Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Huh, Seung-Moo , Jin, Jung-Il , Achard, Marie-France and Hardouin, Francis(1999) 'Synthesis and liquid crystalline properties of new 1,6-bis[2,5-bis(4-alkoxyphenoxycarbonyl)phenoxy] hexanes H-shaped twin compounds: a series of', Liquid Crystals, 26: 6, 919 — 924

To link to this Article: DOI: 10.1080/026782999204615

URL: http://dx.doi.org/10.1080/026782999204615

LIQUID CRYSTALS, 1999, VOL. 26, NO. 6, 919–924

Synthesis and liquid crystalline properties of new H-shaped twin compounds: a series of 1,6-bis[2,5-bis(4-alkoxyphenoxycarbonyl)phenoxy] hexanes

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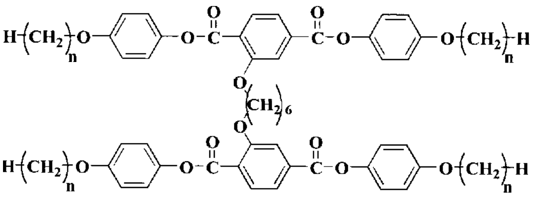
(*Received 2 November 1998; accepted 13 January 1999*)

A new series of laterally linked novel twin mesogenic compounds were synthesized and their liquid crystalline properties studied by differential scanning calorimetry, polarizing microscopy and X-ray analysis. The compounds, 1,6-bis[(2,5-bis(4-alkoxy)phenoxycarbonyl)phenoxy]-hexanes, consisted of two identical mesogenic structures of bis(alkoxyphenoxy)terephthalate linked laterally on the terephthalate centre through a 1,6-dioxyhexane spacer. The length of the terminal alkoxy groups was varied from the ethoxy to the heptyloxy group; the dodecyloxy group was also included in the present study. It was found that the compounds carrying the ethoxy to hexyloxy groups are monotropically nematic whereas that carrying the heptyloxy groups is enantiotropically nematic. Only the compound with the longest dodecyloxy terminals forms the smectic A phase enantiotropically.

1. Introduction

The relationship between molecular structure and properties of liquid crystalline (LC) twin compounds depends very strongly not only on chemical constitution but also on molecular architecture. The two mesogenic units can be interconnected in an end-to-end fashion through a linking spacer unit [1–16] or they can be connected laterally by a spacer [17–19]. There are also other ways to connect two mesogenic units, as demonstrated by Weissflog [17], Demus *et al.* [18], and also by us [19]. Moreover, the structure–LC properties relationship can become even more complicated if the two mesogenic units possess different chemical structures [20, 21]. In a strict sense, the compounds of two different mesogenic structural units [20–25] do not belong to the class of twin LC compounds, and they should rather be called dimesogenic compounds.

In this paper, we report the synthesis and LC properties of the following new series of laterally linked twin mesogenic compounds.



n = 2 - 7 and 12 (BPH-n)

The IUPAC name of the compounds is 1,6-bis-[(2,5-bis(4-alkoxy)phenoxycarbonyl)phenoxy] hexanes. For the sake of convenience, the compounds are called BPH-*n*, where *n* indicates the number of the methylene groups in the tail part. The similar compounds reported earlier by Weissflog [17] and Demus *et al.* [18] are different from the present BPH-*n* series in the chemical structure of mesogenic units and the spacers. Recently, we have reported the synthesis and LC properties of a similar series of compounds that have fixed ethoxy tail groups, but with varying length of the spacers from tetra to octamethylene and dodecamethylene groups, laterally

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connecting the two mesogenic structures [19]. All of them were found to form nematic phases monotropically. Only the compound with the dodecamethylene spacer was able to form a nematic phase enantiotropically.

2. Experimental

2.1. *Synthesis*

The synthetic procedure for the preparation of BPH-2 and the homologous series was described in detail in a previous papers [19]. The present series of compounds were prepared in the same fashion. Therefore, only melting points, elemental analysis, and IR and NMR spectral data are given below for BPH-3 to BPH-7 and BPH-12.

