4)[a]

	$n = 5$					$n = 6$					$n = 10$				
x	ΔH_m	ΔS_m	ΔH_i	ΔS_i	$\Delta S_i/\Delta S_t$ (%)[b]	ΔH_m	ΔS_m	ΔH_i	ΔS_i	$\Delta S_i/\Delta S_t$ (%)[b]	ΔH_m	ΔS_m	ΔH_i	ΔS_i	$\Delta S_i/\Delta S_t$ (%)[b]
1	32.7	78.2	4.0	9.2	11	40.7	91.3	5.0	11	11	47.0	117	5.5	13	10
2	64.0	146	4.5	10	6	32.8	69.5	6.0	12	15	38.4	89.7	6.4	14	14
3	53.8	126	4.2	9.1	7	30.2	67.6	4.7	10	13	51.6	128	5.3	12	9
4	60.5	150	4.4	10	6	34.2	77.8	5.7	12	14	35.0	87.3	6.1	14	14
5	54.0	134	3.5	8.2	6	32.0	77.1	4.5	10	11	45.1	115	4.7	11	9
6	51.4	128	3.8	9.1	7	36.0	89.1	4.8	11	11	55.0	141	5.6	13	8
7	42.1	105	3.2	7.7	7	33.5	82.8	4.4	9.8	11	51.5	131	4.5	11	8

[a] ΔH in kJ mol^{-1}; ΔS in J mol^{-1} K^{-1}. [b] ΔS_t stands for the total entropy change for the phase transitions, *i.e.* $\Delta S_m + \Delta S_i$.

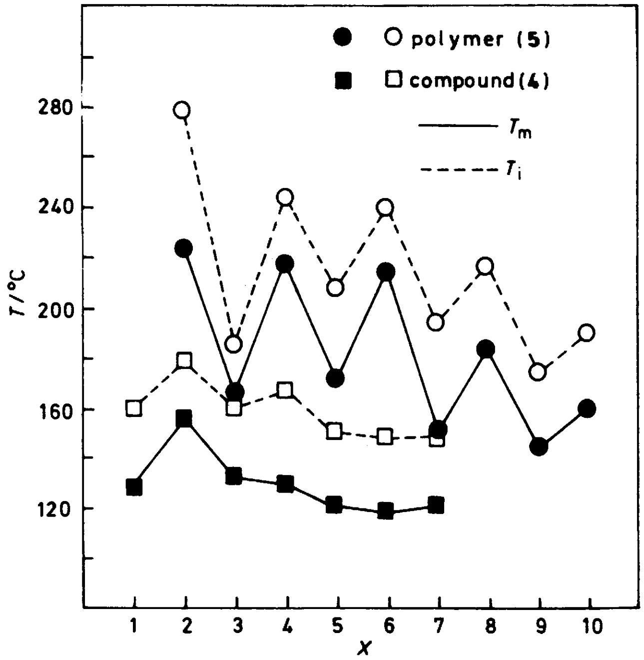


Figure 2. Dependence of transition temperatures of polymers (5) and compounds (4) with n = 10 on the length of the polymethylene spacer, x

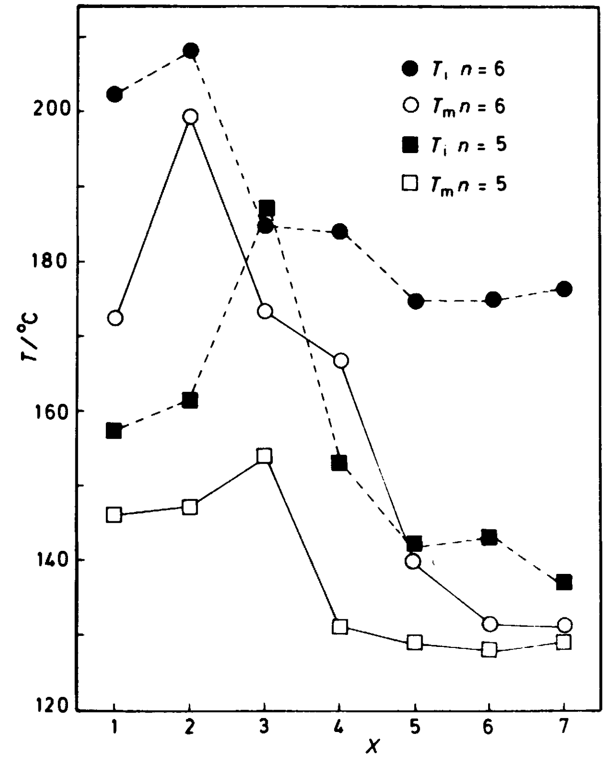


Figure 3. Dependence of transition temperatures of compounds (4) with n = 5 and n = 6 on the length of the polymethylene spacer, x

regular change in ΔH_m or ΔS_m was observed between the successive odd and even homologous members. However, a definite 'odd–even' effect was observed for ΔH_i and ΔS_i in each of the three series of compounds (4) (see Figures 4 and 5).

