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Electroclinic Effect In Unsymmetrical Dimeric Liquid Crystals Composed of Two Non-Identical Chiral Mesogenic Entities

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We report the synthesis and physical characterization of two unsymmetrical dimeric liquid crystals containing two different chiral mesogenic segments, namely, a tolan unit with (*S*)-2-octyloxy tail and a cholesteryl ester unit which are separated by a n-butyl (even) and n-pentyl (odd) spacers respectively. Both the dimers exhibit a smectic A mesophase, with the dimer having the n-pentyl spacer stabilizing this phase over a temperature range of ~150°. Electro-optic studies performed on this compound show that it exhibits an observable electroclinic effect over this entire temperature range. At room temperature, the electroclinic tilt angle and the response time observed are comparable to those exhibited by some monomeric materials.

Keywords: chiral dimeric liquid crystals; electroclinic effect

INTRODUCTION

Among the oligomeric liquid crystals, the dimers composed of either identical (symmerical) or non-identical (unsymmetrical) mesogenic segments connected by a central spacer-such as a polymethylene or a oligo(oxyethylene) or a oligosiloxyl group are now attracting a great deal of attention not only because they are considered as model compounds for polymeric liquid crystals but also due to their unique thermal behavior[1]. Further, there are remarkable differences in the behavior of symmetrical and unsymmetrical dimers.[2–5]

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We have been working on chiral unsymmetrical dimers consisting of the cholesteryl ester unit as a chiral segment and a non-chiral segment containing a Schiffs base, azo, stilbene[2],, tolan[3], biphenyl[4,5], etc., moiety with a polymethylene unit serving as a spacer between the two segments. These investigations reveal that such compounds exhibit a variety of interesting mesophases. For instance, linking of the cholesteryl ester unit and a Schiffs base unit through a n-pentyl spacer has led to the observation of a rich polymorphic sequence including an incommensurate smectic A mesophase[2b]. In contrast the combination of the cholesteryl ester with a tolan unit stabilizes the chiral nematic (N^*) phase over wide temperature range[3], indicating the sensitivity of mesomorphic behavior to the structure of the non-cholesteryl segment in these systems. It would be of much interest to introduce chirality on the non-cholesteryl mesogenic unit as well, to investigate its effect on the thermal behavior and in particular, with a view to exploring the possibility of obtaining ferroelectric properties in these systems. For this purpose, we attached different types of chiral Schiffs base entities to the cholesteryl ester unit through n-pentyl spacer and found that they exhibit chiral smectic A (S_A), chiral smectic C (S_{C^*}), twist grain boundary (TGB) and chiral nematic (N^*) mesophases[6]. However our attempts to observe electroclinic and ferroelectric switching in these materials were not successful as these compounds are sensitive to heat and moisture and tend to decompose. But as mentioned above, the combination of a diphenylacetylene (tolan) mesogen and a cholesteryl ester unit stabilizes N^* mesophase over a wide temperature range (130°) with good thermal stability of the compound. Encouraged by this we introduced chirality in a tolan mesogenic unit and then attached it to a cholesteryl ester unit via alkyl spacers with either even or odd parity. Here we present the synthesis and physical characterization of two such dimers. They consist of a chiral diphenylacetylene segment having (*S*)-2-octyloxy chain as a chiral tail and a cholesteryl ester mesogen joined by an even (C_4) / odd (C_5) methylene spacers.

RESULTS AND DISCUSSION

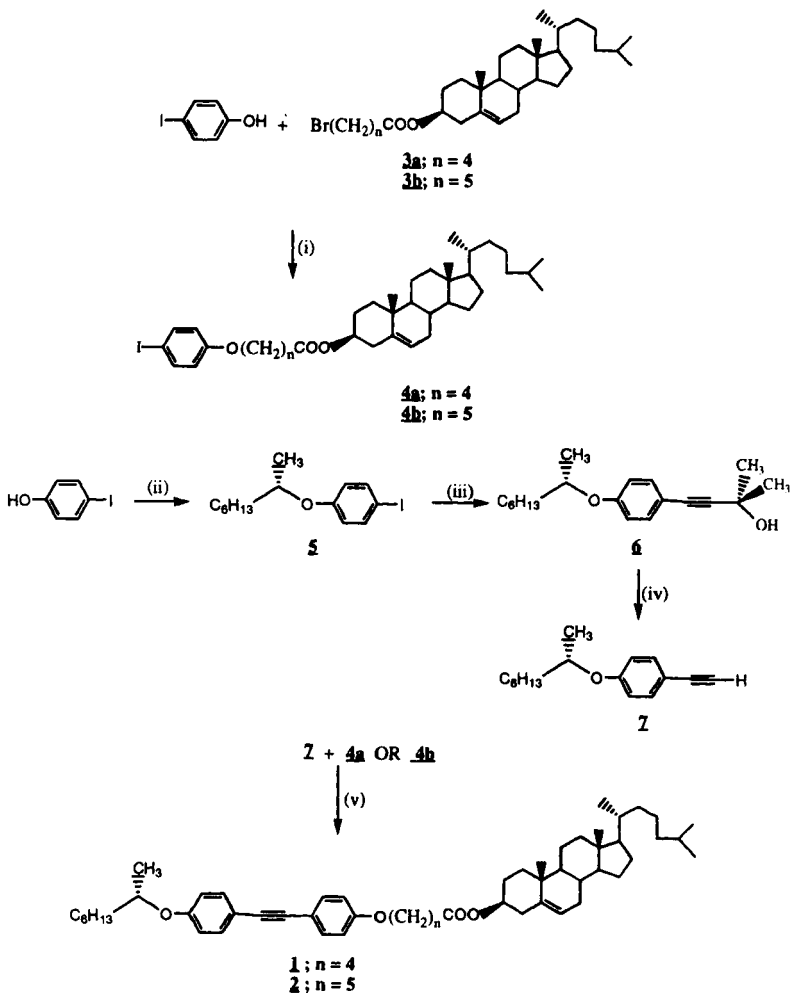
Synthesis

The dimesogens synthesized are cholesteryl 5-{4-[4-(1*S*-methylheptyloxy) phenylethynyl]phenoxy}pentanoate (***1***) and Cholesteryl 6-{4-[4-(1*S*-methylhepty-loxy)phenylethynyl]phenoxy}hexanoate (***2***) The synthetic route employed to prepare these dimesogens is outlined in Scheme-1. Cholesteryl 5-bromopentanoate (***3a***) and cholesteryl 6-bromohexanoate (***3b***) were prepared by esterifica-