2.1.1. *1,6-Bis[2,5-bis(4-propoxyphenoxycarbonyl)-phenoxy]hexane (BPH-3)*

M.p. 128.2°C. Anal: calcd. for $C_{58}H_{62}O_{14}$, C 70.86, H 6.36; found, C 71.02, H 6.14%. IR spectrum (KBr, cm^{-1}): 3079 and 3047 (aromatic C–H stretching), 2935 and 2878 (aliphatic C–H stretching), 1730 (C=O stretching), 1609 and 1503 (aromatic C–C vibration), 1292 (aromatic C–O stretching), 1186 (aliphatic C–O stretching). NMR spectrum (1,1,2,2-tetrachloroethane-d_2, δ ppm): 0.95–1.09 (m, 12H, CH_3), 1.51–1.60 (m, 4H, $-O(CH_2)_2(\underline{CH_2})_2-(CH_2)_2O-$), 1.71–1.89 (m, 12H, $CH_3\underline{CH_2}CH_2O-$ and $-OCH_2\underline{CH_2}(CH_2)_2\underline{CH_2}CH_2O-$), 3.81–4.19 (m, 12H, $ArO\underline{CH_2}$), and 6.85–8.02 (m, 22H, aromatic).

2.1.2. *1,6-Bis[2,5-bis(4-butoxyphenoxycarbonyl)-phenoxy]hexane (BPH-4)*

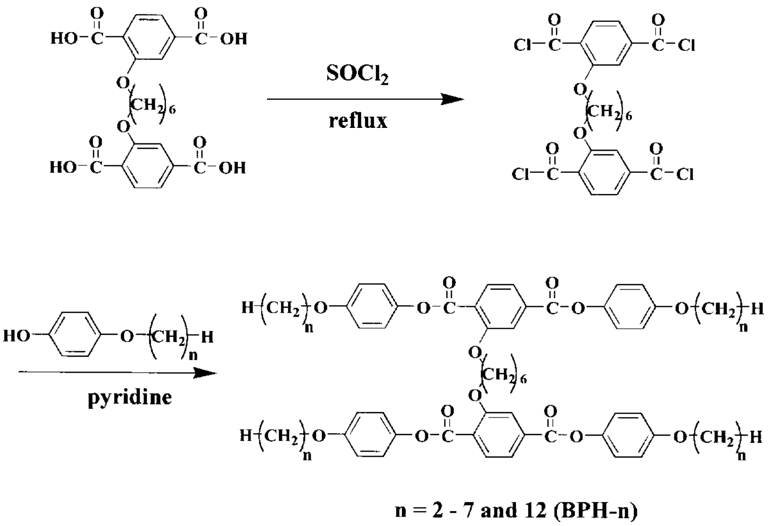
M.p. 134.7°C. Anal: calcd. for $C_{62}H_{70}O_{14}$, C 71.66, H 6.79; found, C 71.33, H 6.57%. IR (KBr, cm^{-1}): 3076 and 3044 (aromatic C–H stretching), 2932 and 2868 (aliphatic C–H stretching), 1743 and 1722 (C=O stretching), 1609 and 1503 (aromatic C=C vibration), 1288 (aromatic C–O stretching), 1186 (aliphatic C–O stretching). NMR (CF_3COOD, δ ppm): 1.01–1.10 (m, 12H, CH_3), 1.50–1.80 (m, 12H, $-OCH_2CH_2-\underline{CH_2}CH_3$ and $-O(CH_2)_2(\underline{CH_2})_2-(CH_2)_2O-$), 1.81–2.10 (m, 12H, $CH_3CH_2\underline{CH_2}CH_2O-$ and $-OCH_2\underline{CH_2}(CH_2)_2\underline{CH_2}CH_2O-$), 4.20–4.40 (m, 12H, $ArO\underline{CH_2}-$), and 7.10–8.30 (m, 22H, aromatic).

