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Dimeric compounds containing malonic acid as the central linking unit: synthesis and mesomorphic properties

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Eight new dimeric compounds containing malonic acid as the central linking unit (series M-*n*-*X*) have been synthesized and their mesomorphic properties studied. All these compounds are found to be liquid crystalline, forming mainly nematic and smectic phases. We have carried out microscopic textural observations, X-ray diffractometry as well as solid state NMR studies on these compounds.

1. Introduction

Liquid crystalline dimeric compounds have emerged as an interesting subject of research in the field of liquid crystals [1, 2]. Both symmetric [3–8] and non-symmetric [9–15] liquid crystalline dimers in which the two monomeric units are linked through a flexible spacer are known in the literature. These are known to be excellent model compounds for thermotropic main chain polymers consisting of similar monomeric units and spacers [16, 17]. Although, extensive research has been reported in this field, the relationships between the liquid crystalline properties of monomers and their dimers are yet to be clearly understood.

As a continuation of our effort to understand the correlation between molecular structure and mesomorphic properties in dimeric compounds, we have synthesized and studied several new compounds. The molecular structures of the dimeric compounds synthesized in the present study are shown in figure 1, and these consist of two identical Schiff's base mesogenic groups linked through a central malonic acid unit and polymethylene spacers. We have introduced different bulky groups, such as methyl, ethyl and phenyl groups, in the middle of the malonic acid moiety of the molecules, and studied their mesomorphic properties with respect to those of the parent compounds (X = H). All the compounds synthesized in this work are found to be liquid crystalline forming nematic and smectic phases. For the sake of simplicity, we designate the compounds as M-*n*-*X* where M, *n* and *X* denote malonic acid, the number of methylene units in the polymethylene spacers and the substituent at the central CH_2 group of the malonic acid moiety, respectively.

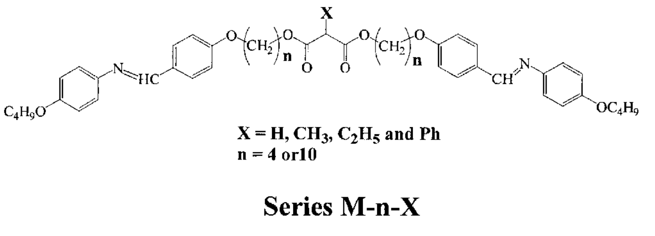

Figure 1. Molecular structures of the M-*n*-*X* series.

2. Experimental

2.1. *General information*

All the intermediate compounds and final products were purified either by column chromatography on silica gel or by repeated recrystallization using suitable solvents. Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F_{254}). The chemical structures of all the compounds synthesized were confirmed by spectroscopy and elemental analysis.

The IR and ^{1}H NMR spectra were recorded on a Bomem MB FTIR instrument and a Varian Gemini 300 NMR spectrometer, respectively. Elemental analyses were performed using an Eager 200 elemental analyser. The optical textural observations of the different mesophases were carried out on a polarizing microscope (Olympus BH-2) equipped with a hot stage (Mettler FP-82 HT) operated by a Mettler FP-90 temperature

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controller. The transition temperatures and associated enthalpy changes of different phase transitions were determined from thermograms recorded on a differential scanning calorimeter (Mettler DSC 821^{e}). The heating and cooling rate was 5°C min^{-1}. X-ray measurements were carried out using synchrotron radiation (1.542 Å) at the Pohang Synchrotron Laboratory, Pohang, Korea. Structural analysis of the compounds was performed by ^{13}C NMR spectroscopy on an Innova Unity (Varian, USA) 200 solid state NMR instrument.