tion of commercial optically pure cholesterol with 5-bromopetanoyl chloride and 6-bromohexanoyl chloride respectively as described in the literature.[2a,5] These bromo compounds ***3a*** and ***3b*** were then reacted with 4-iodophenol to get corresponding iodo compounds ***4a*** and ***4b*** as a key intermediates respectively. The 4-(1*S*-methylheptyloxy)phenylacetylene ***7*** was prepared firstly by alkylating 4-iodophenol with (*R*)-octan-2-ol under the Mitsunobu[7] reaction condition to get ether ***5*** which was then coupled with 2-methyl-3-butyn-2-ol under palladium(0)-copper(I) catalysed[8] reaction conditions to furnish protected phenylacetylene ***6*** which upon refluxing with potassium hydroxide in toulene[9] furnished the phenylacetylenic compound ***7***. The iodo compounds ***4a*** and ***4b*** were then coupled with phenylacetylene ***7*** to get the dimers ***1*** and ***2*** as white crystalline compounds respectively. The molecular structure of these unsymmetrical dimers and all the intermediates were confirmed by spectroscopic analysis (see experimental section for details).

Thermal behavior

Optical microscopic studies of the dimers ***1*** and ***2*** show that on melting, these samples transform into a S_A phase with its characteristic fan shaped texture which remained till the transition to the isotropic (Iso) phase (at 108.4 °C and 146.2 °C respectively). On cooling from the isotropic phase, a slight supercooling was observed and the transition to the S_A phase occurred (at 107.0 °C, ΔH= 5.9 J/g and 145.8 °C ΔH= 10.1 J/g respectively for the two compounds). Neither any other textural change nor crystallization of the samples were seen till room temperature. The fan shaped texture obtained for dimer ***2*** for the two temperatures viz., 140 °C and room temperature are shown in figures 1a and 1b respectively. The differential scanning calorimetric trace shown in figures 3 (top panel) and 2 (top panel) corroborates these observations. In the case of dimer ***2*** the DSC scan shows a small rounded peak at ~ −8°C associated with a very small amount of enthalpy. Thus, the temperature range of the S_A phase is about 153 °C, which is comparable to another wide S_A phase (160° C) range reported by Goodby et al.[10] (It may be stated that the range in both the cases is calculated in the cooling mode). No other transitions have been seen till −65°C, the lowest temperature achievable with our setup. It must be mentioned that on heating the sample from −65°C, the small rounded peak was seen (see the inset in the bottom panel of figure 2) at the same temperature as in the cooling scan and no other peaks were observed till the S_A-Iso transition. These transitions are highly reproducible during repeated heating and cooling cycles. We have checked the chemical stability of the sample by taking DSC scans after keeping the sample at 110°C for 15 hours and found that the transition temperatures agree well with the previous



Reagents and conditions: (i) anhyd.K_2CO_3 cat KI, 2-butanone, 70°C, 24hrs.
(ii) 2-octanol, Ph_3P, DEAD, THF, rt, 12hrs.
(iii) 2-methyl-3-butyn-2-ol, $[(C_6H_5)_3P]_2PdCl_2$,CuI, Ph_3P, Et_3N, THF,65,16hrs
(iv) KOH, toluene, 110°C, 2hrs.
(v) $[(C_6H_5)_3P]_2PdCl_2$, CuI, Ph_3P, Et_3N, THF,75,16hrs.

SCHEME 1

runs. No sign of crystallization was noticed even after keeping the sample at room temperature for more than a week. Further mechanical disturbances seems to have no influence on the stability of S_A mesophase.

