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Dimeric liquid crystalline compounds having a central malonic acid moiety: effect of the length of the spacers and terminal chains

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Dimeric liquid crystalline compounds having a central malonic acid moiety: effect of the length of the spacers and terminal chains

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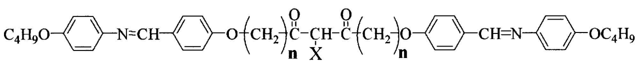
We have studied the liquid crystalline properties of two new series of dimeric compounds consisting of a central malonic acid moiety, polymethylene spacers, and Schiff's base mesogens. In the first series we changed the length of the spacers with the terminal chain fixed as the butoxy group; in the second series we changed the length of the terminal alkyl or alkoxy groups while keeping the spacers fixed as decamethylene groups. In the first series, as the length of the spacer increased, the tendency to form smectic phases grew. In the second series, changing the alkyl terminal chain to the alkoxy terminal group raised the melting and isotropization temperatures. Increasing the length of the terminal group diminished the temperature range for the higher temperature smectic phase. The smectic phases are assigned to be smectic A and crystal smectic E phases.

1. Introduction

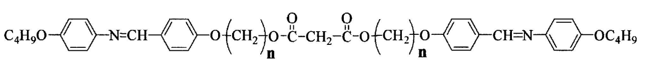
Recently, we reported [1, 2] the liquid crystalline properties of dimeric compounds containing a central malonic acid moiety, polymethylene spacers and Schiff's base mesogenic groups. The central malonic acid moiety bore various substituents such as cholesteryloxyalkyl, alkyl, and phenyl groups:



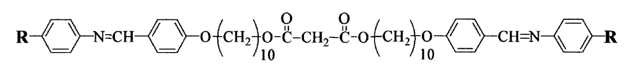
X = H, Chol-O-alkyl, methyl, ethyl and phenyl; n = 4 or 10

Symmetric liquid crystal dimers [3–8] and non-symmetric liquid crystal dimers [9–16] having two different mesogenic units constitute new groups of LCs which exhibit unique types of transitional behaviour and molecular organization in mesophases. The so-called banana-shaped, bent LCs [17–22] may be categorized as a special class of dimeric LC compounds.

In the present investigation we have prepared two series of dimeric compounds, and investigated their LC properties in detail:



Series **I-*n*** (n = 3–8 and 10)



Series **II-*R***

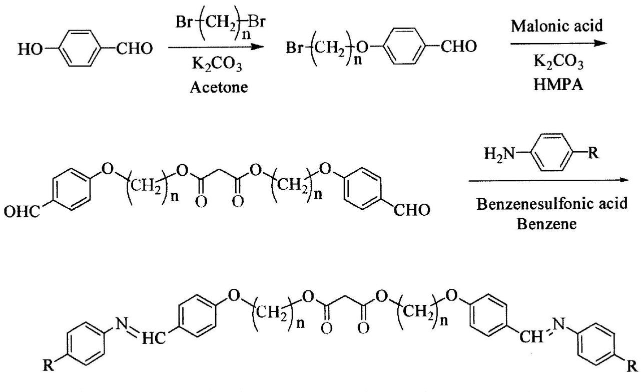
R = n-C_4H_9 (**II-C$_4$**), n-$C_{10}H_{23}$ (**II-C$_{10}$**), and O-n-$C_{10}H_{23}$ (**II-OC$_{10}$**)

In the first series, **I-*n***, the length of the polymethylene spacer was varied, while in the second series, **II-*R***, the nature and length of the terminal chain R was changed. The liquid crystalline properties of **I-4** and **I-10** have been reported in a previous paper [1].

2. Experimental

2.1. *Synthesis of compounds*

The synthetic route to these compounds is shown in the scheme, which is basically the same as we reported earlier [1, 2] for another homologous series of dimers containing the same malonate central linkage. All the final compounds were recrystallized from acetone and their structures were confirmed by FTIR and HNMR



Scheme. Synthetic route to the series **I-*n*** and **II-*R***.