2.2. *Synthesis*

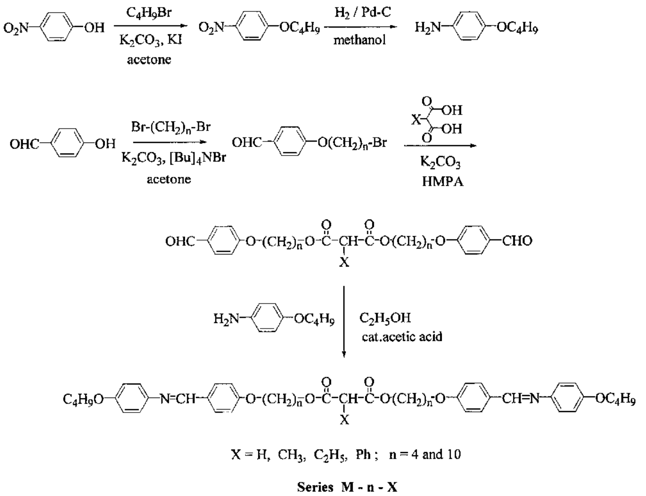
All the compounds shown in figure 1 were synthesized according to the synthetic routes given in the scheme. Since the details of synthetic procedures have already been reported [15] for similar types of compounds, here we provide only the spectral and elemental analysis data for representative compounds of the M-*n*-*X* series and their respective intermediates.

2.2.1. *Di-[10-(4-formylphenoxy)decyl]malonate (X = H, n = 10)*

Yield, 77%; IR (KBr, cm^{-1}): 2932 and 2854 (aliphatic C–H stretch), 1749 (ester C=O stretch), 1691 (aldehyde C=O stretch), 1599 and 1510 (aromatic C=C stretch), 1259 and 1011 (C–O stretch). ^{1}H NMR (CDCl3, δ ppm): 9.88 (s, 1H, –CHO), 6.97–7.84 (d, 8H, Ar–H), 4.14 (t, 4H, –COOCH$_2$–), 4.04 (t, 4H, Ar–OCH$_2$), 3.37 (s, 2H, CH$_2$(COO–)$_2$), 1.25–1.9 (m, 32H, –CH$_2$–).

2.2.2. *Bis-{10-[4-(4-butoxyphenyliminomethynyl)-phenoxy]decyl} malonate, M-10-H*

Yield, 92%; IR (KBr, cm^{-1}): 2935 and 2851 (aliphatic C–H stretch), 1736 (ester C=O stretch), 1512 and 1609 (C=N and C=C stretch), 1254 and 1018 (C–O stretch). ^{1}H NMR (CDCl$_3$, δ ppm): 8.39 (s, 2H, –CH=N–), 6.87–7.81 (m, 16H, Ar–H), 4.14 (t, 4H, –COOCH$_2$–), 3.95–4.02 (m, 8H, Ar–OCH$_2$), 3.37 (s, 2H, CH$_2$(COO–)$_2$), 0.95–1.9 (m, 46H, –CH$_2$– and –CH$_3$). Elemental analysis: calcd. for $C_{57}H_{78}N_2O_8$, C 74.48, H 8.55, N 3.05; found, C 74.46, H 8.53, N 3.09%.



Scheme. Synthetic route to the M-*n*-*X* compounds.

2.2.3. *Di-[10-(4-formylphenoxy)decyl]methylmalonate (X = CH$_3$ and n = 10)*

Yield, 72%, IR (neat, cm^{-1}): 2927 and 2854 (aliphatic C–H stretch), 1731 (ester C=O stretch), 1693 (aldehyde C=O stretch), 1600 and 1508 (aromatic C=C stretch) 1259 and 1024 (C–O stretch). ^{1}H NMR (CDCl$_3$, δ ppm): 9.87 (s, 2H, –CH=O), 7.82 (d, 4H, Ar–H), 6.98 (d, 4H, Ar–H), 4.12 (t, 4H, –COOCH$_2$), 4.03 (t, 4H, Ar–OCH$_2$), 3.44 (q, 1H, CH$_3$C$\underline{H}$(COO–)$_2$), 1.3–1.9 (m, 35H, –CH$_2$– and C$\underline{H}_3$CH(COO–)$_2$).

2.2.4. *Bis-{10-[4-(4-butoxyphenyliminomethynyl)-phenoxy] decyl}methylmalonate, M-10-CH$_3$*

Yield, 91%; IR (KBr, cm^{-1}): 2933 and 2850 (aliphatic C–H stretch), 1733 (ester C=O stretch), 1608 and 1510 (C=C and C=N stretch), 1249 and 1018 (C–O stretch). ^{1}H NMR (CDCl$_3$, δ ppm): 8.39 (s, 2H, –CH=N–), 4.12 (t, 4H, –COOCH$_2$–), 3.95–4.05 (m, 8H, Ar–OCH$_2$–), 3.45 (q, 1H, CH$_3$C$\underline{H}$(COO–)$_2$), 0.98–1.85 (m, 49H, C$\underline{H}_3$CH(COO–)$_2$, and –CH$_3$). Elemental analysis: calcd. for $C_{58}H_{80}N_2O_8$, C 74.68, H 8.58, N 3.00; found, C 74.87, H 8.77, N 3.20%.