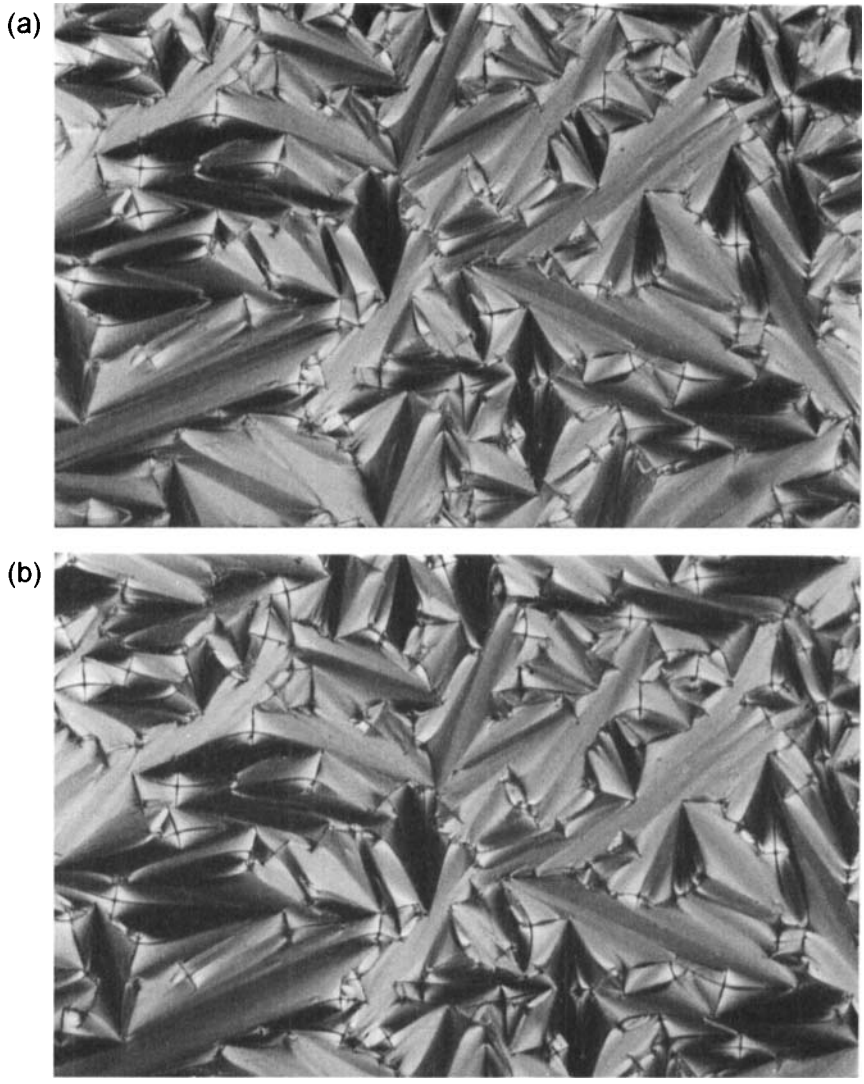


FIGURE 1 Microphotograph of the fan shaped texture observed for dimer ***2*** in the smectic A phase at (a) 140 °C and (b) 30 °C (magnification X100) (See Color Plate I at the back of this issue)

The scan for dimer ***1*** also shows a small rounded peak at about −3 °C indicating stabilization of S_A phase over about 110 °C, which is about 40 °C less than the range obtained for ***2*** but again no other transitions were seen till −65°C. On heating the sample from −65°C, the small rounded peak was seen (see the inset

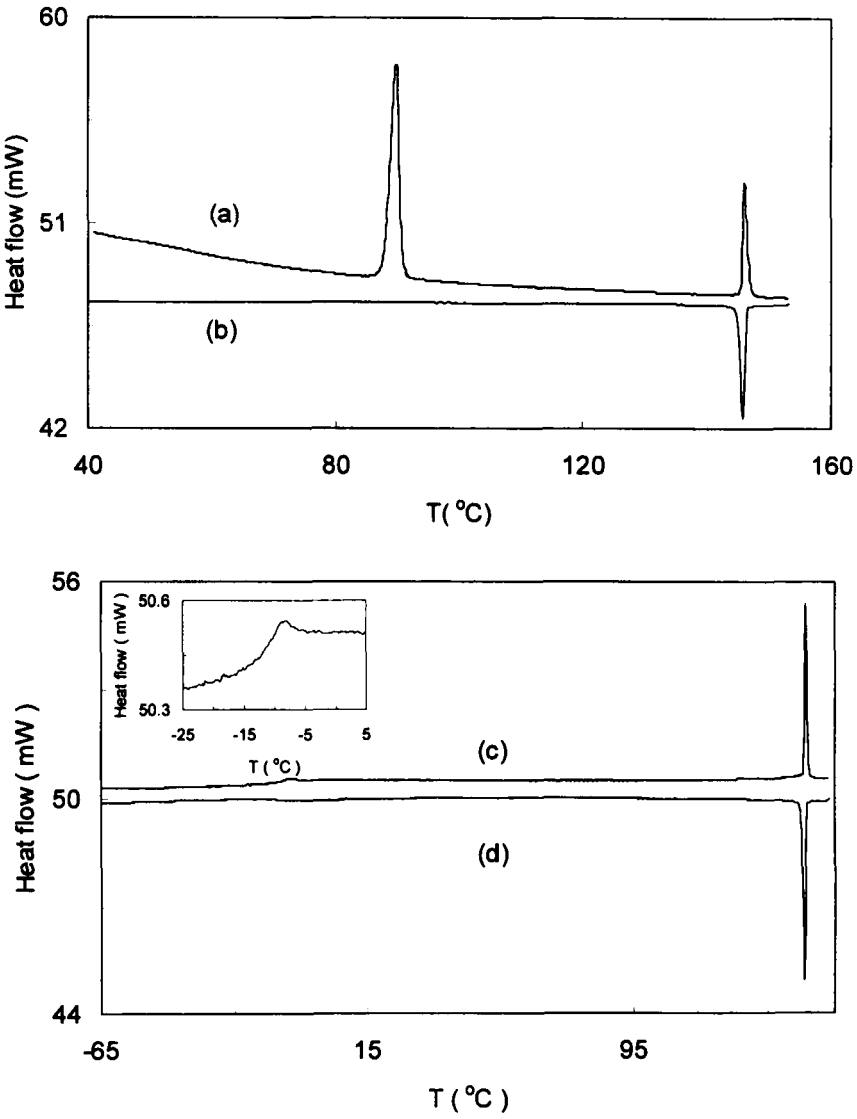


FIGURE 2 Differential scanning calorimeter traces obtained for the dimer ***2*** at a rate of 5°C/min. Top panel: (a) first heating and (b) first cooling scans. Bottom panel: (c) third heating and (d) second cooling run taken from −65°C. The nature of the phase below the small rounded peak seen around −8°C (inset of the bottom panel) is not yet known. Notice that no melting peak is observed

in the bottom panel of figure 3) at the same temperature as in the cooling scan in addition to a exothermic a crystal-melt and S_A-Iso transitions. This sample

remains in the mesophase at room temperature for about 10–15 hr which then crystallizes out. But crystallization occurs immediately in case of any disturbance. It appears that the process of heating itself acts as a mechanical disturbance resulting in crystallization and causing the exothermic peak to appear. This is corroborated by the fact that if the cooling scan is stopped at a temperature > 60°C and the sample is heated the melting peak is not observed. We have not been able to characterize the phase occurring at subambient temperatures owing to the inadequacy of the existing optical setup. Thus out of the two chiral dimers ***1*** and ***2*** synthesized, the dimer ***2*** turns out to be a more interesting system which stabilzes the S_A mesophase over a temperature range of about 150 °C. To confirm that this phase is indeed a S_A we carried out Xray investigation on dimer ***2***.