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spectroscopy, and also by elemental analysis. Here, we give only the spectral and elemental analysis data for representative final compounds of series **I-*n*** and **II-*R***.

2.1.1. *Malonic acid bis(8-[4-{(4-butoxyphenylimino)-methyl}phenoxy]octyl) ester, **I-8***

Yield 1.9 g (88%), m.p. 98.4°C. FTIR spectrum (KBr, cm^{-1}): 2935 (aliphatic C–H stretching), 2872 (C–H stretching of ArO*CH*$_2$), 1732 (ester C=O stretching), 1608 and 1512 (aromatic C=C and C=N stretchings), 1250 and 1028 (C–O stretchings). ^{1}H NMR spectrum ($CDCl_3$, δ ppm): 3.37 (s, 2H, $\underline{CH_2}$–(COO–)$_2$), 3.95–4.02 (m, 8H, Ar–O$\underline{CH_2}$–), 4.14 (t, 4H, COO$\underline{CH_2}$–), 6.89–7.82 (m, 16H, Ar), 8.39 (s, 2H, –CH=N–). Elemental analysis: calc. for $C_{53}H_{70}N_2O_8$ C 73.75, H 8.17, N 3.25; found C 73.81, H 8.49, N 3.59%.

2.1.2. *Malonic acid bis(10-[4-{(4-decylphenylimino)-methyl}phenoxy]decyl) ester, **II-C$_{10}$***

Yield: 2.0 g (96%), m.p. 91°C. FTIR spectrum (KBr, cm^{-1}): 2920 and 2851 (aliphatic C–H stretchings), 1732 (ester C=O stretching), 1605 and 1512 (aromatic C=C and C=N stretchings), 1254 and 1018 (C–O stretchings). ^{1}H NMR spectrum ($CDCl_3$, δ ppm): 2.60 (t, 4H, Ar–$\underline{CH_2}$–), 3.37 (s, 2H, $\underline{CH_2}$–(COO–)$_2$), 4.01 (t, 4H, Ar–O$\underline{CH_2}$–), 4.14 (t, 4H, COO$\underline{CH_2}$–), 6.94–7.83 (m, 16H, Ar), 8.39 (s, 2H, –CH=N–). Elemental analysis: calc. for $C_{69}H_{102}N_2O_6$ C 78.51, H 9.74, N 2.56; found C 78.44, H 9.75, N 2.61%.

2.1.3. *Malonic acid bis(10-[4-{(4-decyloxyphenylimino)-methyl}phenoxy]decyl) ester, **II-OC$_{10}$***

Yield: 1.9 g (87%), m.p. 108°C. FTIR spectrum (KBr, cm^{-1}): 2920 and 2851 (aliphatic C–H stretchings), 1736 (ester C=O stretching), 1609 and 1512 (aromatic C=C and C=N stretchings), 1253 and 1022 (C–O stretchings). ^{1}H NMR spectrum ($CDCl_3$, δ ppm): 3.37 (s, 2H, $\underline{CH_2}$–(COO–)$_2$), 3.96–4.02 (m, 8H, Ar–O$\underline{CH_2}$–), 4.14 (t, 4H, COO$\underline{CH_2}$–), 6.89–7.82 (m, 16H, Ar), 8.39 (s, 2H, –CH=N–). Elemental analysis: calc. for $C_{69}H_{102}N_2O_8$ C 76.20, H 9.45, N 2.58; found C 76.14, H 9.45, N 2.60%.

2.2. *Characterization*

FTIR and HNMR spectra of the compounds were recorded on a Bomem MB spectrometer and on a Varian Gemini 300 spectrometer respectively. Thermal properties were studied in a nitrogen atmosphere using a differential scanning calorimeter (Mettler Toledo DSC 821^e) at a heating and cooling rate of 5°C min^{-1}. The phase transitions and optical textures were examined on a polarizing microscope (Olympus BH-2) equipped with a hot stage (Mettler FP-82HT) controlled by an automatic thermal controller (Mettler FP-90). The X-ray patterns of the compounds were obtained at varying temperatures using synchrotron radiation (1.542 Å) 3C2 beam line at the Pohang Synchrotron Laboratory, Korea.