2.2.5. *Di-[10-(4-formylphenoxy)decyl]ethylmalonate (X = C$_2$H$_5$ and n = 10)*

Yield, 77%; IR (neat, cm^{-1}): 2927 and 2854 (aliphatic C–H stretch), 1732 (ester C=O stretch), 1689 (aldehyde C=O stretch), 1600 and 1508 (aromatic C=C stretch), 1259 and 1018 (C–O stretch). ^{1}H NMR (CDCl$_3$, δ ppm): 9.87 (s, 2H, –CHO), 7.82 (d, 4H, Ar–H), 6.98 (d, 4H, Ar–H), 4.12 (t, 4H, –COOCH$_2$–), 4.03 (t, 4H, Ar–OCH$_2$–), 3.26 (t, 1H, CH$_3$CH$_2$C$\underline{H}$(COO–)$_2$), 0.96–1.9 (m, 37H, –CH$_2$– and –CH$_3$).

2.2.6. *Bis-{10-[4-(4-butoxyphenyliminomethynyl)-phenoxy] decyl} ethylmalonate, M-10-C$_2$H$_5$*

Yield, 90%; IR (KBr, cm^{-1}): 2935 and 2850 (aliphatic C–H stretch), 1733 (ester C=O stretch), 1608 and 1512 (aromatic C=C and C=N stretch), 1251 and 1020 (C–O stretch). ^{1}H NMR (CDCl$_3$, δ ppm): 8.39 (s, 2H, –CH=N–), 6.89–7.82 (m, 16H, Ar–H), 4.12 (t, 4H, –COOCH$_2$–), 3.95–4.0 (m, 8H, Ar–OCH$_2$–), 3.25 (t, 1H, CH$_3$CH$_2$C$\underline{H}$(COO–)$_2$), 0.95–1.9 (m, 51H, –CH$_2$– and –CH$_3$). Elemental analysis: calcd. for $C_{59}H_{82}O_8N_2$, C 74.84, H 8.69, N 2.96; found, C 74.72, H 8.74, N 3.08%.

2.2.7. *Di-[10-(4-formylphenoxy)decyl]phenylmalonate (X = Ph and n = 10)*

Yield, 50%; IR (neat, cm^{-1}): 2927 and 2854 (aliphatic C—H stretch), 1733 (ester C=O stretch), 1693 (aldehyde C=O stretch), 1600 and 1508 (aromatic C=C stretch), 1255 and 1020 (C—O stretch). ^{1}H NMR ($CDCl_3$, δ ppm): 9.87 (s, 2H, —CHO), 6.97–7.83 (m, 13H, Ar—H), 4.0–4.1 (m, 8H, —$COOCH_2$— and Ar—OCH_2—), 3.60 (s, 1H, PhCH$(COO—)_2$), 1.28–1.9 (m, 32H, —CH_2—).

2.2.8. *Bis-{10-[4-(4-butoxyphenyliminomethynyl)-phenoxy] decyl} phenylmalonate, M-10-Ph*

Yield, 85%; IR (KBr, cm^{-1}): 2918 and 2850 (aliphatic C—H stretch), 1745 (ester C=O stretch), 1610 and 1512 (aromatic C=C and C=N stretch), 1247 and 1018 (C—O stretch). ^{1}H NMR ($CDCl_3$, δ ppm): 8.39 (s, 2H, —CH=N—), 6.8–7.8 (m, 21H, Ar—H), 3.9–4.1 (m, 12H, —$COOCH_2$— and Ar—OCH_2—), 3.61 (s, 1H, PhCH$(COO—)_2$), 0.96–1.9 (m, 46H, —CH_2— and —CH_3). Elemental analysis: calcd. for $C_{63}H_{82}N_2O_8$, C 76.06, H 8.25, N 2.82; found, C 76.32, H 8.46, N 2.80%.

