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Liquid crystalline dimeric compounds with an alkylene spacer

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Two series of compounds with dimeric molecules have been synthesized and characterized. These molecules consist of two non-mesogenic units linked by an alkylene spacer through an ester linkage. The effects of varying the terminal as well as the spacer chain length on the mesomorphic properties have been studied. For compounds with an even number of carbon atoms in the spacer chains, the observed textures in the mesophases are reminiscent of those seen for the smectic phases of banana-shaped molecules.

1. Introduction

After the discovery of dimeric liquid crystals [1] over 70 years ago, the next report on such materials [2] generated considerable interest in this class of liquid crystals. These are known to be excellent model compounds for thermotropic main chain polymers consisting of similar monomeric units and spacers [3, 4]. Many series of dimeric liquid crystals have been reported [5–7] wherein identical semi-rigid monomeric units are linked through a flexible alkyl spacer.

A very recent discovery [8] of dimeric compounds with a flexible alkylene spacer between two mesogenic units, giving rise to banana-shaped mesogens forming phases possessing antiferroelectric switching behaviour, is particularly interesting. In the early days of this new field of banana-shaped liquid crystals, it was believed that a central rigid aromatic part in the molecule is essential to obtain such types of mesophase. Most of the examples of banana-shaped mesogens reported so far [9–15] indeed do consist of a central rigid aromatic core. As is known in the field, even a small change in molecular structure can lead to drastic changes in the mesomorphic properties. Therefore we planned to make a small change in the molecular structure of the parent compounds reported by Choi *et al.* [8]. Towards this end, we synthesized several dimeric compounds with an alkylene spacer, and in this paper we report the synthesis and electro-optical switching behaviour of these compounds. In an earlier communication we reported the switching behaviour as well as the X-ray studies on one of the representative compounds from this family [16]. Interestingly, we have now made observations on the electro-optical switching properties for the compounds with alkylene spacers of both odd and even parity. The molecular structures of the different dimeric compounds synthesised are shown in figure 1. In all these molecules, we note that (i) the two identical monomeric units (alkylated phenols A and B, which are non-mesomorphic) have been linked to an alkylene spacer through an ester linkage, and (ii) the carbonyl group of the ester linkage is directly attached to the spacer. It may be mentioned that the latter feature is at variance with the banana-shaped compounds reported by Choi *et al.* [8].

2. Experimental

2.1. *General information*

Chemicals and solvents (analytical quality) were obtained locally and used as such without further purification. All the intermediate compounds and final products were purified either by column chromatography on silica gel, or repeated recrystallization using suitable solvents. Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). The chemical structures of all the intermediates and final compounds were confirmed by spectral data.

^{1}H NMR spectra were recorded using $CDCl_3$ as solvent on a 200 MHz Bruker Aveance Series DPX-200 NMR spectrometer, with Me_4Si as an internal standard. Mass spectra were recorded on a JEOL JMS-600H spectrometer. The transition temperatures were determined using a Mettler FP82HT hot stage and central processor in conjunction with a Leitz DMRXP polarizing microscope. The enthalpies of transitions were determined from thermograms recorded on a differential scanning calorimeter (DSC 7 Perkin-Elmer). The heating and cooling rate was 10° $\min^{-1}$. X-ray measurements were carried out using a MAC Science image plate set up.

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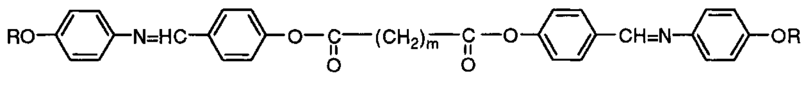
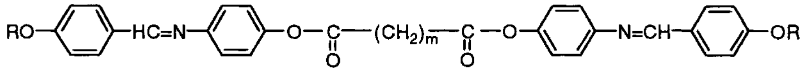


m = 4, 5 and 8
R = C_nH_{2n+1}
n = 10, 12 and 16

Series 1



m = 4 and 8
R = C_nH_{2n+1}
n = 10, 12 and 16

Series 2

Figure 1. Molecular structures of the two series of dimeric compounds.