Xray studies

For Xray diffraction studies the sample ***2*** was aligned by slowly cooling from the isotropic phase in the presence of a magnetic field. The Xray picture obtained at room temperature (figure 4) shows two low-angle sharp spots along the equatorial direction, which is also the magnetic field direction and a wide-angle diffuse arc centered around the meridional direction and orthogonal to the sharp spots. The measured spacings are 42Å, 22 Å and 4.9 Å. The calculated length in the most extended form in the all-*trans* configuration of the molecule, measured using a molecular model is l=46.6 Å. Thus, the 42 Å spacing must be associated with the length of the molecule, with a d/l ratio of 0.9, where d is the spacing. This value of d/l is typical of monolayer smectic A phases and is because the alkyl chains are in a molten state. The 4.9 Å spacing corresponds to the intermolecular separation within the smectic layer arising due to the liquid-like positional correlation within the smectic layer.

The origin of the 22 Å reflection is not as trivial, but could be arising due to a part of the molecule. The length calculated for the four separable regions of the molecule are: (i) 2-octyloxy tail -- 8.8 Å, (ii) diphenyl acetylene moiety -- 12.0 Å, (iii) n-pentyl spacer – - 8.6 Å and (iv) cholesteryl unit -- 17.1 Å. Therefore, the Xray reflection could be coming from a combination of these groups. Such a feature has also been observed for another structurally related compound by Hardouin et al[2]. Hence, one can conclude that the higher temperature phase is indeed a smectic A phase. In over-exposed frames we could observe additional diffuse scattering at low angles also. These are, in fact, reminiscent of the patterns observed in polymeric samples where a variety of factors like layer undulation, fluctuations in the position of alkyl chains acting as spacers, etc. give rise to diffuse scattering[11]. Our material is a dimer, while the results reported in ref. 11 are on polymeric samples and therefore a straightforward comparison is not possible.

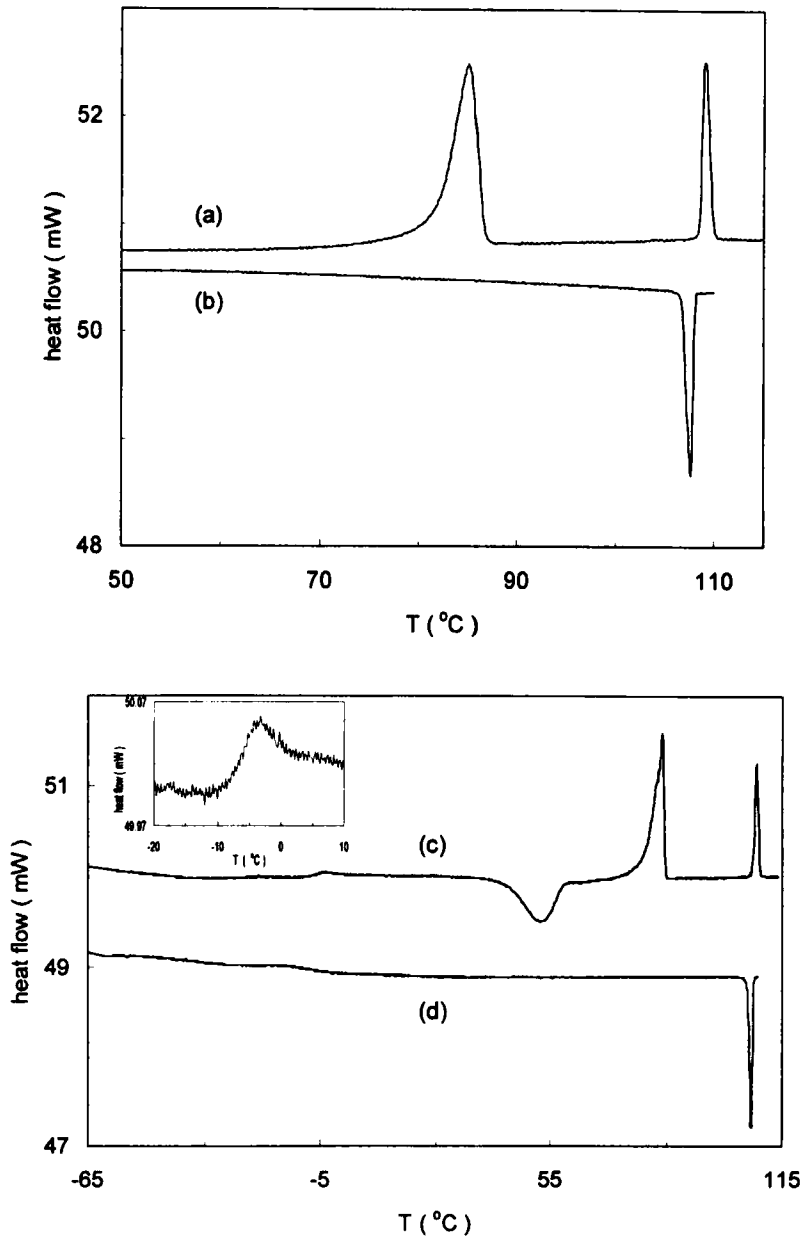


FIGURE 3 Differential scanning calorimeter traces obtained for dimer *I* at a rate of 5°C/min. Top panel: (a) first heating and (b) first cooling scans. Bottom panel: (c) third heating and (d) second cooling run taken from −65°C. The nature of the phase below the small rounded peak seen around −3°C (inset of the bottom panel) is not yet known

FIGURE 4 Xray diffraction photograph of an aligned sample obtained at room temperature showing two sharp spots at low angles (along the equatorial direction, which is also the magnetic field direction) and a diffuse arc at wide angles (along the meridional direction). The sharp spot with the lowest wave vector q_1 corresponds roughly to the length of the dimesogen. The wave vector (q_2) value of the second sharp spot is such that the ratio q_2/q_1 is ~ 1.9. But the value of q_2 also corresponds to the approximate length of each of the moieties. Thus it is not clear whether the second spot is the second harmonic of q_1 or is from the individual moieties

Detailed studies are in progress to understand these phenomena as applied to the present type of molecules.