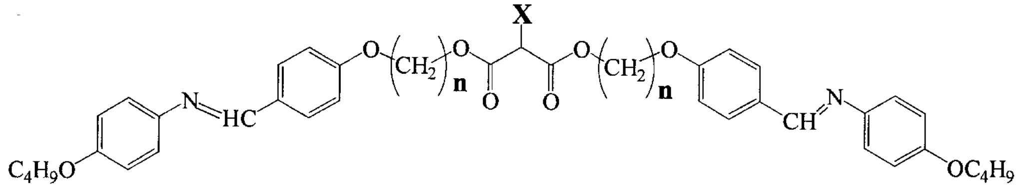
3. Results and discussion

3.1. *Phase behaviour*

The table 1 gives the transition temperatures together with the associated transition enthalpies for the M-n-X series. All eight compounds synthesized in the series were found to be liquid crystalline. They exhibited nematic and smectic phases. The natures of these mesophases were studied by both polarizing optical microscopy (POM) and X-ray diffraction (XRD).

As can be seen from the table, we have performed two different structural variations: (i) the spacer length, n, and (ii) the substituent group X in the centre of the molecule. When the spacer n is fixed at 4 and $X = $H (M-4-H), the compound exhibits two types of mesophase, i.e. an enantiotropic nematic phase and a monotropic smectic A phase. On changing X to CH_3 and C_2H_5 (M-4-CH_3 and M-4-C_2H_5), we again observed two types of mesophase, smectic A and crystal B phases, enantiotropically. The nematic phase is completely destabilized in these two compounds. However, when X is substituted with the Ph group (M-4-Ph), we again

Table 1. Transition temperatures (°C) and enthalpies of transition (kJ mol^{-1}) (in italics) for, M-n-X series. Parentheses indicate monotropic transitions; the numbes in italics represent the enthalpy changes.



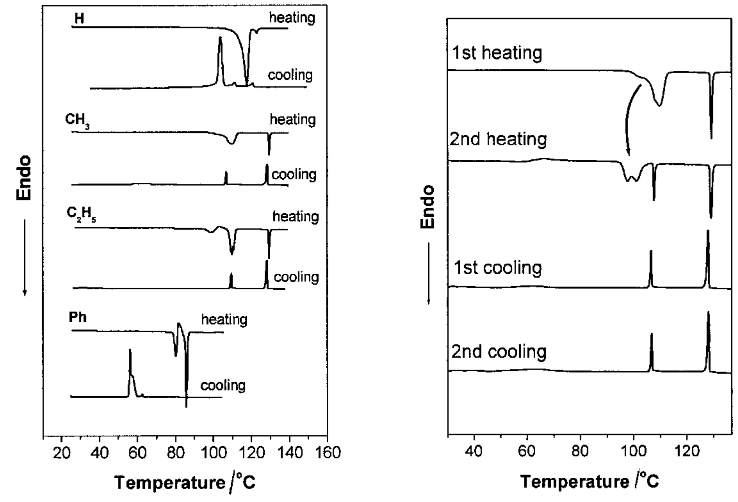
n	X	Cr		CrB		SmA		N		I
4	H	•	117.7 *52.7*	—		(•)	(111.2) *1.50*	•	122.9 *1.2*	•
4	CH_3	•	101.1 *25.1*	•	107.6 *4.9*	•	129.2 *10.9*	—		•
4	C_2H_5	•	109.3 *40.4*[a]	•	110.0	•	129.0 *13.9*	—		•
4	Ph	•	85.6 *76.5*	—	—	—		(•)	(62.5) *1.4*	•

n	X	Cr		CrE		CrB		SmA		I
10	H	•	105.8 *49.6*	(•)	(103.7) 9.2	—		•	121.2 *15.4*	•
10	CH_3	•	119.5 *101.6*[b]	—		(•)	(105.0) 9.5	•	121.5	•
10	C_2H_5	•	126.0 *106.9*	—		—		(•)	(118.0) *15.9*	•
10	Ph	•	*80.3* *117.0*	—		—		(•)	(68.5)[c]	•

[a] Combined enthalpy change for the transitions Cr →CrB and CrB →SmA, since the peaks in DSC could not be resolved.

