Liquid Crystals

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

Antiferroelectric liquid crystals derived from a new optically active (*R*)-3-ethylmercapto-2-methylpropionic acid

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To cite this Article Wu, S. L. , Huang, F. K. , Uang, B. J. , Tsai, W. J. and Liang, J. J.(1995) 'Antiferroelectric liquid crystals derived from a new optically active (*R*)-3-ethylmercapto-2-methylpropionic acid', Liquid Crystals, 18: 5, 715 — 721
To link to this Article: DOI: 10.1080/02678299508036681
URL: http://dx.doi.org/10.1080/02678299508036681

LIQUID CRYSTALS, 1995, VOL. 18, NO. 5, 715–721

Antiferroelectric liquid crystals derived from a new optically active (*R*)-3-ethylmercapto-2-methylpropionic acid

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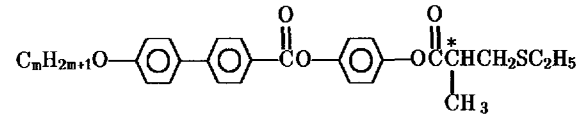
(*Received 27 June 1994; accepted 4 August 1994*)

A new optically active (*R*)-3-ethylmercapto-2-methylpropionic acid has been synthesized using *D*(−)—2,10-camphorsultam as a chiral auxiliary. The optical purity of the acid obtained was greater than 98 per cent. Its derivatives, (*R*)-4-(3-ethylmercapto-2-methylpropionyl)phenyl 4′-alkoxybiphenyl-4-carboxylates (EMMPP*m*BC; $m = 7$–16), have been prepared for the investigation of liquid crystalline properties as a function of peripheral alkyl chain length. Optical studies showed that all members exhibited an antiferroelectric $S_{C_A}^*$ phase. The results also indicate that a lengthened alkyl chain length is favoured for $S_{C_A}^*$ phase formation.

1. Introduction

Antiferroelectric ($S_{C_A}^*$) [1], ferrielectric ($S_{C_\alpha}^*$ and $S_{C_\gamma}^*$) [2] and twist-grain boundary (TGB) [3, 4] phases are recently discovered chiral liquid-crystalline systems. Amongst them, the $S_{C_A}^*$ phase exhibits a tristable switching property and has been extensively studied both experimentally and theoretically because of potential application in electric-optical devices [5–7]. As a consequence, a number of these types of material have been synthesized and an attempt to correlate the molecular structure of the liquid crystals to the appearance of the $S_{C_A}^*$ phase has been carried out.

Goodby and his coworkers [8–11] have demonstrated that the formation of the $S_{C_A}^*$ phase in chiral liquid-crystalline systems depends strongly on the chirality of the molecules. That is, the chiral materials with the $S_{C_A}^*$ phase possess higher chirality. Thus, the $S_{C_A}^*$ phase generally occurs in optically active derivatives of octan-2-ol, 2-methyloctanoic acid, 1,1,1-trifluorooctan-2-ol etc. [1, 12–14], where the chiral centre is relatively close to the central rigid-core moiety of the molecules. In addition, the peripheral alkyl length on the external side of chrial centre is relatively long. Based on this empirical hypothesis, we have designed and synthesized a new optically active compound, (*R*)-3-ethylmercapto-2-methylpropionic acid, as a chiral building block for the preparation of chiral materials. Thus, a homologous series of the derivatives, (*R*)-4-(3-ethylmercapto-2-methylpropionyl)phenyl 4′-alkoxybiphenyl-4-carboxylates (EMMPP*m*BC; $m = 7$–16) were prepared for this study. The chemical structure for EMMPP*m*BC is shown as follows:



2. Experimental

2.1. *Preparation of materials*

Optically active (*R*)-3-ethylmercapto-2-methylpropionic acid **5** was prepared using D(−)-2,10-camphorsultam **1** as a chiral auxiliary according to the procedures outlined in scheme 1. Sultam **1**, prepared from (+)-10-camphorsulphonic acid [15], was *N*-acylated by the treatment of sodium hydride and subsequent addition of methacryloyl chloride to give *N*-methacryloylsultam **2** [16]. Michael addition of mercaptoethane to *N*-methacryloylsultam **2** in the presence of basic promoter *n*-butyllithium gave adducts **3** and **4**. Compound **3**, obtained in pure form after recrystallization from