Electro-optic studies

It is well known that arising from purely symmetry arguments, the S_A phase exhibits the phenomenon called the electroclinic effect[12]. The application of an electric field in the plane of the smectic layer induces the molecules to tilt with respect to the layer normal and in the plane perpendicular to the field. The effect is of much interest because of the associated fast analog electro-optical response with promising applications in spatial light modulation having grey scale capabilities[13]. From the practical point of view, it is obviously an advantage to have a material that exhibits a wide temperature range for the S_A phase. Owing to the stabilization of this mesophase over wide temperature range in dimer ***2***, detailed electro-optic studies were performed on this sample as described below.

The sample was taken between ITO-coated glass plates pre-treated with a polyimide solution and unidirectionally rubbed to get the smectic layers aligned in the bookshelf geometry. The electric-field induced tilt angle (θ) was measured by placing the sample between crossed polarizers such that the layer normal made

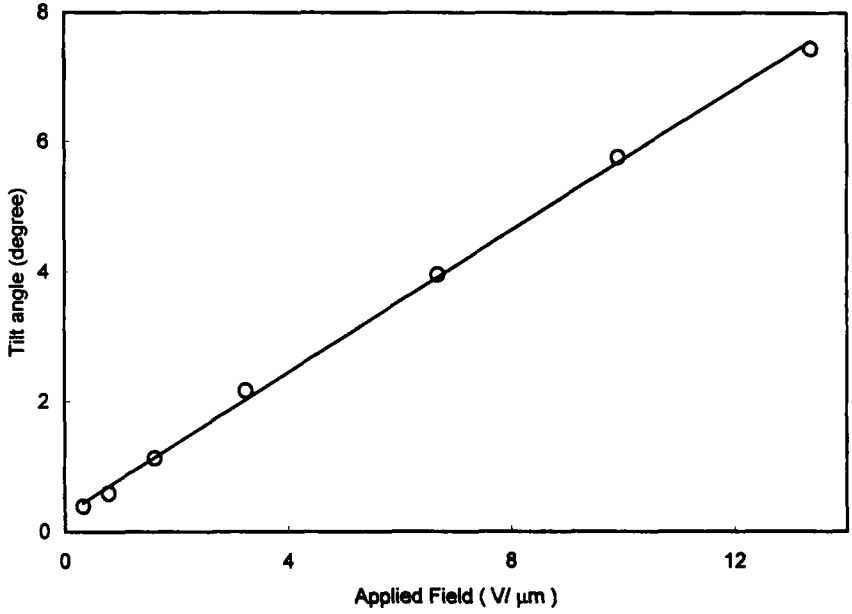


FIGURE 5 Plot of electric field induced tilt angle θ vs. applied field at a constant temperature of 40°C. The solid line is fit to a straight line, describes the data well indicating that the electronic tilt angle is linear with the field

an angle of 22.5° with respect to the first polarizer. The induced tilt angle was calculated[14] by monitoring the intensity change to the applied 22Hz square wave field either as a function of temperature or voltage. Figure 5 shows a plot of θ vs. the amplitude of the field at a constant temperature of 40°C. Considering the fact that this temperature is not in the vicinity of any ferroelectric phase, the values observed are quite significant. The solid line in the figure shows the fit to a straight line and appears to be describing the data well indicating that the electroclinic tilt angle is linear with the field, as is to be expected[14]. Defining the electroclinic coefficient as the slope of this line, we get a value of 0.01 rad μm/V, not different from the values obtained for monomeric materials. The temperature dependence of θ at a fixed field of 6V/μm is shown in figure 6. Over this temperature range θ varies from 0.6 degrees to 6 degrees, values which are not very high, but are again comparable to those obtained for monomeric materials[15–18]. The optical response obtained at 40 °C when a 22 Hz, 7V/μm square wave is applied to the sample is shown in figure 7. The response time, defined as the time for the intensity to increase from 10% to 90% of the maximum value, is 250 μs and is similar to the values seen for room temperature monomeric electroclinic

materials. In contrast, for dimer ***1***, the magnitude of the effect is much weaker resulting in a smaller electroclinic tilt angle. Thus a simple change of the parity of the spacer unit from even to odd causes an appreciable increase in the electroclinic effect. It may be recalled that a case of symmetric dimers connected through a flexible spacer where the parity of the spacer strongly alters the behavior of the system has been reported by Choi et. al.[19]

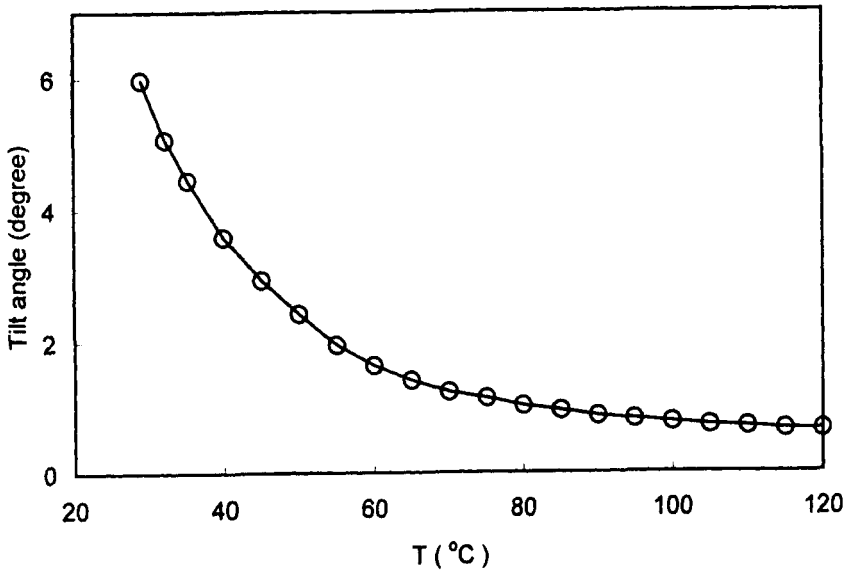


FIGURE 6 Temperature dependence of θ at a fixed field of 6V/μm. Notice that θ varies from 0.6 to 6 degree, which is comparable to the values obtained for monomeric materials. Solid line is guide to the eye

To the best of our knowledge, amongst the numerous chiral liquid crystalline compounds known, monomeric as well as polymeric, the widest temperature range (~ 85°C) over which electroclinic effect has been observed is for a compound reported by Crawford et al[15]. Thus the chiral unsymmetrical dimer ***2*** synthesized in the present investigation exhibits the widest temperature range over which the electroclinic effect is measured.