[b] Combined enthalpy change for the transitions Cr →SmA and SmA →I, since the peaks in DSC could not be resolved.

[c] Enthalpy could not be measured due to the onset of crystallization.



(*a*) (*b*)

Figure 2. DSC thermograms for (*a*) M-n-X compounds with $n=4$, $X=$ H, CH_3, C_2H_5 and Ph and (*b*) M-4-CH_3.

observe the nematic phase which is now monotropic in nature.

The DSC thermograms for the M-4-X series are shown in figure 2(*a*). We observed cold crystallization for the compounds M-4-CH_3 and M-4-C_2H_5. The DSC trace of M-4-CH_3, figure 2(*b*), for the first heating of the ethanol recrystallized sample, reveals a rather broad multiple melting endotherm before a sharp peak at a higher temperature. It shows however, three endothermic peaks on the second heating DSC thermogram. Therefore, it is concluded that the broad multiple endotherm observed in the first heating is a combination of the crystal to crystal B and crystal B to smectic A transition peaks. The peak at 129.2°C corresponds to isotropization.

When the spacer length n was fixed at 10 and $X=$ H, M-10-H, smectic A and crystal E mesophases were observed. The smectic A phase is enantiotropic, whereas the crystal E phase is monotropic in nature. On substituting X with CH_3, C_2H_5 and Ph, the nature of the mesophases exhibited by these compounds did not change significantly compared with those shown by the parent compound with $X=$ H. All of them exhibit the smectic A phase. In addition, M-10-CH_3 exhibits a monotropic crystal B phase. The smectic A phase becomes metastable as the bulk of the substituent X increases, and for M-10-C_2H_5 and M-10-Ph the smectic A phase becomes monotropic. It is very possible that the bulky substituents, for example C_2H_5 and Ph, cause a change in the conformational distribution of the molecules in the melt and hence their effective molecular shape. This will definitely influence their ability to form mesophases. We tried to obtain information on the most probable conformations of the compounds using CS Chem3D Pro (CambridgeSoft Co. USA). Their minimum energy molecular shapes for M-4-X compounds are compared in figure 3, which shows that all are bent and also that the dihedral bend angle between the two arms remains about the same even when the size of the central substituent X increases. Therefore, the larger size of the central substituent appears to be the reason for the reduced ability of M-10-C_2H_5 and M-10-Ph to form mesophases, because they will increase the breadth of the molecule.

Under POM characteristic schlieren textures for the nematic mesophase were seen. For the smectic A phase we observed the focal-conic fan shaped texture which is shown in figure 4. We were also able to observe the homeotropic texture for the smectic A phase. As a characteristic feature of the smectic A to crystal B phase transition, the appearance of concentric arcs on the focal conics was seen during the transition period only [18]. The crystal E mesophase is characterized by the permanent presence of concentric arcs on the focal-conic fan shaped texture [19] even after the phase transition.

Figure 5 shows the X-ray diffractograms obtained at various temperatures for M-10-H. At 95°C, it shows sharp reflections, one each in the small angle and wide angle regions, which suggests that it forms a highly

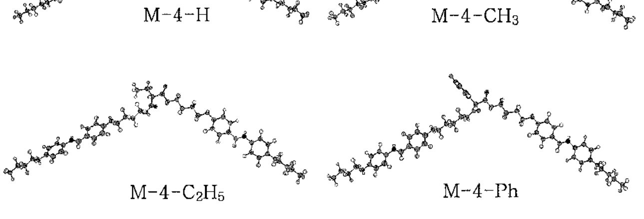


Figure 3. Molecular conformations of M-4-X compounds.