3. Results and discussion

3.1. *Thermal and liquid crystalline properties of the **I-n** series*

All these compounds exhibit clear-cut transition temperatures in their DCS thermograms as shown in figure 1. As representative examples, only the DSC thermograms of **I-3**, **I-6**, and **I-8** are given in the figure. It is clear that as the length of the spacer (i.e. the number *n* of methylene units in the spacer) increases, the number of transition peaks increases from two to three in the heating cycle. In the cooling thermogram of **I-3**, the relative peak area decreases in the order first (lower temperature) peak > the second (higher temperature) peak; and for **I-6**, first peak > second peak > third peak > fourth peak. The DSC thermogram (figure 1) of **I-6** shows a strong crystallization exotherm (lowest temperature, broad) on cooling, whereas the others do not. In the thermogram of **I-8**, however, the relative peak area decreases in the order, first peak > third

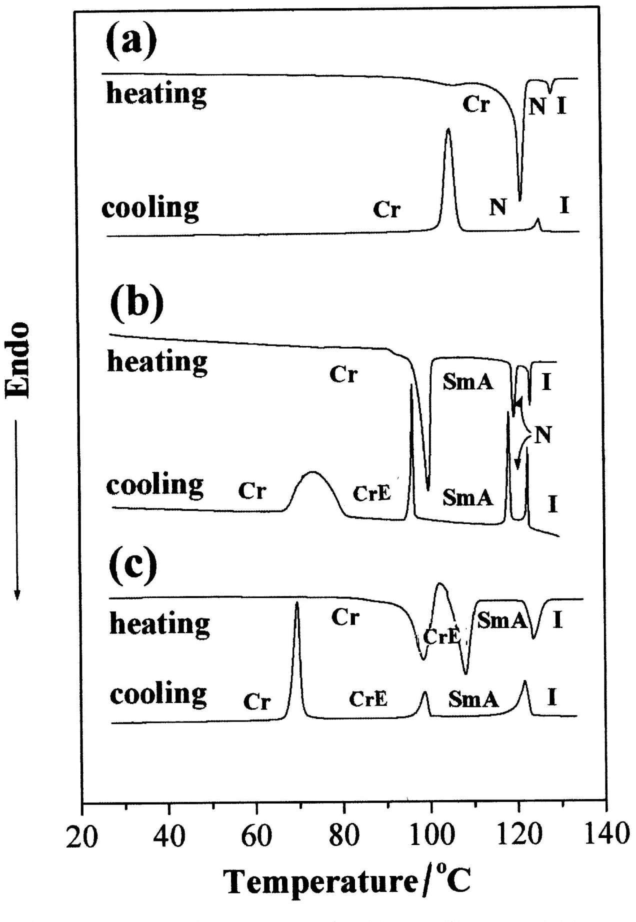


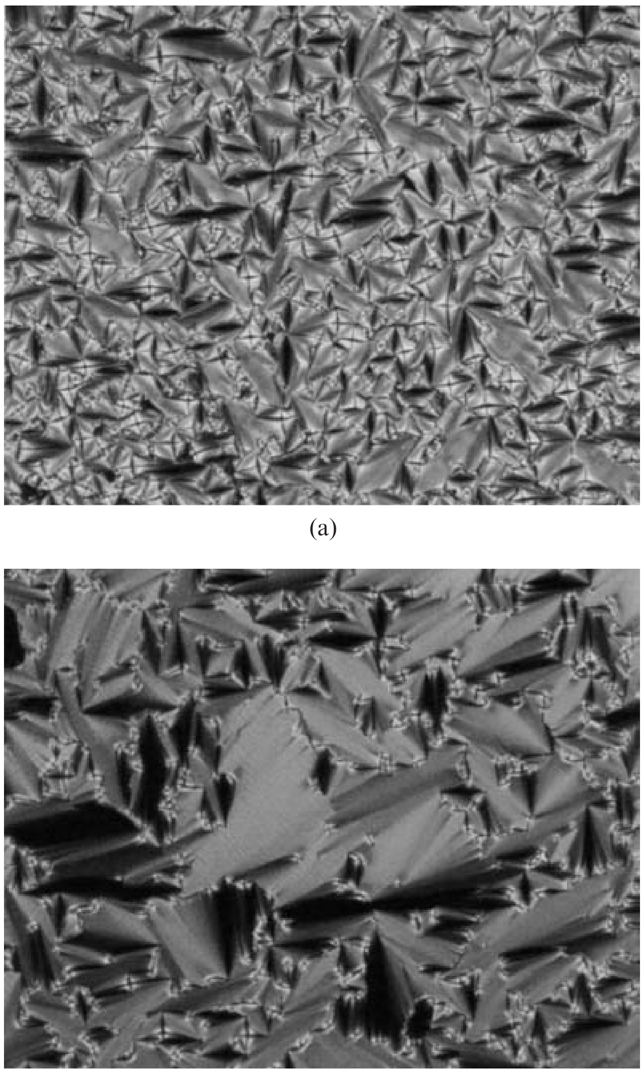
Figure 1. DSC thermograms for (*a*) **I-3**, (*b*) **I-6** and (*c*) **I-8**.

peak > second peak. The crystallization peak in the cooling DSC curve of **I-8** is sharper than that seen for **I-6**, which implies that the longer spacer induces crystallization more effectively. These observations imply that the number of mesophases increase with increasing *n*, and at the same time there is a change in the nature of the mesophases, especially for the members with longer spacers.