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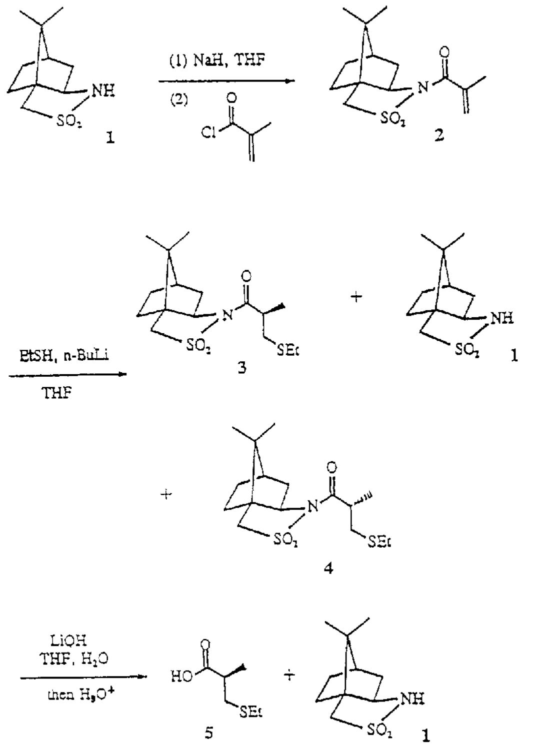


Scheme 1. Mechanistic procedures for the synthesis of compound (*R*)-(+)-3-ethylmercapto-2-methylpropionic acid.

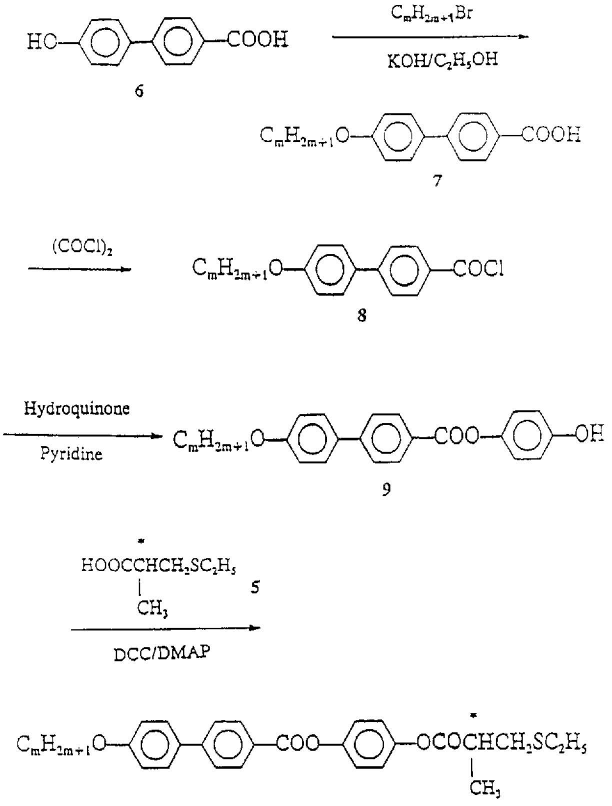
CH_2Cl_2/*n*-hexane, was hydrolyzed with lithium hydroxide in aqueous tetrahydrofuran to give chiral acid **5**.

The derivatives of the acid **5**, (*R*)-4-(3-ethylmercapto-2-methylpropionyl)phenyl 4′-alkoxybiphenyl-4-carboxylates (EMMPP*m*BC; *m* = 7–16), were prepared according to the procedures outlined in scheme 2. 4′-Hydroxybiphenyl-4-carboxylic acid **6** was treated with sodium hydroxide and n-alkylbromide to give the 4′-alkoxybiphenyl-4-carboxylic acids **7**. The acids **7** were then converted to acid chlorides **8** by reacting with oxalyl chloride. Addition of acid chlorides **8** to excess amount of hydroquinone in the presence of pyridine gave alcohols **9**. Esterification of the acid **5** and the alcohols **9** by the treatment of *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) gave the target compounds EMMPP*m*BC.

Detailed synthetic procedures are described below.