In summary, we have synthesized unsymmetrical dimeric liquid crystalline compounds composed of two different chiral entities joined by an odd / even alkyl spacers. The unsymmetrical dimer ***2*** with an odd (C_5) spacer exhibits a chiral smectic A phase over the temperature range of ~150°. Interestingly, electroclinic effect is observed over this entire temperature range, with the magnitude of

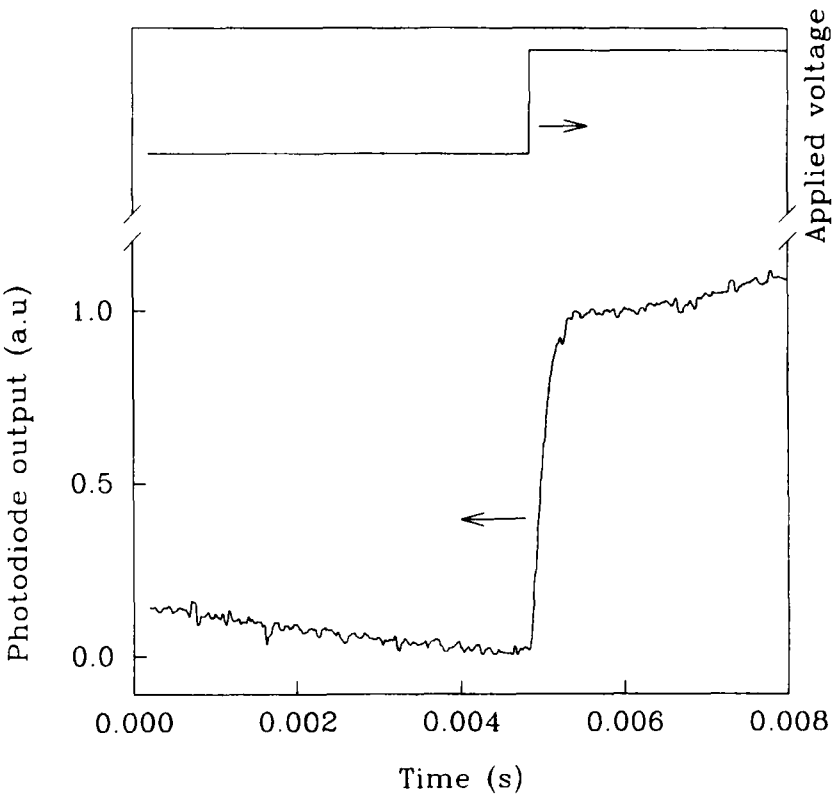


FIGURE 7 Electro-optic response obtained at 40°C when a square wave 7V/μm, 22 Hz AC field is applied. The response time, defined as the time for the intensity to increase from 10% to 90% of the maximum value, is 250 μs

the induced tilt angle, the electroclinic coefficient and the response times being comparable to monomeric substances.

EXPERIMENTAL

General information

Chemicals were obtained from Fluka or Aldrich Company or a local source and used as such without any purification, while solvents were dried following standard procedures. Column chromatographic separations were performed using

either silica gel or neutral aluminium oxide. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselge60, F254). IR spectra were recorded using Perkin Elmer Spectrum 1000 FT-IR spectrometer. ^{1}H NMR spectra were recorded using a Bruker DRX-500 (500 MHz) or Bruker AMX-400 (400 MHz) or Bruker Aveance series DPX-200 (200MHz) spectrometers. For ^{1}H NMR spectra, the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on Jeol JMS-600H spectrometer. The compound was investigated for liquid crystalline behaviour with the help of optical polarizing microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90) and by differential scanning calorimetry (Perkin Elmer DSC7). Optical observations were made with two different surface coated slides, one treated for homogeneous alignment and another with homeotropic alignment. Xray diffraction studies were carried out using an Image Plate Detector (MAC Science, Japan) equipped with a double mirror focussing optics and the sample contained in a Lindemann capillary tube.

Cholesteryl 5-(4-iodophenoxy)pentanoate (4a)

A mixture of cholesteryl 5-bromopetanoate ***3a*** (1.95g, 3.55 mmol), 4-iodophenol (0.78g, 3.55 mmol), anhyd. potassium carbonate (1.96g, 14.2 mmol) and potassium iodide (30mg, 0.18 mmol, 5%) in dry 2-butanone (40ml) was heated at 70°C for 24 hrs. under argon atmosphere. The reaction mixture was filtered through celite bed when hot. The filtrate was evaporated *in vacuo*to get solid residue which was poured onto water. The off-white solid separated was collected by filtration. It was purified by recrystallization in a mixture of CH_2Cl_2-ethanol (1:10). R_f=0.45 (10% EtOAc-hexanes). A white solid; m.p. 100–102°C; yield:1.52g (60 %); IR (KBr pellet): γ_{max} 3135, 2867, 1731 and 1584cm^1; ^{1}H NMR ($CDCl_3$, 400MHz): 7.53 (d, *J*=8.92Hz, 2H, Ar), 6.66 (d, *J*=8.96, Hz, 2H, Ar), 5.36 (brd, *J*=4.1Hz, 1H, Olefinic), 4.62 (m, 1H, -CH-OCO-), 3.92 (t, *J*=6.34Hz, 2H, – OCH_2-), 2.31 (m, 4H, 2× allylic methylene), 2.02–1.15 (m, 30H, 6×-CH-, 12×-CH_2-), 1.01 (s, 3H, -CH_3), 0.91 (d, *J*=6.52, 3H, -CH_3), 0.86 (d, *J*=1.84Hz, 3H, 1×-CH_3) 0.85 (d, *J*=1.76Hz, 3H, 1×-CH_3) and 0.67 (s, 3H, -CH_3); FAB Mass: 710.5 $[M+Na]^+$, ($C_{38}H_{57}IO_3$),