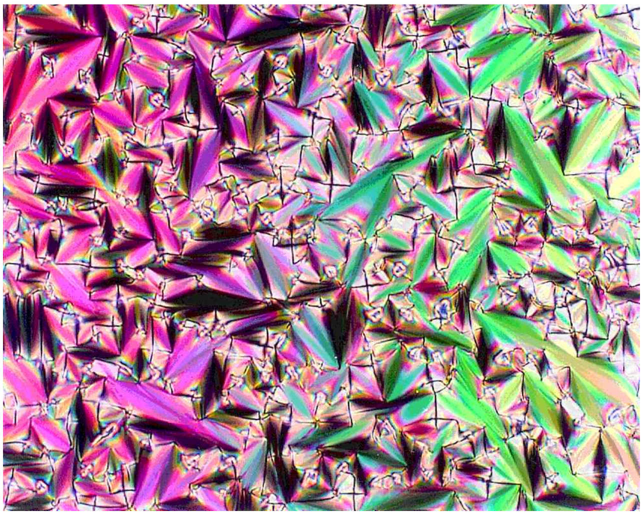


Figure 4. Optical microscopic texture showing the focal-conic fan shaped pattern for the smectic A phase of 17-10-C_2H_5 at 116.5°C (magnification 200 ×).

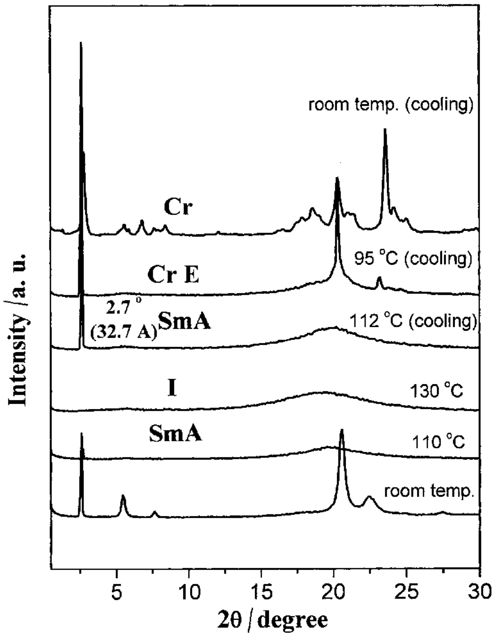


Figure 5. X-ray diffractograms for M-10-H at different temperatures.

ordered smectic phase (CrE). At 112°C, it shows a sharp reflection only in the small angle region (*c.* $2\theta = 2.7°$; $d = 32.7$ Å) and a very broad one in the wide angle region (*c.* $2\theta = 15$–$22°$; $d = 5.9$–4.4 Å), which suggests that it forms a fluid smectic phase (SmA). In addition, a very small, most probably a second order diffraction peak, is seen in all the diffractograms of this compound in the liquid crystalline phase. The smectic periodicity d estimated from the small angle peaks is 32.7 Å. This value is significantly smaller than the estimated end-to-end length of the molecule ($l = 66$ Å) assuming the all-*trans* conformation and the d/l value is approximately 0.50. This suggests that the smectic A phase exhibited by this compound may be of the intercalated type. Although non-symmetric dimers often form intercalated smectic phases, few symmetric dimers are known to form intercalated phases. Date *et al.* studied the LC properties of a series of symmetric dimers consisting of aromatic Schiff's base mesogens [8]. They suggested an empirical rule that, if the total length of the two terminal groups is equal to or less than the length of the central spacer, the dimeric compound could form an intercalated smectic phase. They did not in fact observe such behaviour although the view is in accord with our present observation. Figure 6 shows the X-ray diffractograms obtained in the liquid crystalline phases of the compound M-4-CH_3. In the high temperature mesophase at 120°C on cooling, it also shows a sharp diffraction in the small angle region (*c.* $2\theta = 3.35°$; $d = 26.4$ Å). This pattern is almost same as that of the high temperature phase of the compound M-10-H, indicating that the smectic A phase may be intercalated in nature.