2.1.1. *N-Methacryloyl-*{[*3aS-*(*3aα, 6α, 7aβ*)]*-hexahydro-8,8-dimethyl-3H-3a,6-methano-2,1-benzisothiazole-*2,2*-dioxide*}, **2**

Sultam **1** (10·75 g, 0·05 mol) was dissolved in anhydrous tetrahydrofuran (THF 10 ml) in a 250 ml flask under nitrogen. The flask was cooled in an ice bath. A mixture of sodium hydride (1·44 g, 0·06 mol) in anhydrous THF (40 ml) was then added dropwise to the flask and stirred for another 30 min at 0°C. After removal of the ice bath, methacryloyl chloride (6·27 g, 5·86 ml, 0·06 mol) was added to the reaction mixture and stirred further for 4 h at room temperature. The reaction was quenched by the addition of saturated sodium bicarbonate solution (100 ml), and then extracted by ethyl acetate (3 × 75 ml). The combined ethyl acetate solution was dried over anhydrous sodium sulphate, filtered and concentrated *in vacuo*. The product was isolated by silica gel (Merck Art 7734) column chromatography using a mixture of *n*-hexane, ethyl acetate and methylene chloride (6 : 2 : 3 by volume). White precipitates was obtained with m.p. 145–145·2°C and yield of 85 per cent. Elemental analysis (per cent): calculated, C 59·34, H 7·47, N 4·94, S 11·26; found, C 59·27, H 7·48, N 4·96, S 11·26. ^{1}H NMR ($CDCl_3$): δ(ppm) 5·69 (s, 1 H), 5·65 (s, 1 H), 4·02–4·05 (dd, 1 H, $J = 4{\cdot}8$, 7·6 Hz), 3·51, 3·40 (ABq, 2 H, $J = 13{\cdot}6$ Hz), 1·86–2·08 (m, 5 H), 1·99 (s, 3 H), 1·34–1·45 (m, 2 H), 1·23 (s, 3 H), 1·00 (s, 3 H). Specific rotation: $[\alpha]_D^{22}$ − 94·01 (c1, $CHCl_3$).



Scheme 2. Mechanistic procedures for the synthesis of compound (*R*)-(+)-4-(3-ethylmercapto-2-methylpropionoyloxy)phenyl 4′-alkoxybiphenyl-4-carboxylates, EMMPP*m*BC

2.1.2. *M-(3-Ethylmercapto-(R)-2-methyl)propionyl-{[3aS-(3aα, 6α, 7aβ)]-hexahydro-8,8-dimethyl-3H-3a,6-methano-2,1-benzisothiazole-2,2-dioxide}*, **3**

A mixture of mercaptoethane (0·97 g, 1·15 ml, 95·5 mmol) and anhydrous THF (70 ml) in a 250 ml flask was mixed with *n*-butyl-lithium (1·5 M, 1·14 ml, 2·12 mmol) and stirred for 10 min at −78°C under nitrogen. Compound **2** (4·00 g, 14·13 mmol) dissolved in anhydrous tetrahydrofuran (71 ml) was added to the mixture and further stirred for 2 h at −78°C. The reaction was then quenched by a 5 per cent solution of sodium hydroxide (50 ml) at 0°C. The organic layer was separated, and the water layer was extracted with methylene chloride (4 × 40 ml). The combined organic solution was then washed with saturated brine solution, dried over anhydrous sodium sulphate, filtered and concentrated *in vacuo*. The residue was purified by silica gel (Merck Art 7734) column chromatography using a mixture of methylene chloride, ethyl acetate and *n*-hexane (6 : 1 : 14 by volume) as eluent. A 97 per cent yield of stereoisomeric solid mixtures **3** and **4** (4·53 g, 13·13 mmol) was obtained and compound **1** (0·13 g, 0·6 mmol) was recovered. After recrystalization by methylene chloride and *n*-hexane, optically pure compound **3** was obtained with a m.p. of 103·6–103·9°C. Elemental analysis (per cent): calculated, C 55·62, H 7·88, N 4·05, S 18·56; found, C 55·66, H 7·90, N 4·12, S 18·61. ^{1}H NMR (CDCl$_3$): δ (ppm) 3·90–3·93 (dd, 1 H, $J = 7·8$, 4·8 Hz), 3·55, 3·41 (Abq, 2 H, $J = 13·8$ Hz), 3·35–3·42 (m, 1 H), 2·85 (dd, 1 H, $J = 9·0$, 13·2 Hz), 2·64 (dd, 1 H, $J = 5·6$, 13·2 Hz), 2·54–2·64 (m, 2 H), 2·18–2·19 (m, 1 H), 2·06 (dd, 1 H, $J = 7·6$, 14·0 Hz), 1·86–1·94 (m, 3 H), 1·35–1·43 (m, 2 H), 1·24 (d, 3 H, $J = 6·4$ Hz), 1·21 (t, 3 H, $J = 7·4$ Hz), 1·23 (s, 3 H), 0·98 (s, 3 H). Specific rotation: $[\alpha]_D^{22}$ + 10·04 (c2, CHCl$_3$).