2.1.3. *1,6-Bis[2,5-bis(4-pentoxyphenoxycarbonyl)-phenoxy]hexane (BPH-5)*

M.p. 131.1°C. Anal: calcd. for $C_{66}H_{78}O_{14}$, C 72.37, H 7.18; found, C 72.26, H 7.25%. IR (KBr, cm^{-1}): 3079 and 3047 (aromatic C–H stretching), 2937 and 2866 (aliphatic C–H stretching), 1736 (C=O stretching), 1609 and 1505 (aromatic C=C vibration), 1287 (aromatic C–O stretching), 1185 (aliphatic C–O stretching). NMR (1,1,2,2-tetrachloroethane-d_2, δ ppm): 0.89–0.95 (m, 12H, CH_3), 1.31–1.90 (m, 32H, $CH_3(\underline{CH_2})_3CH_2O-$ and $OCH_2(\underline{CH_2})_4CH_2O-$), 3.90–4.20 (m, 12H, $ArO\underline{CH_2}-$), and 6.90–8.15 (m, 22H, aromatic).

2.1.4. *1,6-Bis[2,5-bis(4-hexyloxyphenoxycarbonyl)-phenoxy]hexane (BPH-6)*

M.p. 129.6°C. Anal: calcd. for $C_{70}H_{86}O_{14}$, C 73.02, H 7.53; found, C 72.81, H 7.58%. IR (KBr, cm^{-1}): 3075 and 3046 (aromatic C–H stretching), 2935 and 2857 (aliphatic C–H stretching), 1744 and 1721 (C=O stretching), 1609 and 1505 (aromatic C=C vibration), 1291 (aromatic C–O stretching), 1186 (aliphatic C–O stretching). NMR (CF_3COOD, δ ppm): 0.90–1.00 (m, 12H, CH_3), 1.30–2.00 (m, 40H, $CH_3(\underline{CH_2})_4CH_2O-$ and $-OCH_2(\underline{CH_2})_4CH_2O-$), 4.20–4.31 (m, 12H, $ArO\underline{CH_2}-$), and 7.10–8.25 (m, 22H, aromatic).



Scheme.

2.1.5. *1,6-Bis[2,5-bis(4-heptyloxyphenoxycarbonyl)-phenoxy]hexane (BPH-7)*

M.p. 99.4°C. Anal: calcd. for $C_{74}H_{94}O_{14}$, C 73.60, H 7.85; found, C 73.28, H 7.83%. IR (KBr, cm^{-1}): 3079 and 3047 (aromatic C–H stretching), 2937 and 2866 (aliphatic C–H stretching), 1736 (C=O stretching), 1609 and 1505 (aromatic C=C vibration), 1287 (aromatic C–O stretching), 1185 (aliphatic C–O stretching). NMR (tetrachloroethane-d_2, δ ppm): 0.85–0.95 (m, 12H, CH_3), 1.31–1.90 (m, 48H, $CH_3(\underline{CH_2})_5CH_2O$– and –$OCH_2(\underline{CH_2})_4$–$CH_2O$–), 3.90–4.18 (m, 12H, $ArO\underline{CH_2}$–), and 6.90–8.05 (m, 22H, aromatic).