The transitions seen in the DSC thermograms were confirmed by polarizing optical microscopy (POM). The optical textures observed for each phase could be used for phase assignment. The first member of the series, **I-3**, showed a typical nematic (N) schlieren texture. **I-4** and **I-5** exhibited only the nematic schlieren texture when the crystalline solids were heated, while on cooling the isotropic liquid showed the focal-conic texture typical of the smectic A (SmA) phase in addition to the nematic texture, figure 2 (*a*). Thus the compounds form the SmA phase monotropically and the nematic phase enantiotropically. In contrast, **I-6** and **I-7** were found to form both the SmA and N phases enantiotropically. Therefore, it is clear that longer spacers favour the formation of the SmA phase [8]. They also formed the crystal E phase monotropically.

Further increase in the length of the spacer enables the compound **I-8** to form two smectic phases enantiotropically. The high temperature mesophase exhibited a focal-conic texture and the lower temperature phase a similar focal-conic texture but with concentric arc lines, figure 2 (*b*), which is known to be the characteristic texture of the crystal E (CrE) phase [23]. Surprisingly, **I-10**, containing the decamethylene spacers, formed the SmA phase enantiotropically but the CrE phase only monotropically. The crystal E mesophase is characterized by the permanent presence of concentric arcs on the focal-conic fan texture even after the phase transition is complete.