2.1.3. *(R)-3-Ethylmercapto-2-methylpropionic acid*, **5**

Compound **3** (1 g, 2·9 mmol) was dissolved in a solution of THF (16 ml) and distilled water (4 ml) in a 250 ml flask. The flask was cooled to 0 ∼ − 5°C. A mixture of lithium hydroxide (0·21, 8·7 mmol) in distilled water (4 ml) was then added to the flask. After the reaction mixture was stirred at 0 ∼ − 5°C for 32 h, distilled water (10 ml) was added to quench the reaction. The mixture was extracted by methylene chloride (3 × 40 ml). The organic solution was dried over anhydrous sodium sulphate, filtered and concentrated *in vacuo*. Quantitative amount of compound **1** (0·62 g, 2·88 mmol) was recovered. The water solution was acidified by the addition of 2 M HCl (8·5 ml) and extracted by ethyl ether (4 × 40 ml). The combined ethereal solution was then washed by saturated brine solution, dried over anhydrous sodium sulphate, filtered and concentrated *in vacuo*. The yellowish liquid residue was distilled under vacuum. A 95 per cent yield of compound **5** was obtained, b.p. 90°C/0·2 mm Hg. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 10·60 (br, 1 H), 2·79 (dd, 1 H, $J = 6·9$, 12·7 Hz), 2·59–2·66 (m, 1 H), 2·52 (dd, 1 H, $J = 6·9$, 12·7 Hz), 2·49 (q, 2 H, $J = 7·2$ Hz), 1·22 (d, 3 H, $J = 6·8$ Hz), 1·18 (t, 3 H, $J = 7·4$ Hz). Specific rotation: $[\alpha]_D^{22}$ + 26·45 (c2, CHCl$_3$).

2.1.4. *4′-Alkoxybiphenyl-4-carboxylic acids*, **7**

4′-Hydroxybiphenyl-4-carboxylic acid (17 mmol) was treated with sodium hydroxide (2·2 g) and then reacted with alkyl bromide (51 mmol) in ethanol (400 ml) under reflux. The products were recrystallized from glacial acetic acid and ethanol with a 60–70 per cent yield of compounds **5** obtained.

2.1.5. *4′-Alkoxybiphenyl-4-carboxylic acid chloride*, **8**

The acids **7** (6 mmol) were reacted with oxalyl chloride (2·66 ml) in methylene chloride (6 ml) at reflux for 2 h under nitrogen atmosphere. After excess oxalyl chloride was completely removed, the precipitates were used immediately for the folllow-up reaction.

2.1.6. *4-Hydroxyphenyl 4′-alkoxybiphenyl-4-carboxylates*, **9**

Compound **8** (6 mmol) dissolved in methyl chloride was added dropwise to a mixture of hydroquinone (30 mmol), dried pyridine (5 ml) and THF (30 ml). The reaction mixture was cooled in a refrigerator for 2 d. Silica gel was then added to the mixture, dried and powdered. The product was collected by column chromatography over silica gel (70–230 mesh) using methylene chloride as eluent. Recrystalization from ethanol yielded 60–70 per cent of white precipitates was obtained.

2.1.7. *(R)-4-(3-Ethylmercapto-2-methylpropionyloxy)-phenyl 4′-alkoxybiphenyl-4-carboxylates, EMMPPmBC*

Compounds **7** (1·49 mmol) were reacted with compound **4** (0·2 g 1·35 mmol) by the treatment of DCC (0·389 g, 1·89 mmol) and DMAP (0·0165 g, 0·135 mmol) in anhydrous THF (6 ml) at room temperature for 2 d. After the work-up procedure, the products were isolated by silica gel (70–230 mesh) column chromatography using methylene chloride as eluent and purified by recrystallization from absolute ethanol. 30–50 per cent yield of white precipitates were obtained.