2.2. *Synthesis*

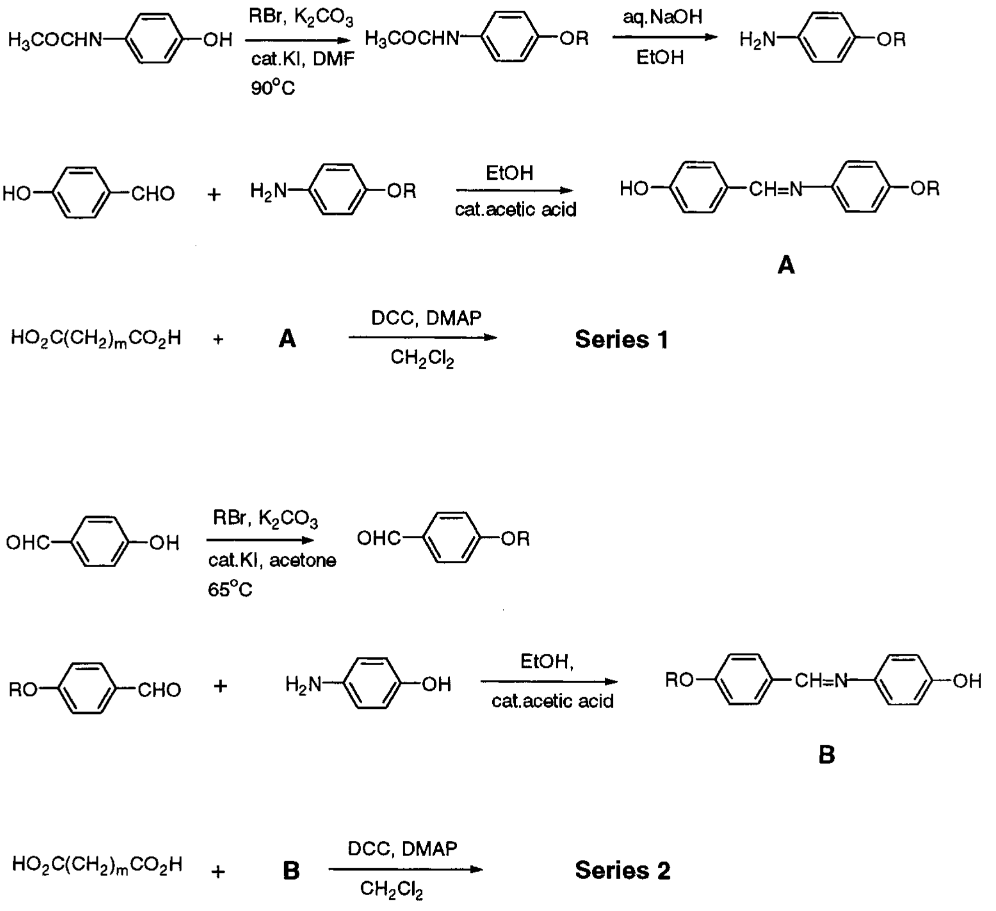
The two series of compounds, 1 and 2, were synthesized following the routes shown in the scheme. Thus, 4-hydroxyacetanilide was *O*-alkylated with the appropriate *n*-alkyl bromides. The *O*-alkylated products on hydrolysis gave the corresponding anilines. The monomers A, were obtained by condensing 4-hydroxybenzaldehyde with the appropriate *O*-alkylated anilines. The compounds of series 1 were obtained by esterification of appropriate diacids with the monomeric phenols A, following a procedure described by Hassner and Alexanian [17]. The compounds of series 2, were obtained by starting with the *O*-alkylation of 4-hydroxybenzaldehyde with appropriate *n*-alkyl bromides. The *O*-alkylated products were condensed with 4-aminophenol to obtain the monomers B. These monomeric phenols B, were used in the esterification of the appropriate diacids, to obtain the compounds of series 2. The detailed synthetic procedure as well as the analytical data for one of the homologues of series 1 and 2 are given below.