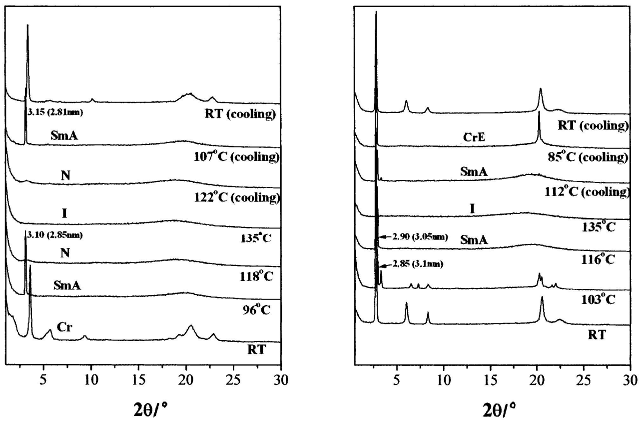
The wide-angle X-ray patterns of **I-6** and **I-8** obtained at different temperatures are shown in figure 3. The diffractogram shown in figure 3 (*a*) reveals gradual changes from the crystal to fluid smectic phase and finally to the isotropic phase. At room temperature (25°C), the diffractogram shows a typical crystalline pattern. As the temperature is increased, the pattern changes to a similar diffractogram that shows a sharp peak in the small angle region ($2\theta = 3.15°$; $d = 28.1$ Å) and a very broad peak centered around $2\theta = 15°–23°$ ($d = 5.9–3.9$ Å) at 107°C, indicating that the mesophase is a fluid smectic in nature. The long spacing of 28.1 Å corresponds to about one half the length l (56.6 Å) of the molecule in an extended conformation. Our previous report [1] discussed the molecular conformation of a similar compound studied by NMR spectroscopy; thus the fluid smectic phase is an intercalated SmA phase. The X-ray pattern at 122°C, i.e. in the temperature range of the higher temperature phase, reveals a very broad halo ($2\theta = 14°–25°$; $d = 6.3–3.6$ Å) in the wide angle region and a broad, weak peak centered around $2\theta = 3.3°$ ($d = 26.8$ Å). This pattern is a characteristic of the nematic phase. This sequence of phase transitions was observed to be reversible when the isotropic liquid was cooled as shown in figure 3 (*a*). Unfortunately, we did not obtain the diffractogram for the CrE phase of **I-6** formed monotropically. Therefore, it is not seen in figure 3 (*a*). Although it is not given, the X-ray diffraction pattern of **I-7** showed a temperature dependence exactly the same as that described for **I-6**.



(a)

(b)

Figure 2. Optical photomicrographs of the fan textures of (*a*) **I-4** (cooling, 108°C) and (*b*) **I-8** (cooling, 80°C) (magnification 200 ×).



(a) (b)

Figure 3. X-ray diffractograms of (*a*) **I-6** and (*b*) **I-8**.

The X-ray patterns of **I-8** given in figure 3(*b*) are typical of SmA and CrE phases. We could obtain better defined patterns on the cooling cycle than are shown in the figure. The diffractogram obtained at 116°C reveals that the mesophase is a fluid smectic phase in nature. The sharp peak at $2\theta = 2.90°$ ($d = 30.5$ Å) corresponds to the interlayer spacing. This spacing is again about one-half the length l (61.7 Å) of the molecules assuming a fully extended conformation. Another peak is very broad and centered around $2\theta = 15°–22°$ ($d = 5.9–3.9$ Å). This diffraction corresponds to the intermolecular spacing. This indicates that the layered morphology of this phase is of the intercalated SmA type. Based on the observed d/l ratio, a proposed packing model for **I-8** in the SmA phase is shown in figure 4. We have observed previously a similar structural organization for another series of dimeric compounds having central malonic ester linkages [1]. This is a rather surprising observation and not fully understood. The next diffractogram measured at 95°C, however, exhibits two sharp peaks: one at $2\theta = 2.85°$ ($d = 31.0$ Å) and the other at $2\theta = 20.5°$ ($d = 4.3$ Å). The presence of two sharp peaks implies that the mesophase is not fluid but solid-like. The optical texture of this phase and the X-ray diffraction pattern lead to the conclusion that this mesophase is the CrE phase.

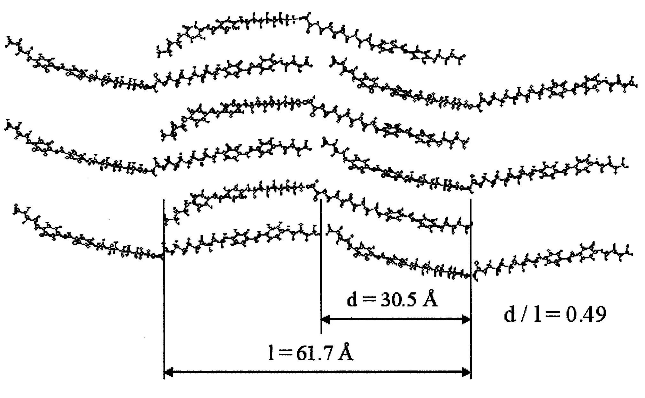


Figure 4. Schematic representation of the possible packing of **I-8** in the SmA phase.