2.2. *Characterization of materials*

The chiral acid **5** was purified by vacuum distillation. The remaining intermediates and final products were isolated by column chromatography and further purified by recrystallization. All melting and boiling points were uncorrected. The purity of the final products was checked by thin layer chromatography (TLC) and further confirmed by elemental analysis using a Perkin–Elmer 2400 spectrometer. The chemical structures of all materials were analysed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy using a Bruker WP100SY FT-NMR spectrometer. The magnitudes of specific rotations were measured in dichloromethane using a JASCO DIP-360 digital polarimeter.

Transition temperatures and enthalpies were determined by differential scanning calorimetry (DSC) using a DuPont DSC-910 calorimeter at a rate of 3°C min^{-1}. Mesophases were identified by optical microscopy using a Nikon Microphot-FXA optical microscope under crossed polarizers with a Mettler FP82HT hot stage in connection with a Mettler FP82HT heat controller. Sample cells of each liquid crystal were fabricated by ITO glasses coated with unidirectionally buffed polyimide film. The cell gap is 5 μm and the electrically conducting area is 0·25 cm^2. D–E hysteresis loops were obtained by Diamant bridge method [17] when measured at both low and high frequencies.

3. Results and discussion

3.1. *Synthesis*

Michael addition reaction of mercaptoethane to *N*-methacryloylsultam **2** gave an excellent yield of diastereoisomeric mixtures, **3** and **4**. The isomeric ratio of **3**/**4** was found to be 19/1 based on the ^{1}H NMR spectrum. This result suggested that the reaction was carried out with a high degree of diastereoselectivity. In order to confirm the optical purity of the chiral acid **5**, the hydrolysis of **3** using lithium hydroxide was investigated in D_2O/THF solution. ^{1}H NMR analysis showed no deuterium incorporation in the product suggesting that no epimerization occurred during hydrolysis. The optical purity of the acid **5** could therefore be expected to be greater than 98 per cent. Chiral auxiliary **1** was recovered quantitatively after the hydrolysis of **3**, and could be used repeatedly after recrystallization form CH_2Cl_2/*n*-hexane. ^{1}H NMR spectroscopic analyses of the final products EMMPP*m*BC were consistent with the expected structures. The results of elemental analyses for EMMPP*m*BC, are shown in table 1. The percentage errors for carbon and hydrogen contents were satisfactorily less than 2 per cent as compared to the calculated results. All EMMPP*m*BC were expected to posssess high optical purity, since the esterification using DCC/DMAP [18] has been demonstrated to be free from epimerization. The specific rotations measured in dichloromethane are also summarized in table 1.

Table 1. Results of calculated (and found) elemental analyses and physical data of specific rotation for compounds EMMPP*m*BC.

Compounds	Elemental analysis/per cent		$[\alpha]_D^{26}$(conc.)†
	C	H	
EMMPP7BC	71·91 (70·74)	7·13 (7·26)	+ 36·1 (0·600)
EMMPP8BC	72·26 (71·66)	7·30 (7·29)	+ 33·9 (0·602)
EMMPP9BC	72·60 (71·96)	7·47 (7·35)	+ 32·4 (0·596)
EMMPP10BC	72·92 (72·64)	7·64 (7·70)	+ 29·3 (0·596)
EMMPP11BC	73·20 (72·60)	7·80 (7·67)	+ 28·4 (0·602)
EMMPP12BC	73·51 (72·82)	7·95 (7·94)	+ 32·6 (0·602)
EMMPP13BC	73·78 (73·64)	8·11 (8·07)	+ 29·7 (0·608)
EMMPP14BC	74·04 (73·82)	8·24 (8·14)	+ 28·8 (0·602)
EMMPP16BC	74·54 (74·85)	8·48 (8·55)	+ 25·8 (0·606)

† Solvent: dichloromethane, conc. units: g 100 ml^{-1}.

3.2. *Transition temperatures and mesophases*

The transition temperatures of the mesophases for EMMPP*m*BC were determined by DSC in conjunction with optical microscopy. The mesophase identification was carried out principally by optical microscopy. The Antiferroelectric $S_{C_A}^*$ phase was further characterized by D–E hysteresis loops [19].