2.2.1. *4-(4-n-Decyloxyphenyliminomethyl)phenol (A)*

4-Hydroxybenzaldehyde (1.22 g, 0.01 mol) and 4-*n*-decyloxyaniline (2.49 g, 0.01 mol) were taken up in ethanol (50 ml) containing a few drops of acetic acid. The mixture was boiled under a nitrogen atmosphere for 6 h. After cooling the reaction mixture, the solid which separated out was filtered off and recrystallized from ethanol. Yield 64%, m.p. 162°C. ^{1}H NMR ($CDCl_3$) δ: 8.39 (s, 1H, –CH=N–), 7.78 (d, J = 8.6 Hz, 2H, Ar–H), 7.19 (d, J = 8.6 Hz, 2H, –ArH), 6.91 (d, J = 8.6 Hz, 2H, Ar–H), 6.90 (d, J = 8.6 Hz, 2H, Ar–H), 5.44 (brS, 1H, –OH), 3.96 (t, J = 6.4 Hz, 2H, –OCH_2–), 1.79 (m, 2H, –OCH_2CH_2–), 1.3 (m, 14H, –CH_2–), 0.88 (m, 3H, –CH_3). Mass (FAB): m/z 353 $[M]^+$ [calcd. for $C_{23}H_{31}NO_2$].

2.2.2. *1,6-Bis[4-(4-n-decyloxyphenyliminomethyl)-phenyl] adipate (Series 1)*

Adipic acid (0.147 g, 0.001 mol) and 4-(4-*n*-decyloxyphenyliminomethyl)phenol (0.706 g, 0.002 mol) were dissolved in dichloromethane (100 ml). Dicyclohexylcarbodiimide (0.453 g, 0.0022 mol) and a catalytic amount of 4-dimethylaminopyridine were added and the mixture was stirred at room temperature for 24 h under nitrogen. The dicyclohexylurea formed was filtered off. The filtrate was washed with distilled water (100 ml × 3) and dried (Na_2SO_4). The crude product obtained on evaporation of the solvent was purified by flash chromatography on neutral aluminium oxide. Finally the product was recrystallized repeatedly from CH_2Cl_2/ethanol; yield 57%. ^{1}H NMR ($CDCl_3$) δ: 8.46 (s, 2H, –CH=N–), 7.91 (d, J = 8.6 Hz, 4H, Ar–H), 7.23 (d, J = 3.5 Hz, 4H, Ar–H), 7.19 (d, J = 3.5 Hz, 4H, Ar–H), 6.92 (d, J = 8.6 Hz, 4H, Ar–H), 3.97 (t, J = 6.5 Hz, 4H, –OCH_2–), 2.67 (m, 4H, –$OCOCH_2$–), 1.91 (m, 4H, –OCH_2CH_2–), 1.77 (m, 4H, –$OCOCH_2CH_2$–), 1.27 (m, 28H, –CH_2–), 0.88 (m, 6H, –CH_3). Mass (FAB): m/z 817.2 $[M]^+$ [calcd. for $C_{52}H_{68}O_6N_2$].



Scheme.

2.2.3. *4-(4-n-Decyloxybenzylideneamino)phenol (B)*

4-*n*-Decyloxybenzaldehyde (2.62 g, 0.01 mol) and 4-aminophenyl (1.09 g, 0.01 mol) in ethanol (50 ml) containing a few drops of acetic acid were heated at reflux under nitrogen for 6 h. After cooling the mixture, the solid which separated out was filtered off and recrystallized from ethanol. Yield 61%, m.p. 102.0°C. ^{1}H NMR ($CDCl_3$) δ: 8.38 (s, 1H, –CH=N–), 7.80 (d, $J = 8.8$ Hz, 2H, Ar–H), 7.15 (d, $J = 8.8$ Hz, 2H, Ar–H), 6.96 (d, $J = 8.8$ Hz, 2H, Ar–H), 6.84 (d, $J = 8.8$ Hz, 2H, Ar–H), 4.0 (t, $J = 6.4$ Hz, 2H, $-OCH_2-$), 1.8 (m, 2H, $-OCH_2CH_2-$), 1.3 (m, 14H, $-CH_2-$), 0.88 (m, 3H, $-CH_3$). Mass (FAB): *m/z* 354.3 $[MH]^+$ [calcd. for $C_{23}H_{31}NO_2$].