Table 1 summarizes the sequence of phase transitions of the **I-*n*** series determined from DSC, X-ray, and POM analyses. The sequences include the phase transitions observed both on heating as well as cooling cycles. Figure 5 correlates the long spacing in the SmA phase with the length of the spacers *n*. This figure clearly shows that the layer spacing increases linearly with increasing *n*. On average, the increment of the long spacing per methylene unit of the spacers is 1.3 Å which is very close to those for other reported homologous series [24].

In summary, increasing the spacer length favours the formation of smectic phases, and when the spacer is octamethylene or longer, the compounds have a tendency to form the solid crystal E phase. It is also noted that increase in *n* decreases the nematic temperature range, whereas it increases the smectic temperature range.

3.2. *Thermal and liquid crystalline properties of series **II** compounds*

In the second series we briefly studied the influence of the length and polarity of the terminal chain on LC properties. Since we are comparing the phase transition behaviour of only three compounds, our discussion and conclusions are based on a rather limited number of data and observations.

Table 1 summarizes the sequence of phase transitions of the three compounds based on the characterization results obtained by DSC, X-ray, and microscopic analyses. From a close examination of the phase transitions and sequences given in the table we see that: (1) all the

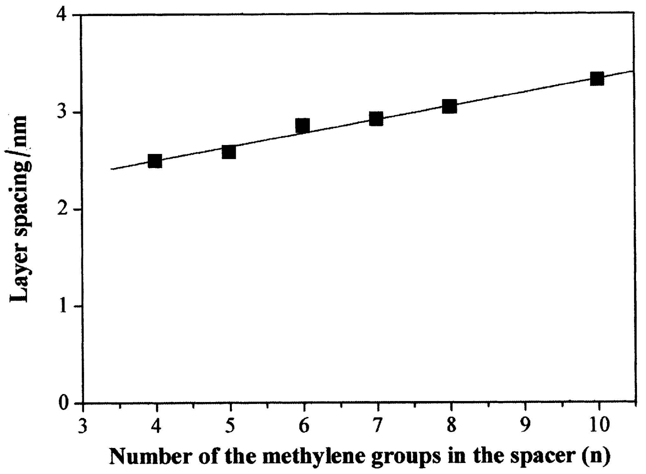


Figure 5. Layer spacing vs number *n* of methylene groups in the spacers for series **I-*n***.

Table 1. Transition temperatures and enthalpy changes for the **I-*n*** and **II-*R*** series: measured at a heating/cooling rate of 5°C min^{-1}, under a 15 ml min^{-1} flow of nitrogen. [] indicates a monotropic phase.

Compound	Transition temperature (°C) and enthalpy change (kJ mol^{-1})						
I-3	Cr	(31.1) 121.5	N	(1.7) 128.6	I		
I-4	Cr	(52.7) 117.7	N	(1.2) 122.9	I		
	[SmA]	111.2	↵(1.5)				
I-5	Cr	(63.9) 123.0	N	(2.0) 127.2	I		
	[SmA]	111.1	↵(1.6)				
I-6	Cr	(70.8) 99.3	SmA	(4.6) 120.3	N	(1.7) 123.5	I
	[CrE]	96.2	↵(5.0)				
I-7	Cr	(75.0) 118.6	SmA	(3.5) 121.6	N	(2.7) 125.0	I
	[CrE]	93.8	↵(4.2)				
I-8	Cr	(44.2) 98.5	CrE	(36.8) 108.2	SmA	(11.2) 123.6	I
I-10	Cr	(49.6) 105.8	SmA	(15.4) 121.2	I		
	[CrE]	103.7	↵(9.2)				
II-C4	Cr	(26.9) 71.2	CrE	(8.2) 80.0	SmA	(15.0) 90.8	I
II-OC10	Cr	(94.8) 108.1	SmA	(13.1) 116.5	I		
	[CrE]	103.5	↵(10.0)				
II-C10	Cr	(38.8) 65.6	CrE	(13.5) 88.4	SmA	(13.3) 91.8	I