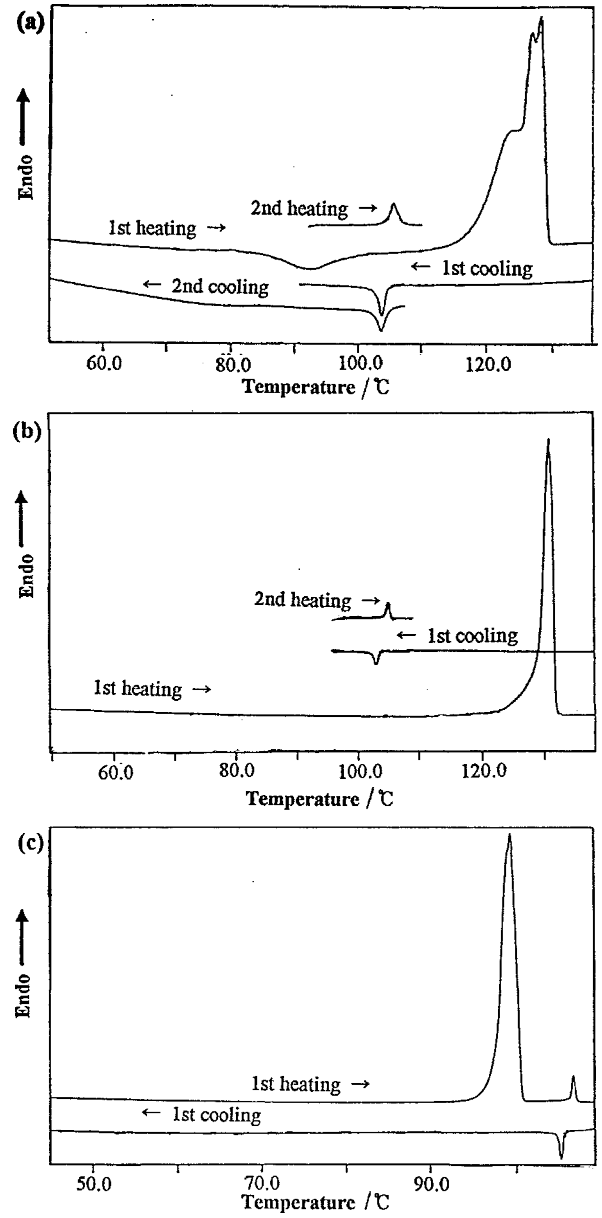


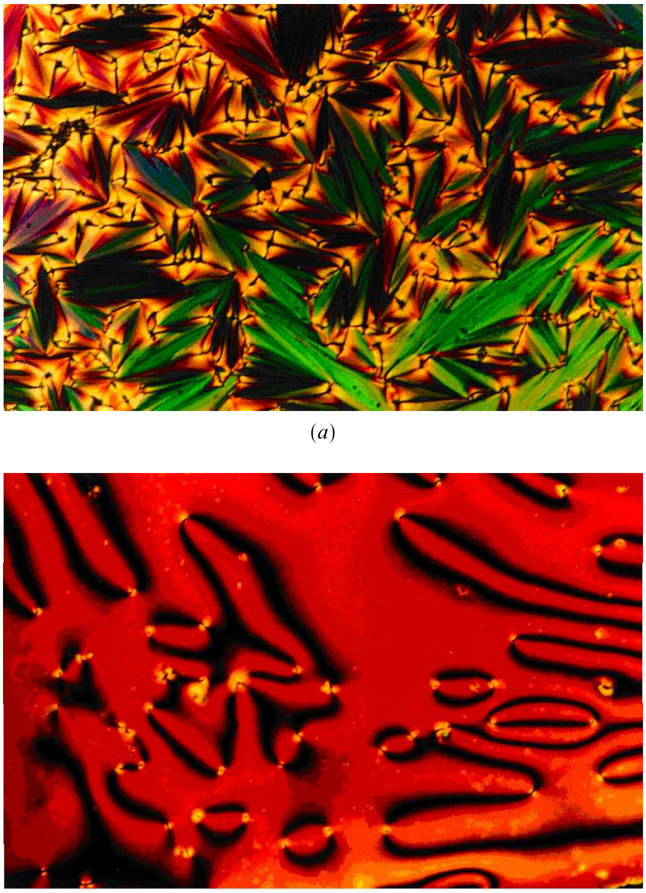
Figure 1. DSC thermograms of (*a*) BPH-3, (*b*) BPH-5 and (*c*) BPH-7 heating and cooling rate: 3°C min^{-1}.

2.1.6. *1,6-Bis[2,5-bis(4-dodecyloxyphenoxycarbonyl)-phenoxy]hexane (BPH-12)*

M.p. 44.1°C. Anal: calcd. for $C_{94}H_{134}O_{14}$, C 75.87, H 9.08; found, C 75.54, H 8.82%. IR (KBr, cm^{-1}): 3074 and 3050 (aromatic C–H stretching), 2922 and 2850 (aliphatic C–H stretching), 1739 (C=O stretching), 1609 and 1506 (aromatic C=C vibration), 1292 (aromatic C–O stretching), 1190 (aliphatic C–O stretching). NMR (CF_3COOD, δ ppm): 0.89–1.00 (m, 12H, CH_3), 1.30–2.10 (m, 88H, $CH_3(\underline{CH_2})_{10}CH_2O$– and –$OCH_2(\underline{CH_2})_4CH_2O$–), 4.20–4.39 (m, 12H, $ArO\underline{CH_2}$–), and 7.13–8.23 (m, 22H, aromatic).