2.2.4. *1,6-Bis[4-(4-n-decyloxybenzylideneamino)phenyl] adipate (Series 2)*

The procedure followed was similar to that for the compounds of series 1 described above; yield 54%. ^{1}H NMR ($CDCl_3$) δ: 8.36 (s, 2H, –CH=N–), 7.82 (d, $J = 8.8$ Hz, 4H, Ar–H), 7.20 (d, $J = 8.8$ Hz, 4H, Ar–H), 7.1 (d, $J = 8.8$ Hz, 4H, Ar–H), 6.97 (d, $J = 8.8$ Hz, 4H, Ar–H), 4.02 (t, $J = 6.6$ Hz, 4H, $-OCH_2-$), 2.66 (m, 4H, $-OCOCH_2-$), 1.9 (m, 4H, $-OCH_2CH_2-$), 1.77 (m, 4H, $-OCOCH_2CH_2-$), 1.27 (m, 28H, $-CH_2-$), 0.88 (m, 6H, $-CH_3$). Mass (FAB): *m/z* 817.2 $[M]^+$ [calcd. for $C_{52}H_{68}O_6N_2$].

3. Results and discussion

The transition temperatures together with the associated transition enthalpies for the compounds of series 1 and 2 are given in tables 1 and 2, respectively. All the compounds in both series were found to be liquid crystalline. The mesophases were characterized by optical polarizing microscopy, as well as by optical observation of switching. Owing to the high ionic conductivity of the samples, we were unable to carry out electrical switching studies involving measurement of current, because the ionic contribution to the current swamps the true switching characteristics.

We have recently reported [16] optical, electro-optical and X-ray measurements on one of the compounds mentioned in table 1, viz. the compound with $m = 4$ and $n = 10$; we now briefly recall these results. This compound shows two mesophases: while the high temperature mesophase is a tilted smectic phase (X_1) exhibiting

Table 1. Transition temperatures (°C) and enthalpies of the transitions (kJ mol^{-1}) for the compounds of series 1.

m	n	Cr		X_2		X_1				I
4	10	•	149.0 (32.64)	•	177.4 (10.98)	•	225.3 (22.99)			•
4	12	•	144.8 (35.80)	•	173.0 (10.17)	•	222.0 (23.28)			•
4	16	•	140.2 (52.59)	•	162.7 (11.0)	•	212.4 (27.15)			•
				E		SmC				
5	10	•	165.0 (61.0)	—		•	182.5 (16.97)			•
5	12	•	155.5 (11.98)	•	162.7 (52.41)	•	182.3 (18.45)			•
5	16	•	149.5 (20.42)	•	156.2 (51.66)	•	178.5 (20.19)			•
				X_2		X_1		SmA		
8	10	•	139.0 (36.93)	•	173.0 (15.31)	•	176.2 (0.28)	•	181.5 (23.84)	•
8	12	•	135.5 (43.49)	•	170.0 (15.05)	•	181.0 (27.12)	—		•
8	16	•	132.8 (58.77)	•	162.8 (14.60)	•	177.3 (30.55)	—		•

Table 2. Transition temperatures (°C) and enthalpies of the transitions (kJ mol^{-1}) for the compounds of series 2.

m	n	Cr		X_2		X_1		I
4	10	•	134.0 (36.20)	•	173.5 (8.76)	•	210.5 (25.68)	•
4	12	•	133.3 (44.70)	•	169.7 (9.24)	•	209.5 (27.5)	•
4	16	•	130.3 (59.45)	•	158.0 (8.41)	•	203.0 (28.55)	•
8	10	•	124.5 (40.92)	•	170.1[a]	•	171.0 (40.52)	•
8	12	•	124.0 (45.98)	•	168.3 (10.99)	•	172.7 (28.7)	•
8	16	•	123.8 (66.04)	•	158.7 (10.93)	•	170.0 (32.62)	•

[a] This transition is observed only by microscopy.