Representative DSC heating and cooling thermograms obtained for EMMPP9BC are depicted in figure 1, and show that for the cooling process, the phase transitions are the isotropic liquid (I) to the S_A phase at 157·52°C, subsequently to the $S_{C_A}^*$ phase at 134·70°C, and followed by another two more ordered, unidentified smectic phases, S_3 and S_4. The transition from S_A to $S_{C_A}^*$, which appeared as a small step along the base line of the cooling trace, was further identified by the observation of textural changes from optical microscopy. In the case of heating run, the crystal (C) was first melted to the S_3 phase followed by successive transitions of S_3– $S_{C_A}^*$–S_A–I. The S_3 phase was rather unstable in the heating run as can be seen as a shoulder of the C–$S_{C_A}^*$ transition peak with a narrow temperature range. As a whole, the thermograms obtained

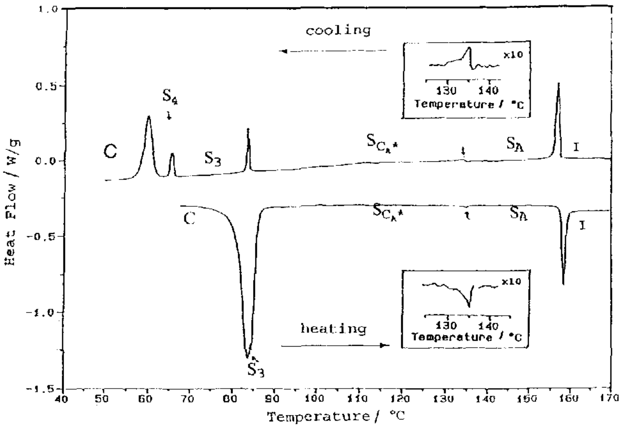


Figure 1. Heating and cooling thermograms for compound EMMPP9BC. The heating and cooling rate was 3°C min^{-1}.

Table 2. Transition temperatures (°C) and enthalpies (in parentheses) ($J\,g^{-1}$) for EMMPP*m*BC series on cooling.

Compound	I		S_A		$S^*_{C_A}$		S_3		S_4		C
EMMPP7BC	●	161·23 (6·12)	●	112·22 (0·077)	●	94·73 (4·16)	●	71·11 (3·30)			●
EMMPP8BC	●	160·36 (7·82)	●	125·53 (0·098)	●	91·33 (5·34)	●	71·69 (4·83)			●
EMMPP9BC	●	157·52 (10·38)	●	134·70 (0·297)	●	83·93 (5·91)	●	66·17 (6·89)	●	61·42 (54·69)	●
EMMPP10BC	●	156·19 (7·07)	●	137·38 (0·132)	●	82·22 (4·23)	●			64·94 (45·75)	●
EMMPP11BC	●	151·13 (5·52)	●	133·32 (0·100)	●					80·56 (58·27)	●
EMMPP12BC	●	153·06 (7·16)	●	140·46 (0·202)	●					82·89 (62·58)	●
EMMPP13BC	●	151·53 (5·79)	●	139·99 (0·094)	●					86·33 (60·30)	●
EMMPP14BC	●	150·94 (6·41)	●	139·91 (0·054)	●					86·46 (63·67)	●
EMMPP16BC	●	150·62 (5·49)	●	140·63 (0·030)	●					91·52 (53·50)	●

for the EMMPP*n*BC compounds show that the S_A, $S^*_{C_A}$ and S_3 mesophases are enantiotropic, whereas S_4 is monotropic.

The phase transition temperatures measured for all materials on the cooling stage are summarized in table 2. A phase diagram as function of the peripherial alkyl chain length *m* is plotted in figure 2. It shows that as *m* ascends, the I–S_A transition temperature falls, but as the S_A– $S^*_{C_A}$ transition temperature rises, the thermal stability of the S_A phase decreases. In the case of the $S^*_{C_A}$ phase, the thermal stability rises with increasing *m* from 7 to 10 and then remains unchanged upon further increases to 16. These results strongly suggest that a lengthened peripheral alkyl chain is favourable for the formation of the $S^*_{C_A}$ phase. Figure 2 also shows that the S_3 and S_4 phases occur at lower alkyl chain lengths; the former appears at $m < 10$ and the latter at $m < 9$, demonstrating that shorter alkyl chain length is favourable for the formation of higher ordered smectic phases.