Since the relative magnitude of ΔS_i can be taken as an indirect index of the degree of order when the mesophase is in equilibrium with the isotropic phase, we can conclude that the mesophases of compounds with an even number of carbon atoms in the terminal alkoxy groups are of higher degree of order at T_i regardless of whether the central spacer consists of an odd or an even number of methylene units. Another interesting feature in Figure 5 is that the longer the central spacer, the higher the value of ΔS_i. This indicates that longer central spacers favour a better organized molecular orientation in the mesophase. This could be ascribed to the greater degree of freedom given by the longer spacer for the mesogens to attain a higher degree of organization. Recently Roviello and Sirigu[4] propounded that the orientational contribution to ΔS_i is much more important than the conformational one. Chang *et al.*[10] had earlier demonstrated that, for a series of Schiff-base type compounds in which the lengths of the terminal alkyl groups were varied, the order parameters for molecules with even-numbered terminal groups were consistently higher at T_i than for those with odd-numbered groups. Direct comparison of ΔS_i with other quantities, such as order parameters, and conformational analysis of the compounds could be helpful in making a more definitive conclusion in this aspect. It is also worth noting that the fractional magnitude of ΔS_i ranges from 6 to 15% of the total ΔS_t for the phase transitions. These values are significantly higher than those of other low molar mass liquid crystalline compounds which have only one mesogenic unit.[11] The same can be said of ΔH_i. A similar phenomenon has been repeatedly observed earlier by us.[1–3]

The Nature of the Mesophases of Compounds (**4**).—The nature of the mesophases of compounds (4) was judged from the optical textures observed on the hot-stage of a polarizing microscope. The results are summarized in Table 6. All

Table 6. Mesophases formed by compounds (**4**)[a]

x	$n = 5$	$n = 6$	$n = 10$
1	S_A	N	S_A
2	S_A	N	S_A
3	S_A	N	S_A
4	S_A	N	N
5	S_A	S_A	N
6	S_A	S_A	N
7	S_A	S_A	N

[a] N = nematic; S_A = smectic A.

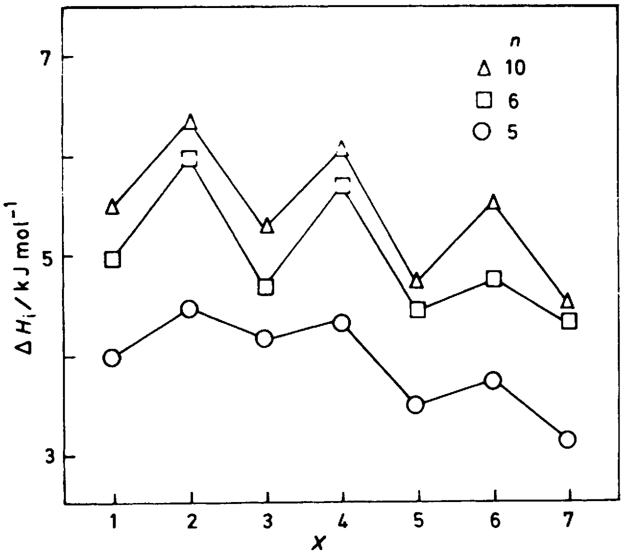


Figure 4. Dependence of ΔH_i of compounds (**4**) with n = 5, 6, or 10 on the length of the polymethylene spacer, x