2.2. *Characterization*

The infrared and ^1H NMR spectra were recorded on a Bomen MR-Series FTIR instrument and AMS 300 spectrometer, respectively. Elemental analysis was performed by the Korea Basic Science Institute, Seoul Branch, Seoul, Korea. Thermal properties of the compounds were studied under a nitrogen atmosphere on a differential scanning calorimeter (DSC; Perkin-Elmer 7) at heating



(*a*)

(*b*)

Figure 2. Optical photomicrographs of (*a*) BPH-12 (101°C) and (*b*) BPH-3 (112°C) (magnification 200×).

and cooling rates of 3°C min^{-1}. Thermal transitions and the optical textures of the compounds were also observed through a polarizing microscope (Olympus BH-2) equipped with a hot stage (Mettler FP82HT) controlled automatically by a Mettler FP90HT central unit. X-ray scattering experiments were performed using a CuK_{α} radiation of an 18 kW rotating anode X-ray generator. The experimental detail can be found elsewhere [20].

3. Results and discussion

3.1. *Synthesis*

The present compounds were synthesized by converting 1,6-bis[2,5-dicarboxyphenoxy] hexane [19] to the corresponding acid chloride, which was then reacted with 4-alkoxyphenols in the presence of pyridine as an HCl acceptor, as shown in the scheme. The final compounds were recrystallized from a mixture of ethanol and tetrahydrofuran (v/v = 3/2). Their purity and structure were confirmed by TLC, elemental analysis, and IR and ^{1}H NMR spectroscopy, as described in §2.

3.2. *Thermal and liquid crystalline properties*

Thermal and LC properties of BPH-2 were described earlier by us [19]. It is a monotropic LC compound that forms the nematic phase in the supercooled state. The nematic phase could easily be vitrified by cooling the mesophase to room temperature and below. The thermal transition behaviour of the compounds from BPH-3 to BPH-6 was found to be different from that of BPH-7 and BPH-12. The DSC thermograms of the first group of compounds exhibit only strong melting endothermic peaks on heating the freshly prepared samples or those annealed to crystallization. Moreover, BPH-3 and BPH-4 exhibited multiple melting transitions implying polymorphic crystalline nature, see figure 1 (*a*). In comparison, the melting endotherms of BPH-5 and BPH-6 were much sharper and single-peaked, figure 1 (*b*). But all showed much weaker exothermic peaks on cooling the melts, and the mesophase formed during cooling remained down to room temperature without crystallization. BPH-6 alone underwent crystallization over a very broad temperature range (90–60°C) on cooling the mesophase melt. This thermal behaviour implies that the compounds are monotropically liquid crystalline and that their crystallization is rather sluggish. Among the present compounds, BPH-7 and BPH-12 are the only ones that show two endothermic peaks on heating; one strong melting peak and the other comparatively very weak isotropization peak. When their melts were cooled, the high temperature transitions reappeared. The lower temperature transitions, however, did not appear reversibly, figure 1 (*c*), because the LC phase remained down to room temperature without being transformed to a crystalline phase. Thus, crystallization did not occur readily. Besides, these two compounds appeared to be enantiotropically liquid crystalline.