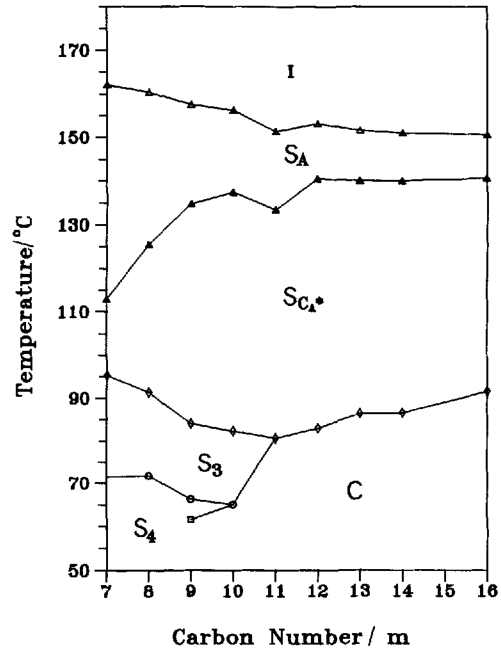


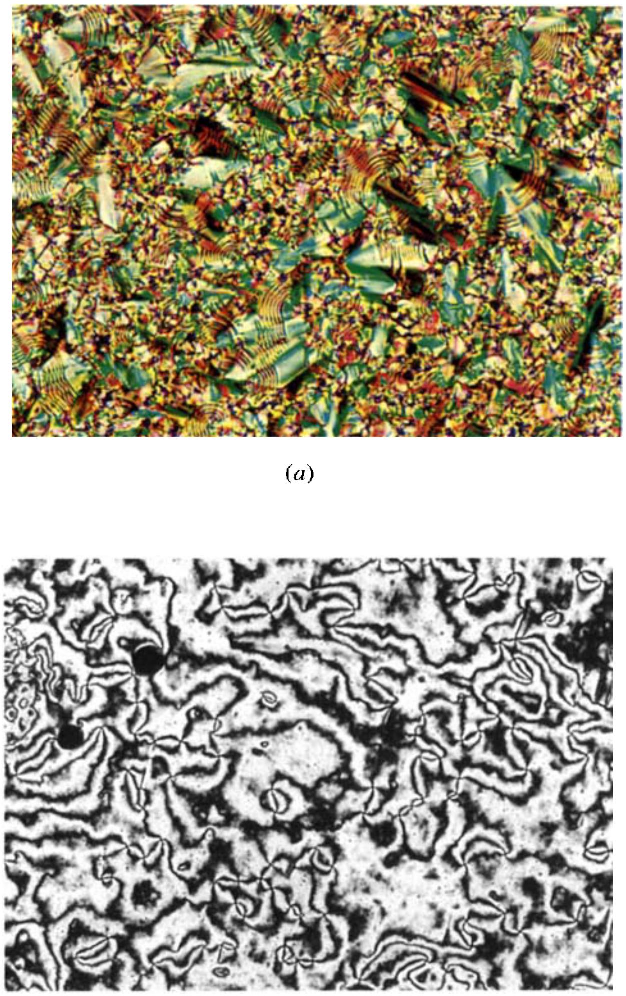
Figure 2. A plot of transition temperatures as function of the alkyl chain length for EMMPP*m*BC on cooling. △, I–S_A; ▲, S_A–$S^*_{C_A}$; ◇, $S^*_{C_A}$–S_3 or C; ○, S_3–S_4 or C; □, S_4–C.

The enthalpies were measured for each phase transition, the results of which obtained for the cooling scans are listed in table 2. It shows that the enthalpies for the I–S_A, $S^*_{C_A}$–S_3 and S_3–S_4 transitions are significantly large, and hence these transitions are first order. In the case of the S_A– $S^*_{C_A}$ transition, the enthalpy is rather small and is of second order. These small enthalpies for the S_A– $S^*_{C_A}$ transition are consistent with the view [9] that this phase change is not driven by a structural change as in other liquid crystalline transitions.