The general observation made earlier for symmetric dimers is that increasing the length of the alkyl spacer decreases the tendency towards smectic phase formation and favours nematic phase formation [1]. Also, to observe smectic phases in such dimers, the terminal chains should be at least half the length of the spacer

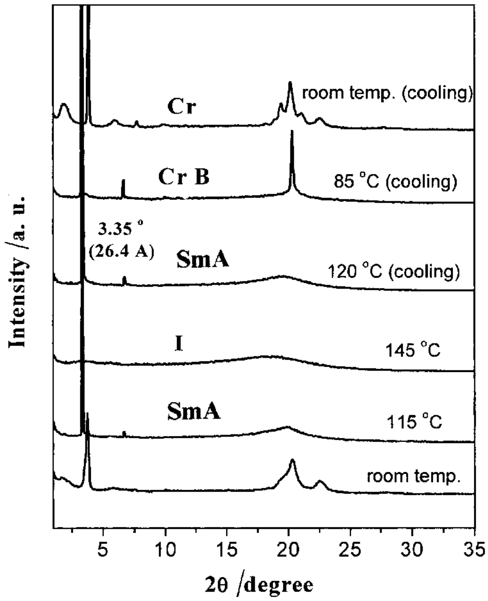


Figure 6. X-ray diffractograms for M-4-CH_3 at different temperatures.

chain length. In contrast, in the present series of compounds we observe that increasing the length of the alkyl spacer did not affect the tendency towards smectic phase formation, whereas the nematic phase has been completely destabilized. As mentioned already, part of the interest in dimers arises from their ability to act as model compounds for semiflexible main chain liquid crystal polymers. Indeed, it has been found that increasing the length of the alkyl spacer in a semiflexible polymer increases the tendency towards smectic phase formation [1].

3.2. ^{13}C *NMR studies of M-10-H and M-10-CH*$_3$

Using ^{13}C NMR we tried to compare the molecular motions of M-10-H and M-10-CH$_3$ in the smectic A and the low temperature crystalline smectic phases. The ^{13}C NMR spectra of M-10-H and M-10-CH$_3$ in the smectic phase are shown in figures 6 and 7, respectively. The spectrum can be divided into four groups of peaks: (1) $-CH_3$ and $-CH_2-$ (10–30 ppm), (2) $-OCH_2-$ (50–70 ppm), (3) tertiary aromatic (130–170 ppm) and (4) quarternary aromatic, the Schiff's base and carbonyl carbons (> 190 ppm).

As shown in figures 7 and 8, in the low temperature crystalline phases of M-10-H and M-10-CH$_3$, we only observe broad NMR lines with poor resolution. The only meaningfully resolved sites are the four tertiary aromatic carbons for M-10-H. Thus, taken together with the X-ray results, the NMR peaks showing dipolar broadening indicate a solid-like LC phase. In addition, for M-10-CH$_3$, this low temperature phase signal shows no fine structure associated with a magnetically aligned mesophase. Thus M-10-CH$_3$ appears to experience more barriers to molecular motion in the crystalline smectic phase than does M-10-H. This is rather in contrast to the earlier report that molecules in the crystalline B