The thermal behaviour of these compounds observed on DSC analysis could be confirmed by microscopy. In addition, it was learned that the compounds from BPH-2 to BPH-7 form a nematic phase, whereas BPH-12 forms a smectic phase, figures 2 (*a*) and 2 (*b*). The smectic phase formed by BPH-12 was identified as the smectic A (SmA) phase by X-ray analysis, figures 3 (*a*) and 3 (*b*). Figures 3 (*a*) and 3 (*b*) show the X-ray diffraction pattern in the small angle region and the diffractogram, respectively. Both were obtained at 90°C. The symbol q of figure 3(*b*) is the momentum transfer vector that is defined by the equation, $q = 4\pi \sin \theta / \lambda$. The q value of 0.150 corresponds to the long spacing of 41.8 Å ($2\theta = 2.1°$), which is only slightly shorter than the molecular length (42.4 Å) of BPH-12 when the terminal dodecyl groups are in a fully extended *trans*–anti conformation. The

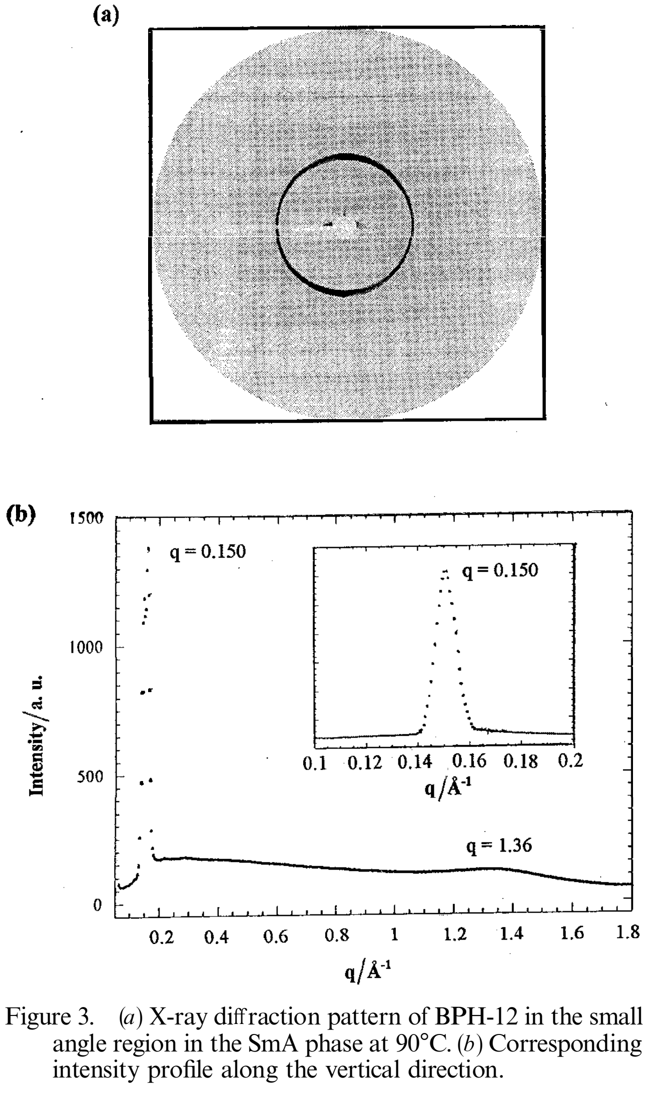


Figure 3. (*a*) X-ray diffraction pattern of BPH-12 in the small angle region in the SmA phase at 90°C. (*b*) Corresponding intensity profile along the vertical direction.

other broad diffraction around $q = 1.36$ (4.6 Å; $2\theta = 19.2°$) is the short spacing corresponding to intermolecular distance.

The table summarizes the thermal transition temperatures of the compounds together with values of $\Delta H_{\text{I-M}}$ for isotropic phase → mesophase transitions. The compounds from BPH-2 to BPH-7 have $\Delta H_{\text{I-N}}$ values of 1.5–2.3 J g^{-1}, but BPH-12 has a much greater value of $\Delta H_{\text{I-S}} = 7.0\ \text{J g}^{-1}$. This coincides with the general observations [4, 6, 12] that the heat of transition for isotropic-to-smectic phases is significantly higher than that for isotropic-to-nematic phases. Another point to be noted is that the melting points and the isotropic-to-mesophase transition temperatures do not exhibit the so-called odd–even dependence on the number of methylene groups in the terminal alkoxy groups.