3.3. *Characterization of* $S^*_{C_A}$ *phase*

The first assignment of $S^*_{C_A}$ for EMMPP*m*BC was evidenced by polarizing optical microscopy. Test samples for each compound were prepared separately in a way such that thick and thin films formed on top of the slide covered with a cover slip without any surface treatment. The textures that appeared, for example of EMMPP10BC, are presented in figure 3. Figure 3 (*a*) shows the texture observed from a thick film, and figure 3 (*b*) from the thin film. A broken focal-conic fan texture was observed with the thick film, typical of the S^*_C phase. However, in the case of the thin film, a schlieren texture was observed. Furthermore, this schlieren texture appears to have singularities associated with both two ($s = \pm 1/2$) and four ($s = \pm 1$) brushes. The above textures provide evidence to the existence of the antiferroelectric $S^*_{C_A}$ phase [20].

Further investigation for the existence of the antiferroelectric phase for EMMPP*m*BC was performed using a Diamant Bridge by applying a sinewave with variant frequencies. Test samples were homogenously aligned in sandwich-packed glass cells coated with a buffed polyimide film. The cell gap was 5 μm and the electrically conducting area was $0{\cdot}25\,cm^2$. The results obtained for compound EMMPP10BC, as a typical example, are shown in figure 4. Figure 4 (*a*) shows a double hysteresis loop at a frequency of 1·05 KHz. This corresponds to a tristable switching between the antiferroelectric and ferroelectric



(*a*)

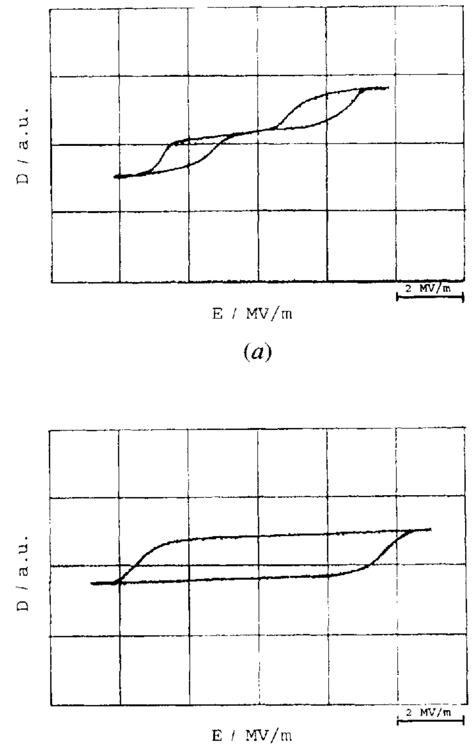
(*b*)

Figure 3. Optical micrographs of EMMPP10BC at 116°C, magnification × 400. (*a*) is a broken focal-conic fan texture for a thick film, and (*b*) is a schileren texture for a thin film.

states, and is characteristic of a stable antiferroelectric phase. This double loop changes to a single loop, as shown in figure 4(*b*), when the frequency is increased to 10·1 KHz. The change of switching behaviour has also been observed by several groups [10, 19, 21].

4. Conclusion

We have successfully synthesized a new chiral group, *R*-3-ethylmercapto-2-methylpropionic acid, with a high optical purity through the aid of chiral auxiliary D-(−)-2,10-camphorsultam. The derivatives of this chiral acid, EMMPP*m*BC, have been shown to exhibit the antiferroelectric $S_{C_A}^*$ phase by (i) the observance of a schlieren texture associated with both two and four brushes in a thin film, and (ii) the switching phenomena of a double hysteresis loops in D–E measurements. So far as we are aware, antiferroelectric liquid crystals containing an ester linkage with the –OCOC*– unit in the chiral tail of the molecules, instead of the –COOC*– unit found in most of the chiral materials [1, 7–12], are the first examples in this field of study. Moreover, the elongation of the alkyl chain length has been found to favour the formation of the $S_{C_A}^*$ phase in this series.



(*a*)

(*b*)

Figure 4. Hysteresis loops obtained by changing the frequecies, (*a*) 1·05 KHz and (*b*) 10·1 KHz, of applied voltage for compound EMMPP10BC at 119·1°C.

This work was supported by Tatung Company (Grant No. 81-1409-27) and the National Science Council (Grant No. NSC 82-0417-E036-022).

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