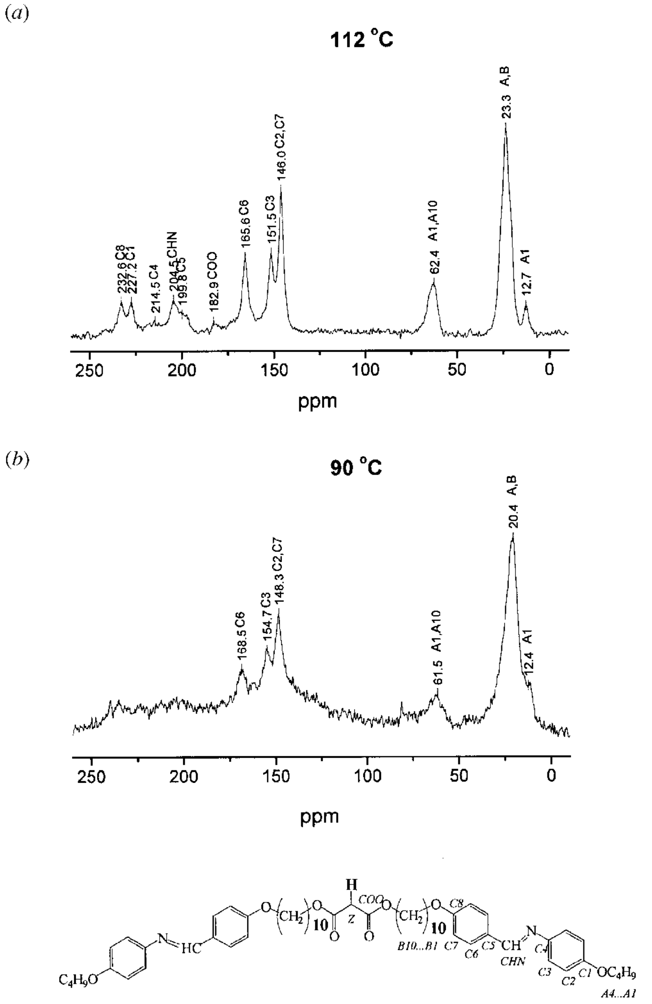


Figure 7. ^{13}C NMR spectra of M-10-H: (*a*) in the smectic A phase at 112°C, (*b*) in the crystal E phase at 90°C.

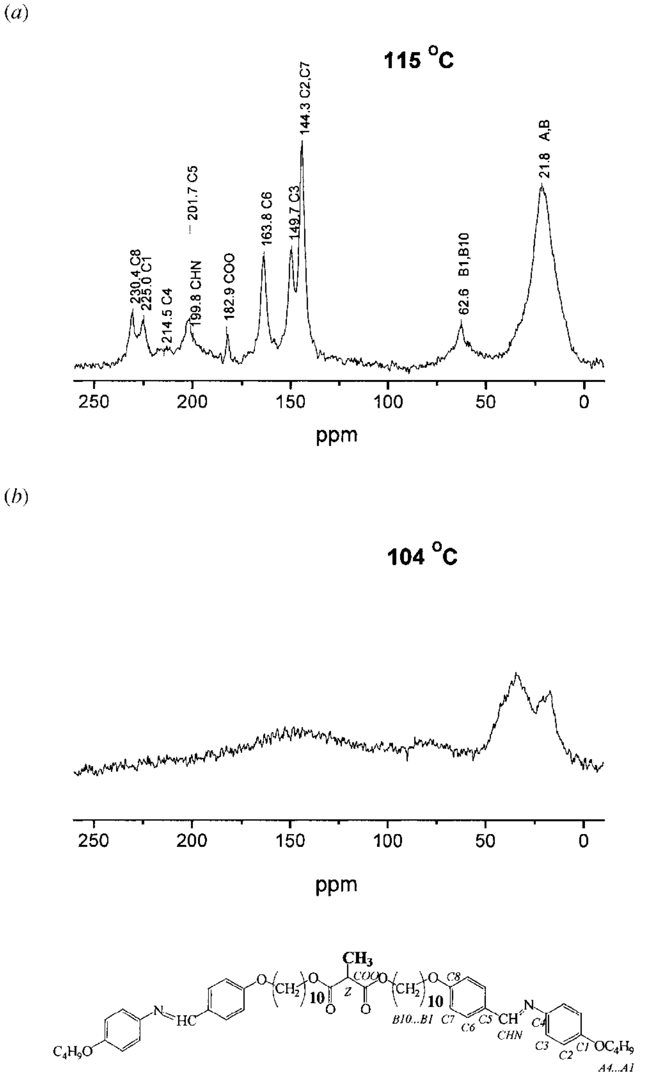


Figure 8. ^{13}C NMR spectra of M-10-CH$_3$: (*a*) in the smectic A phase at 115°C, (*b*) in the crystal B phase at 104°C.

phase are more motional than in the crystalline E phase [20]. It appears very probable that the presence of the methyl group in the centre of M-10-CH_3 exerts a steric hindrance to molecular motions. The NMR peaks obtained for the compounds in the smectic A phase are much sharper, implying faster molecular motion.

4. Conclusions

We have synthesized a series of dimeric compounds which have all been found to be liquid crystalline. They mainly exhibit nematic and smectic phases. From microscopic textural observations combined with the XRD results we have identified these smectic phases as smectic A, crystal B and crystal E types. The smectic A phase has an intercalated structure. Increasing the alkylene spacer favoured only smectic phase formation and destabilized the nematic phase completely. This result is in contrast to the general observation made for other symmetric dimers that an increase in length of the alkylene spacer decreases the tendency towards smectic phase formation and favours nematic phase formation. The solid state NMR studies verify the formation of crystalline LC phases by M-10-H and M-10-CH_3 at lower temperatures.

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