compounds are able to form the solid-like crystal E phase and also the fluid smectic A phase; (2) the alkoxy terminal chain stabilize the formation of the CrE phase to a greater extent than alkyl chains, as reflected by higher CrE–SmA transition temperatures, although the former compounds tend to give monotropic CrE phases; (3) while the CrE phase temperature range increases with the length of the alkyl chain, it decreases with the length of the alkoxy chain; (4) regardless of the nature of the terminal chains, longer chains tend to decrease the temperature range of the SmA phase [8], although the alkoxy chains give much wider temperature ranges for the SmA phase than do the alkyl groups; (5) the melting and clearing transition temperatures are significantly higher for the alkoxy compounds than for the alkyl compounds—the melting points of the alkoxy compounds are higher, resulting in narrower mesophase temperature ranges.

The SmA phases exhibited focal-conic textures, while the CrE phases showed the same textures but with concentric arcs. Figure 6 compares the DSC thermograms of **I-10** and **II-C$_4$**, and figure 7 the wide angle X-ray diffractograms of the same compounds obtained at different temperatures. They are all consistent with the data given in table 1 and the preceding discussions. The heating DSC thermogram of **I-10** reveals a multiple melting transition, figure 6(*a*).

Table 2 also lists the enthalpy changes (ΔH) associated with the phase transitions. For the sake of comparison, the values obtained from heating as well as cooling DSC thermograms are included. The enthalpy changes for the melting of **I-10** and **II-C$_4$** are much exaggerated because they were estimated from the very broad endotherms that are most probably overlapped peaks for the crystal → CrE and CrE → SmA transitions. Therefore, it is more informative to compare the values obtained from the cooling DSC curves. Firstly, the relative magnitudes of the enthalpy changes for isotropization ($\Delta H_{\text{I-SmA}}$) compared with those for the CrE → Cr transitions ($\Delta H_{\text{CrE-Cr}}$) are very high (*c* 41.5–54.5%). For monomesogenic smectic compounds this value is about 30% [25, 26].

Similar trends have been observed for other dimers [1], and attributed to enhanced molecular interactions among the larger dimer molecules. When the values are

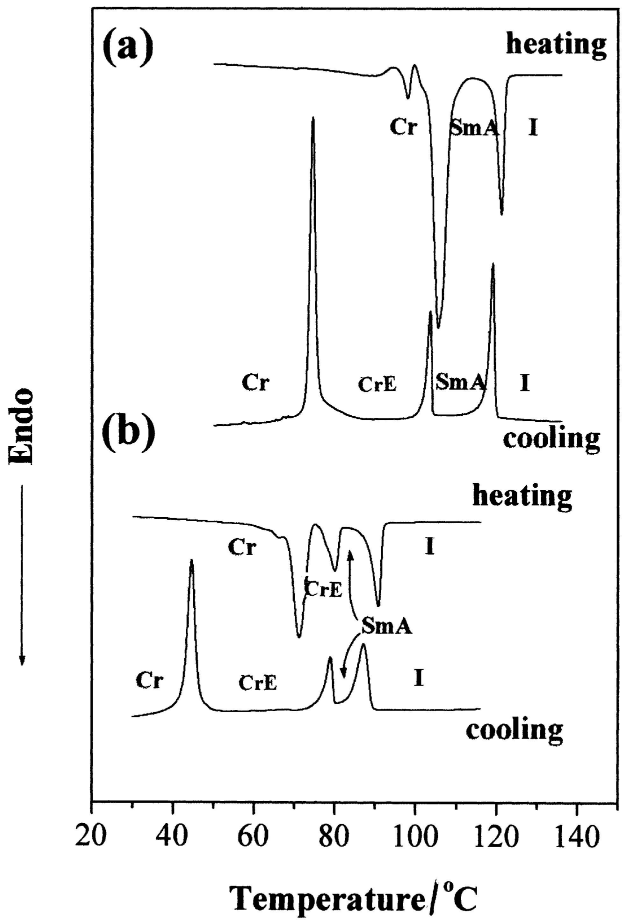
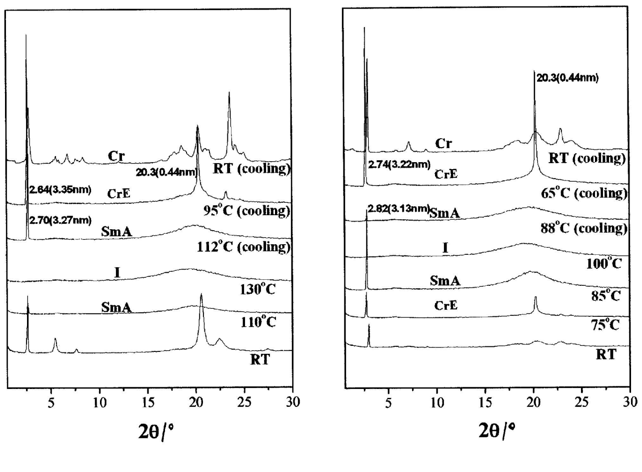