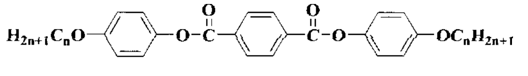
It is interesting to learn, however, that $\Delta H_{\text{I-N}}$ values for the compounds with even-numbered spacers are consistently higher than for those with odd-numbered spacers. The same phenomenon is often observed for monomeric LC compounds [26–28] as well as for linearly linked dimeric twin compounds [1, 4, 9, 29].

Examination of the thermal and LC properties of the present series of compounds clearly demonstrates that longer alkoxy tails lead to enantiotropic LCs whereas shorter tails result in monotropic LCs. Moreover, much longer tails, as in BPH-12, appear to favour the formation of smectic phases. The same trend is observed in the LC behaviour of monomeric compounds [30].

Table. Thermal behaviour of BPH-*n* compounds.

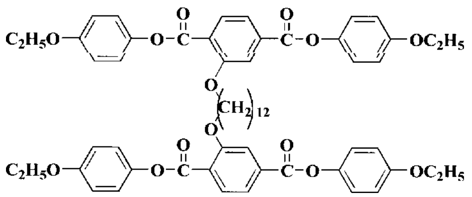
Compound (*n*)	Transition temperature[a]/°C	$\Delta H_{\text{I-M}}/\text{J g}^{-1}$
2 [19]	$\text{Cr} \xrightarrow{188.5} \text{I}$ $\text{I} \xrightarrow{124.6} \text{N} \xrightarrow{110.0} \text{SmX} \xrightarrow{77.8} \text{Cr}$	2.3
3	$\text{Cr} \xrightarrow{128.2} \text{I}$ $\text{I} \xrightarrow{104.0} \text{N}$	1.5
4	$\text{Cr} \xrightarrow{134.7} \text{I}$ $\text{I} \xrightarrow{117.7} \text{N}$	1.9
5	$\text{Cr} \xrightarrow{131.1} \text{I}$ $\text{I} \xrightarrow{103.4} \text{N}$	1.5
6	$\text{Cr} \xrightarrow{129.6} \text{I}$ $\text{I} \xrightarrow{105.8} \text{N} \xrightarrow{90.5} \text{Cr}$	1.9
7	$\text{Cr} \xrightarrow{99.4} \text{N} \xrightarrow{106.5} \text{I}$ $\text{I} \xrightarrow{105.1} \text{N}$	1.5
12	$\text{Cr} \xrightarrow{44.1} \text{SmA} \xrightarrow{117.1} \text{I}$ $\text{I} \xrightarrow{115.8} \text{SmA}$	7.0

[a] Obtained by DSC at heating and cooling rates of 3°C min^{-1}. The ΔH values were obtained from the cooling DSC runs.



n = 1 - 4 : nematic
n = 5 and 6 : smectic-C, smectic-A and nematic

This observation is in great contrast to our earlier observation [19] that the compound having a dodecyl spacer between the two mesogenic units, and carrying ethoxy tails, forms only the nematic phase, not the smectic phase. Therefore, it can be said that longer tails are more efficient in inducing the formation of smectic phases than are the longer spacers laterally linking the two mesogenic units.



$\text{Cr} \xrightarrow{110.0\ °\text{C}} \text{N} \xrightarrow{119.7\ °\text{C}} \text{I}$ (heating)

$\text{I} \xrightarrow{85\ °\text{C}} \text{N}$ (cooling)

4. Conclusion

Thermal and LC properties of 1,6-bis[2,5-bis(4-alkoxyphenoxycarbonyl)phenoxy] hexanes reveal the importance of the length of the alkoxy tails in controlling the nature of mesophases formed by these compounds. Shorter tails tend to make the compounds monotropically nematic, while longer tails produce smectic phases enantiotropically.

Compared with monomeric compounds, the diversity of the mesophases formed by the 'H-shaped' compounds is diminished. Combinations of longer lateral spacers and longer tails are expected to lead to the formation of a greater variety of LC phases, which are presently under investigation.

This research (BSRI-97-3402) was supported by the Korea Research Foundation through the Basic Science Research Institute of Korea University.

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