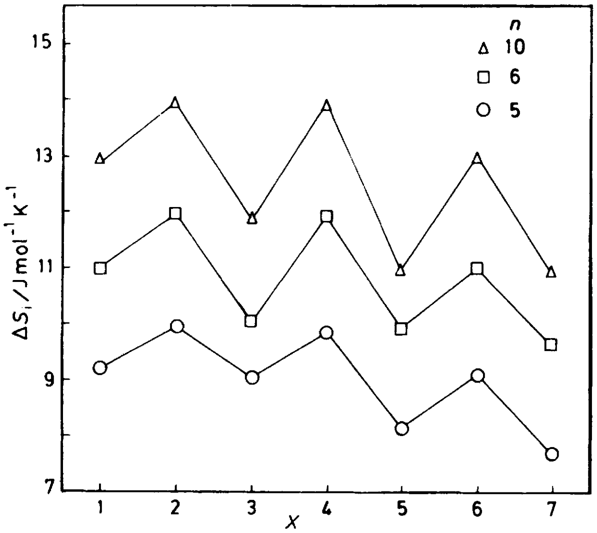
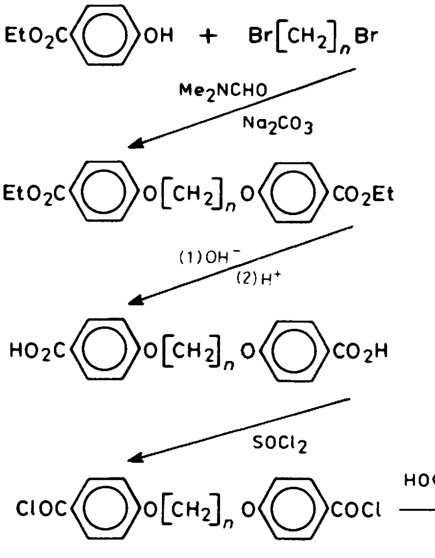


Figure 5. Dependence of ΔS_i of compounds (**4**) with n = 5, 6, or 10 on the length of the polymethylene spacer, x



Scheme.

compounds with a pentamethylene (n = 5) spacer formed an S_A phase; those with a hexamethylene (n = 6) spacer a nematic or smectic phase, depending on the lengths of the terminal alkoxy groups. The compounds with a decamethylene (n = 10) spacer formed an S_A or a nematic phase; S_A up to $x = 3$ and nematic for higher x values. We could not find any regular dependence of the nature of the mesophases on the lengths of central spacers and terminal alkoxy groups.

Conclusions

(1) All the compounds reported here are enantiotropic and thermotropic. (2) They do not show 'odd–even' effects in T_m, T_i, ΔH_m, or ΔS_m, but do in ΔH_i and ΔS_i. (3) Their thermal behaviour does not simulate that of polymers having a sequence of the same mesogenic units alternating with polymethylene spacers. (4) They exhibited different mesophases depending on the lengths of both the central spacers and the terminal alkoxy groups.

Experimental

Synthesis of Compounds (**4**).—The compounds were synthesized *via* the route shown in the Scheme. Since other steps of these reactions were reported earlier,[8] only the final two steps will be described, for a representative procedure. The α,ω-bis-(*p*-carboxyphenoxy)alkane (0.012 mol) was refluxed in thionyl chloride (17 ml) for 5 h under nitrogen. The excess of thionyl chloride was removed by distillation at reduced pressure. Dry light petroleum (20 ml) was added and the mixture was vigorously stirred. It was then distilled at reduced pressure. The solid diacid dichloride was dissolved in dry pyridine (20 ml) and added dropwise to a solution (10 ml) of *p*-alkoxyphenol (0.024 mol) in pyridine at room temperature with stirring. The final step of the reaction was conducted under dry nitrogen. After being stirred for 2 h at room temperature and then 2 h more at 70 °C, the mixture was poured into a large amount of distilled water. The precipitates were collected and washed thoroughly with 0.1M-sodium hydroxide solution. The product was washed further with distilled water. After being dried at 50 °C and under reduced pressure, the compound was recrystallized from toluene–ethanol (v/v 95:5). Yields and elemental analyses are shown in Tables 1—3.

Identification and Characterization of Compounds (**4**).—Compounds were identified by elemental analysis and i.r. and n.m.r. spectra. I.r. spectra were obtained with a JASCO spectrophotometer and n.m.r. spectra with a Varian EM360A spectrometer. Thermal behaviour of the compounds was studied by DSC analysis on a du Pont 910 thermal analyser and on the hot-stage (Mettler FP-2) of a polarizing microscope (Leitz, Ortholux). All the DSC runs were carried out under nitrogen with both heating and cooling rates of 10 °C min^{-1}. Indium was employed as a reference for estimation of thermodynamic parameters for the phase transitions. The nature of the mesophases formed by the compounds was identified by the optical texture observed on the polarizing microscope.

Acknowledgements

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