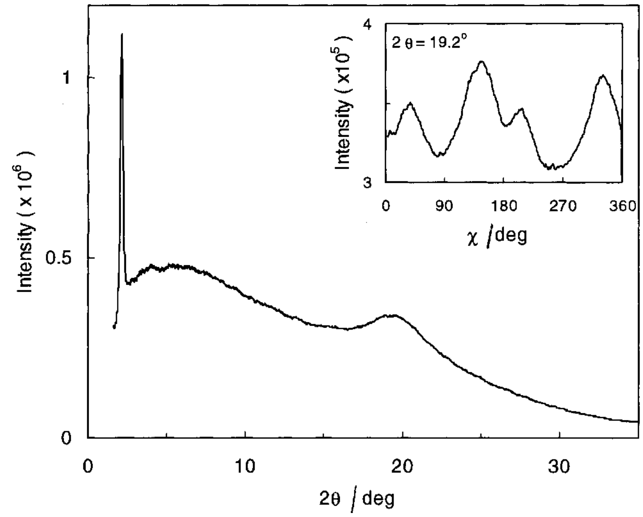


Figure 2. Intensity vs. 2θ plot in the X_1 phase at 180°C, for the compound with $m = 4$ and $n = 10$ of series 1. The inset shows the intensity profile as a function of χ with 2θ fixed at the peak value (= 19.2°) of the diffuse wide angle peak.

ferroelectric switching characteristics, the low temperature phase (X_2) is a more ordered phase with textural features similar to that of the B_3 banana phase. The X-ray measurements in the high temperature phase showed (figure 2) a sharp low angle Bragg reflection and a diffuse wide angle ring. In fact, the profile obtained (see the inset in figure 2) by plotting the intensity versus χ angle, taken by keeping 2θ fixed at 19.2°, showed four peaks. The tilt of the molecule calculated from the angular separation between two peaks was found to be about 36°. On applying an electric field it was found that optically, the equilibrium states for the opposite signs of the field appear identical, with only a transient change. Such a feature has also been observed by Choi *et al.* [8] for the electro-optical switching in a banana-shaped compound.