Cholesteryl 6-(4-iodophenoxy)hexanoate (4b)

This was synthesized similar to that of ***4a*** with same stoichiometric amount of reactants R_f=0.4 (10% EtOAc-hexanes). A white solid; m.p. 122–123°C; yield:

2.1g (84 %); IR (KBr pellet): γ_{max} 2940, 2875, 1731 and 1578cm^{-1}; ^{1}H NMR ($CDCl_3$, 200MHz): 7.53 (d, *J*=8.92Hz, 2H, Ar), 6.66 (d, *J*=8.9Hz, 2H, Ar), 5.38 (brd, *J*=4.3Hz, 1H, Olefinic), 4.6 (m, 1H, -CH-OCO-), 3.91 (t, *J*=6.34Hz, 2H, -OCH_2-), 2.29 (m, 4H, 2× allylic methylene), 2.04–1.1 (m, 32H, 6×-CH-, 13×-CH_2-), 1.01 (s, 3H, -CH_3), 0.91 (d, *J*=6.48, 3H, -CH_3), 0.87 (d, *J*=6.54Hz, 6H, 2×-CH_3) and 0.68 (s, 3H, -CH_3). FAB Mass: 725 $[M+Na]^+$, ($C_{39}H_{59}IO_3$).

4-(1S-Methylheptyloxy)iodobenzene (5)

To a cooled (10–15°C) and magnetically stirred solution of 4-iodophenol (0.85g, 3.86 mmol), (*R*)-2-octanol (0.5g, 3.86 mmol), triphenylphosphine (1.2g, 4.6mmol) in dry THF (5ml) added diethylazodicarboxylate (0.73ml, 4.6mmol) dropwise over a period of 5min. under argon atmosphere. The reaction mixture was allowed to attain room temperature and stirred for 18hrs. The solvent was removed *in vacuo* and a mixture of ether (10ml) and hexanes (10ml) was added. The solid that was separated was removed by filtration and the filtrate was washed with 5% $NaOH_{(aq)}$ solution (10ml×2), water (10ml×2), brine (10ml) and was then dried over anhyd. Na_2SO_4. The evaporation of solvent furnished crude oil which was purified by column chromatography using silica gel (230–400 mesh). Elution with a mixture of 10% CH_2Cl_2-hexanes afforded a colourless oil. R_f=0.54 (15% CH_2Cl_2-hexanes). Yield = 0.96g (75%); IR(Neat): γ_{max} 2928, 2860 and 1579 cm^{-1}: ^{1}H NMR ($CDCl_3$, 200MHz): 7.53 (d, *J*=9Hz, 2H, Ar), 6.7 (d, *J*=9Hz, 2H, Ar), 4.3 (m, 1H, – OCH-), 1.75–1.2 (m, 10H, 5×-CH_2-), 1.27 (d, *J*=6.04Hz, 3H, -CH_3) and 0.88 (t, *J*=6.82Hz, 3H, -CH_3). FAB Mass: 332 $[M]^+$ ($C_{14}H_{21}IO$).

4-[4-(1S-Methylheptyloxy)phenyl]-2-methyl-3-butyn-2-ol (6)

A mixture of 4-(1*S*-methylheptyloxy)iodobenzene (*5*) (0.75g, 2.26mmol), 2-methyl-3-butyn-2-ol (0.21g, 2.48mmol), bis(triphenylphosphine)palladium(II)chloride (8mg, 0.01mmol, 0.5%), triphenylphosphine (14.8mg, 0.056 mmol, 2.5%), and copper(I)iodide (8.6mg, 0.045mmol, 2%) in dry triethylamine (5ml) was stirred at 65°C under argon atmosphere for 16 hrs. The reaction mixture was cooled and filtered through celite bed. The filtrate was evaporated *in vacuo* to get a pale yellow oil which was then purified by column chromatography using silica gel (100–200 mesh). Elution with a mixture of 10% EtOAc-hexanes furnished a colourless oil. R_f = 0.38 (20% EtOAc-Hexane). Yield: 0.58g (89%); IR(Neat): γ_{max} 3361, 2929, 2862, 2228 and 1604 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500MHz): 7.36 (d, *J*=8.85Hz, 2H, Ar), 6.83 (d, *J*=8.8Hz, 2H, Ar), 4.39

(m, 1H, -OCH), 2.06 (s, 1H, -OH), 1.78–1.3 (m, 10H, 5×-CH_2), 1.65 (s, 6H, 2×-CH_3), 1.32 (d, J=6.05, 3H, -CH_3), and 0.92 (t, J=7.1Hz, 3H, -CH_3). FAB Mass: 288$[M]^+$ ($C_{19}H_{28}O_2$).

4-(1S-Methylheptyloxy)phenylacetylene (7)

A mixture of protected phenylacetylene (***6***) (0.5g, 1.73mmol), potassium hydroxide (0.117g, 2.08 mmol) and toluene (5ml) was heated to reflux for 2hrs. under argon atmosphere. The solvent was evaporated to dryness *in vacuo* and the brown semi-solid obtained was poured into a ice-cold water (50ml). The aqueous layer was extracted with hexanes (10ml×2). The organic layer was then washed with water (10ml×2), brine and dried over anhyd. Na_2SO_4. Evaporation of solvent furnished a pale brown oil which was purified by column chromatography using alumina (neutral). Hexanes elution furnished a pale voilet colour oil. R_f=0.27 (hexanes). Yield:0.28gm (70%), IR(Neat): γ_{max} 3316, 2928, 2856, 2107 and 1604 cm^{-1}; ^1H NMR ($CDCl_3$, 500MHz): 7.43 (d, J=8.7Hz, 2H, Ar), 6.84 (d, J=8.65Hz, 2H, Ar), 4.38 (m, 1H, -O-CH-), 3.0 (s, 1H, -C≡CH), 1.78–1.23 (m, 10H, 5×-CH_2-), 1.31 (d, J=6Hz, 3H, -CH_3) and 0.91 (t, J=6.95Hz, 3H, -CH_3). FAB Mass: 230 $[M]^+$ ($C_{16}H_{22}O$).