Figure 6. DSC thermograms for (*a*) **I-10** and (*b*) **II-C$_4$**.

scaled by the number of mesogenic units, i.e. $\Delta S_i/R/2$, they range from 2.1 to 2.5 (see table 2). Similar values have been reported for other trimers and tetramers [27, 28]. The absolute magnitudes of the enthalpy changes are also greater for the dimers described here than those of monomeric compounds. In addition, it is noted that the $\Delta H_{\mathrm{Cr\text{-}CrE}}$ values are much greater than either the $\Delta H_{\mathrm{CrE\text{-}SmA}}$ or $\Delta H_{\mathrm{SmA\text{-}I}}$ values, although the CrE phase is solid-like. Needless to say, breaking the crystal lattice requires much more energy than do the phase transitions between LC phases.



(a) (b)

Figure 7. X-ray diffractograms for (*a*) **I-10** and (*b*) **II-C$_4$**.

4. Conclusion

From the results of this investigation the following conclusions are drawn.

(1) The tendency of the dimers to form smectic phases increases on increasing the length of the spacers. The compounds having long spacers (octamethylene and longer) favour the formation of the solid-like CrE phase, while the nematic phase is destabilized.

Table 2. Thermodynamic data for the phase transitions of series **I-10** and **II-*R***: measured at a heating/cooling rate of 5°C min^{-1}, under a 15 ml min^{-1} flow of nitrogen.

Compound		T_m /°C	T_t^c /°C	T_i /°C	ΔH_m /kJ mol^{-1}	ΔH_t^c /kJ mol^{-1}	ΔH_i kJ mol^{-1}	ΔS_m J mol^{-1} K^{-1}	ΔS_t^c /J mol^{-1} K^{-1}	ΔS_i /J mol^{-1} K^{-1}	ΔS_i /R
I-10	h[a]	105.8	—	121.2	49.6	—	15.4	131.0	—	38.9	2.34
	c[b]	74.5	103.7	119.1	33.5	9.2	13.9	96.3	24.3	35.4	2.13
II-C$_4$	h	71.2	80.0	90.8	26.9	8.2	15.0	78.2	23.3	41.3	2.48
	c	44.6	78.9	87.1	26.6	8.2	14.5	83.6	23.2	40.2	2.42
II-OC$_{10}$	h	108.1	—	116.5	94.8	—	13.1	248.8	—	33.5	2.02
	c	84.9	103.5	113.1	70.5	10.0	16.0	197.0	26.7	41.4	2.49
II-C$_{10}$	h	65.6	88.4	91.3	38.8	13.5	13.3	114.5	37.4	36.5	2.20
	c	37.5	87.0	88.9	34.2	13.1	12.7	110.4	36.3	35.2	2.12

[a] Heating.
[b] Cooling.
[c] Liquid crystal to liquid crystal transition.

(2) Alkyl terminal chains tend to give enantiotropic CrE phases, whereas alkoxy chains give rise to monotropic phases. The alkoxy chains tend to increase the melting and isotropization temperatures, implying the existence of stronger intermolecular interactions due to their polar nature.

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