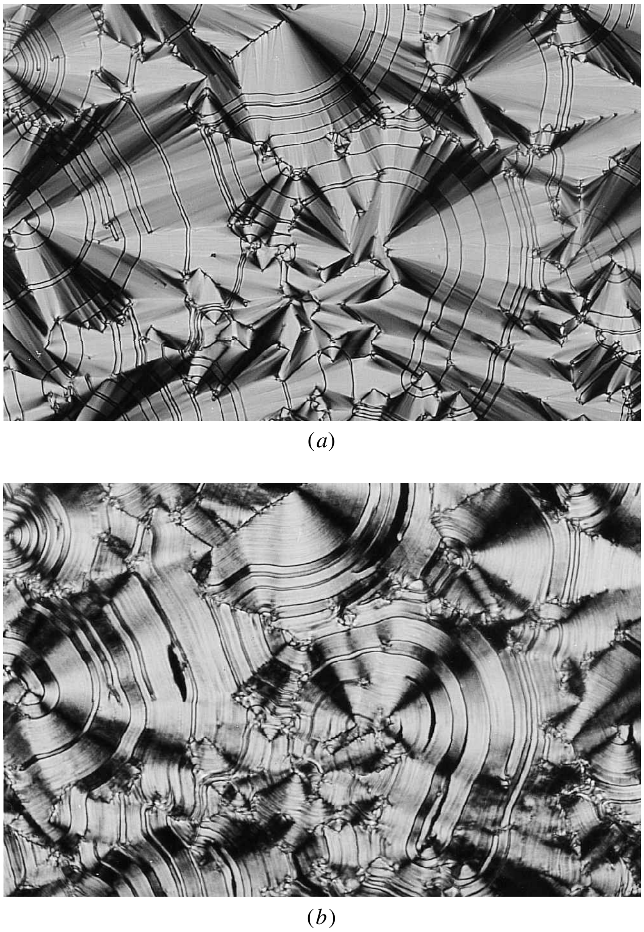
In the present studies we find that when the spacer length m is kept fixed at 4 and the value of the terminal chain length n is varied, i.e. $n = 10$, 12 and 16, the compounds (series 1) exhibit two mesophases. The textures in the two mesophases are quite similar to those seen for the compound $m = 4$, $n = 10$, discussed above. While the higher temperature X_1 phase is electro-optically switchable, the low temperature X_2 phase did not show any switching. In contrast, when the spacer has an odd parity with $m = 5$, the compounds with $n = 10$, 12 and 16 exhibit classical smectic phases. We observed both the broken focal-conic and schlieren textures for the smectic C phase; the observed schlieren texture had only four brush patterns. Based on the microscopic textural observations, these phases have been identified as smectic C and crystal E.

To check the influence of the length of the even spacer on the mesomorphic properties, we synthesized three more compounds with $m = 8$ and $n = 10$, 12 and 16. The compounds with $n = 12$ and 16 show two mesophases and the $n = 10$ material has three mesophases. From microscopic textural observations combined with electro-optical switching studies, we infer that the two mesophases of the $n = 12$ and 16 compounds and the lower temperature mesophases of the $n = 10$ compound are similar to the X_1 and X_2 phases of the series with $m = 4$. The high temperature mesophase of the compound with $n = 10$ is a smectic A phase, and the phase sequence here is Cr–X_2–X_1–SmA–I with increasing temperature.

From table 1, it is seen that the mesophase range of X_1 increases marginally with increasing n, but decreases considerably as m increases. In contrast, the mesophase range of X_2 decreases only slightly with increasing n, but increases appreciably as the value of m increases. The isotropic temperature falls a little as we increase the value of n, but shows a drastic decrease when m is changed from 4 to 5; further increase of m to 8 has hardly any effect. These features are in agreement with the general tendency observed for dimeric compounds, i.e. an increase in the length of the terminal alkyl/alkyloxy chain results in a slow monotonic decrease in the isotropization temperature, while an increase in the length of the spacer chain leads to a strong odd–even effect [18].

Table 2 shows thermal data for the compounds of series 2. Here, we have simply reversed the direction of the imino linkage with respect to the compounds of series 1. When compared with similar compounds of series 1, it is seen that the series 2 compounds show only two mesophases X_1 and X_2, but no smectic A phase. It can be seen from table 2 that, by reversing the imino linkage with respect to the isomeric compounds of series 1, the temperatures are lower for the compounds of series 2. From tables 1 and 2 we see that the X_1 phase is stabilized when the spacer chain is shorter and the X_2 phase is stabilized if the spacer chain is longer.

Figure 3 shows photomicrographs obtained for the two mesophases of the representative compound of series 2 with $m = 8$ and $n = 12$. For all the compounds studied, it was difficult to get good textures. Hence the sample was cooled in the presence of an electric field (a typical field is of the order of $\sim 9\ \mathrm{V\ \mu m^{-1}}$, 20 Hz, square wave) to yield a broad focal-conic texture. The sample was sandwiched between two ITO coated glass plates pretreated with polyimide solution, and unidirectionally rubbed for homogeneous alignment of the liquid crystalline molecules. A photomicrograph taken in the high temperature mesophase X_1 (170°C), exhibiting a broken focal-conic texture is shown in figure 3(*a*). There was no fringe pattern, but a few strands were seen on the focal-conics. Figure 3(*b*) shows the photomicrograph of the X_2 phase taken at 162°C with a strong, banded, fringe pattern superimposed on the focal-conics. These features are more reminiscent of the phases of banana-shaped molecules than classical smectic phases.