Cholesteryl 6-{4-[4-(1S-methylheptyloxy)phenylethynyl] phenoxy}pentanoate (1)

A mixture of cholesteryl 6-(4-iodophenoxy)pentanoate (***4a***) (0.5g, 0.73 mmol), phenylacetylene ***7*** (0.213g, 0.93mmol), bis(triphenylphosphine)palladium (II) chloride (20mg, 0.028mmol, 4%), triphenylphosphine (37mg, 0.14mmol), 20%), copper(I)iodide (23mg, 0.12mmol, 16.8%) and triethylamine (10ml) was heated at 75°C under argon atmosphere for 16 hrs. The reaction mixture was filtered through celite bed when hot. The filtrate was evaporated under vaccum and the pale yellow solid obtained was dissolved in $CHCl_3$ (20ml) and the resultant solution was washed with a 0.1M $HCl_{(aq)}$ (10ml×2u), 5% solution of $NaOH_{(aq)}$ (10ml×2u), water (10ml×2), brine and then was dried over anhyd. Na_2SO_4. Evaporation of solvent furnished pale yellow solid which was purified by column chromatography using alumina (neutral). Elution with a mixture of 10% EtOAc-hexanes furnished a white solid which was further purified by repeated recrystallizations in n-butanol. R_f = 0.38 (10% EtOAc-hexanes). A white solid; m.p.: 108–109 °C; yield: 0.49gm (86%); IR (KBr pellet): γ_{max} 2931, 2861, 1725 and 1607cm^{-1}; ^{1}HNMR (500MHz, $CDCl_3$): 7.43 (d, J=3.36Hz, 2H, Ar), 7.41 (d, J=3.4, 2H, Ar), 6.85 (d, J= 4, 2H, Ar), 6.82 (d, J=3.88, 2H, Ar), 5.37 (brd, J=4.4,

1H, Olefinic), 4.61 (m, 1H, – CH-O-CO-), 4.37 (m, 1H, -CH-O-), 3.98 (br t, J=6.0, 2H, -OCH_2-), 2.31 (m, 4H, 2 × allylic methylene), 2.01–0.92 (m, 43H, 1×CH_3-, 17×-CH_2-, 6×-CH-), 1.3 (d, J=6.08, 3H, -CH_3), 1.02 (s, 3H, -CH_3), 0.91 (d, J=6.56, 3H, -CH_3), 0.87 (d, J=1.8, 3H, -CH_3), 0.85 (d, J=1.8, 3H, -CH_3), and 0.67 (s, 3H, -CH_3); ^{13}CNMR (100MHz, $CDCl_3$, Spin Echo FT): 172.86 (CO), 158.78 (C), 158.17 (C), 139.7 (C), 132.91 (CH), 122.72 (CH), 115.8 (CH), 115.4 (C), 114.54 (CH), 88.11 (C), 87.88 (C), 74.02 (CH), 67.5 (CH_2), 56.75 (CH), 56.20 (CH), 50.10 (CH), 42.37 (C), 39.79 (CH_2), 39.56 (CH_2), 38.21 (CH_2), 37.04 (CH_2), 36.65 (C), 36.47 (CH_2), 36.24 (CH_2), 35.84 (CH), 34.32 (CH_2), 31.97 (CH_2), 31.91 (CH), 31.83 (CH_2), 29.31 (CH_2), 28.61 (CH_2), 28.28 (CH_2), 28.06 (CH), 27.87 (CH_2), 25.52 (CH_2), 24.34 (CH_2), 23.89 (CH_2), 22.86 (CH_3), 22.65 (CH_2), 22.61 (CH_3), 21.75 (CH_2), 21.08 (CH_2), 19.74 (CH_3), 19.37 (CH_3), 18.77 (CH_3) 14.12 (CH_3); and 11.91 (CH_3); FAB Mass: 789.9 $[M]^+$ (C_{54} $H_{78}O_4$).

Cholesteryl 6-{4-[4-(1S-methylheptyloxy)phenylethynyl] phenoxy}hexanoate (2)

This was synthesized similar to that of dimer ***1*** with same stiochiometric amount of reactants. R_f=0.35 (10% EtOAc-hexanes). A white solid; m.p. 146–147°C; yield: 0.49gm (85%); IR (KBr pellet): γ_{max} 2939, 2860, 2356, 1725 and 1605cm^{-1}; ^{1}HNMR (500MHz, $CDCl_3$): 7.43 (d, J=3.25Hz, 2H, Ar), 7.41 (d, J=3.25, 2H, Ar), 6.85 (d, J=2.95, 2H, Ar), 6.83 (d, J=2.9, 2H, Ar), 5.38 (brd, J=4.45, 1H, Olefinic), 4.61 (m, 1H, -CH-O-CO-), 4.37 (m, 1H, -CH-O-), 3.97 (t, J=6.4, 2H, -OCH_2-), 2.32 (m, 4H, 2 ×-CH_2=C-), 2.01–0.9 (m, 45H, 1×CH_3-, 18×-CH_2-, 6×-CH-), 1.3 (d, J=6.05, 3H, -CH_3), 1.02 (s, 3H, -CH_3), 0.92 (d, J=6.5, 3H, -CH_3), 0.88 (d, J=2.1, 3H, -CH_3), 0.87 (d, J=2.1, 3H, -CH_3), and 0.68 (s, 3H, -CH_3); ^{13}CNMR (125MHz, $CDCl_3$): 172.89, 158.73, 158.0, 139.57, 132.76, 132.73, 122.53, 115.63, 115.56, 115.26, 114.37, 87.92, 87.75, 73.87, 73.72, 67.57, 56.59, 56.05, 49.94, 42.22, 39.64, 39.42, 38.07, 36.89, 36.32, 36.09, 35.69, 34.46, 31.80, 31.77, 31.68, 29.15, 28.78, 28.13, 27.90, 27.72, 25.48, 25.36, 24.68, 24.18, 23.74, 22.71, 22.46, 20.94, 19.59, 19.21, 18.61, 13.96 and 11.75; FAB Mass: 804 $[M]^+$ (C_{55} $H_{80}O_4$).

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