(*a*)

(*b*)

Figure 3. Photographs taken in the (*a*) X_1 (170°C) and (*b*) X_2 (162°C) phases of the compound with $m = 8$ and $n = 12$ of series 2.

Figure 4 shows a plot of the electro-optic switching obtained for the same compound, viz. $m = 8$ and $n = 12$ of series 2 at a temperature of 169°C. The sample was contained in a thin cell (~4 μm thick) made of ITO coated glass plates, treated with a polyimide solution. The sample was slowly cooled (~0.1°C min^{-1}) from the isotropic phase in the presence of an electric field (9 V $\mu\mathrm{m}^{-1}$, 20 Hz, triangular wave) to obtain broad focal-conic groups. Then the sample was rotated by 22.5° from the position of minimum transmitted intensity in the absence of the electric field. The electro-optic profile is very similar to those obtained for materials exhibiting an antiferroelectric type of switching [19, 20]. Similar switching behaviour was seen for all the compounds of table 2.

We have discussed above the mesomorphic properties of two series of dimeric compounds with even as well as odd numbers of carbon atoms in the spacer chain. We have found that the compounds with an even number of carbon atoms in the spacer chain exhibit mesophases which have characteristics like those of banana-shaped compounds. In contrast the compounds with an odd number of carbon atoms in the spacer chain show classical smectic phases. As for other liquid crystalline compounds, the length of the end chain affects the type and the transition temperatures of the mesophases observed. However, a more important role is played by the parity of the central alkylene spacer. It must be mentioned that Choi *et al.* [8] observed the banana phase when the spacer chain contained an odd number of carbon atoms, and only classical smectic phases when the carbon atoms were even in number. In contrast, we observe the features of banana phases for the compounds with an even number of carbon atoms in the spacer chain and classical smectic phases when the number of carbon atoms is odd. This contrasting behaviour is perhaps associated with the flip in the orientation of the ester linkages between the compounds of Choi *et al.* and those described in this paper.

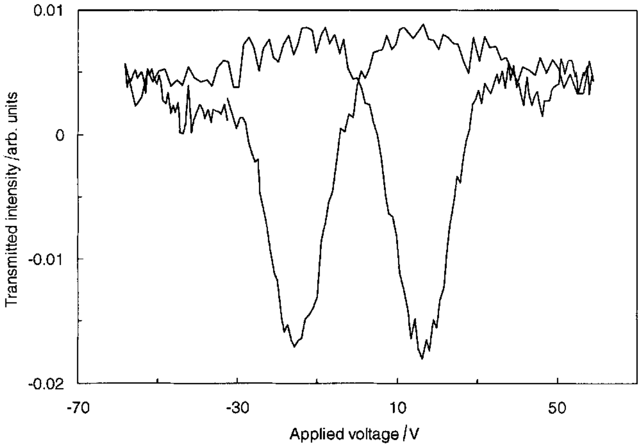


Figure 4. Electro-optic response in the X_1 phase (T = 169°C) of the compound with $m = 8$ and $n = 12$ of series 2. The applied electric field was 9 V $\mu\mathrm{m}^{-1}$, 20 Hz triangular wave. The profile is typical of an antiferroelectric type of switching.

4. Conclusions

In summary, we have reported two series of compounds with dimeric molecules. All the compounds synthesized are found to be liquid crystalline. The effect of varying the terminal as well as the spacer chain length, on the mesomorphic properties has been studied. From the physical studies performed here, we believe that the mesophases observed for the compounds with an even number of carbon atoms in the spacer chain may be different from classical smectic phases. To reveal the exact nature of these mesophases, however, more structural studies need to be performed.

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