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

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To cite this Article Wu, S. -l. and Chen, F. -d.(2003) 'Novel chiral swallow-tailed amide liquid crystals possessing antiferroelectricity', Liquid Crystals, 30: 8, 991 — 995
To link to this Article: DOI: 10.1080/0267829031000148135
URL: http://dx.doi.org/10.1080/0267829031000148135

Liquid Crystals, Vol. 30, No. 8, August, 2003, 991–995

Novel chiral swallow-tailed amide liquid crystals possessing antiferroelectricity

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(*Received 17 March 2003; accepted 16 April 2003*)

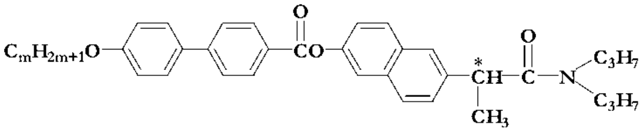
Novel chiral swallow-tailed amide materials, *N*,*N*-dipropyl-(*S*)-2-{6-[4-(4-alkoxyphenyl)-benzoyloxy]-2-naphthyl}propionamides, DP*m*PBNPA ($m = 9$–13), have been designed and synthesized for the investigation of mesomorphic properties. The materials DP*m*PBNPA ($m = 9$–11) display a monotropic phase sequence of I–SmA*–SmC$_A$*–Cr. The antiferroelectric SmC$_A$* phase for the materials was characterized by microscopic texture, switching behaviour, dielectric permitivity and electro-optical response. The measured maximum $\mathbf{P}_s$ values in the SmC$_A$* phase of the materials are in the range 80–87 nC cm^{-2}.

1. Introduction

It is generally acknowledged that the amide linkage in low molecular mass molecules may not be easily conductive to mesomorphism due to hydrogen bonding and/or the high polarization of the amide group leading to ease of crystallization. Consequently, only a few liquid crystal materials containing an amide linkage have been reported [1–4]. Among those materials, only one chiral liquid crystal has been reported to possess monotropic SmA* and unidentified SmX* phases [4]. So far as we are aware, no chiral liquid crystal materials with an amide linkage in the molecules and possessing an antiferroelectric SmC$_A$* phase have yet been found and reported.

The antiferroelectric SmC$_A$* phase in chiral liquid crystals exhibits a tristable switching property and has been extensively studied both experimentally and theoretically because of potential application in electric-optical devices [5]. Thus, many chiral materials, based on the first discovered structures of MHPOBC [5] and TFMHPOBC [6], have been synthesized and investigated. Subsequently, a correlation between the molecular structure of the materials and the appearance of antiferroelectric liquid crystals has been successfully reviewed [7].

In this work, we provide, for the first time, novel chiral swallow-tailed amide liquid crystals, the *N*,*N*-dipropyl-(*S*)-2-{6-[4-(4-alkoxyphenyl)benzoyloxy]-2-naphthyl}propionamides, DP*m*PBNPA ($m = 9$–13), that exhibit antiferroelectric properties. The characteristics of the molecular structure for these materials, as depicted below, are that (i) the chiral centre is directly attached to the naphthalene ring of the rigid core and (ii) an *N*,*N*-dipropylamino group serves as a swallow-tailed group reacting with (*S*)-2-(6-hydroxy-2-naphthyl)propionic acid to form an amide linkage that is directly attached to the chiral centre of the molecule. It has been reported that some non-chiral materials with swallow-tailed terminal moieties [8–10] are favourable for the formation of an 'antiferroelectric-like', so-called SmC$_{alt}$ phase, and can be doped with a small quantity of antiferroelectric liquid crystal to induce antiferroelectricity. Moreover, structurally similar chiral swallow-tailed materials, EP10PBNP, derived from (*S*)-2-(6-hydroxy-2-naphthyl)propionic acid with a swallow-tailed alcohol also exhibit an antiferroelectric phase [11, 12].



DP*m*PBNPA(m=9~11)

2. Experimental

2.1. *Synthesis*

The synthetic procedures for these chiral materials were carried out as depicted in the scheme. (*S*)-2-(6-Methoxy-2-naphthyl)propionic acid was treated with oxalyl chloride, in dichloromethane to give the acid chloride. The resulting acid chloride was then added dropwise to a solution of *N*,*N*-dipropylamine and triethylamine in dry dichloromethane to produce

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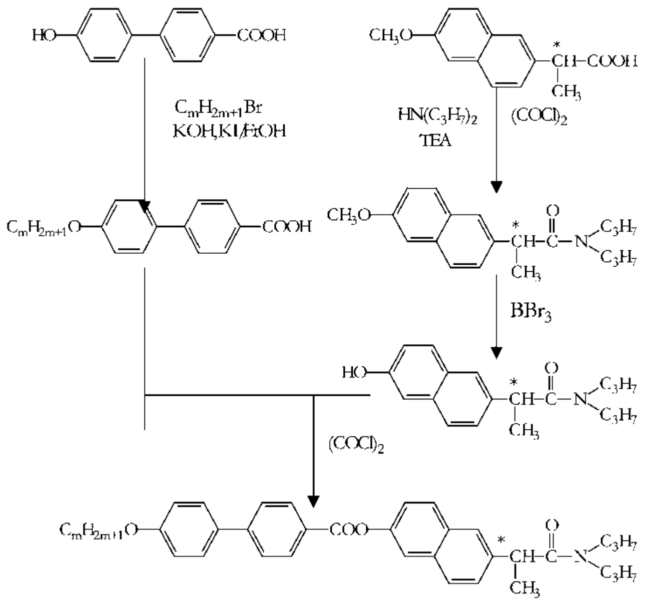
Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2003 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/0267829031000148135



DP*m*PBNPA(*m*=9~13)

Scheme. Synthetic procedures for the chiral amide materials DP*m*PBNPA ($m = 9$–13).

(*S*)-2-(6-methoxy-2-naphthyl)propionamide. The methoxy group of this amide was demethylated by treatment with boron tribromide [13], and hydroxy group of the resulting compound *N*,*N*-dipropyl (*S*)-2-(6-hydroxy-2-naphthyl)propionamide was treated with 4-(4-alkoxyphenyl)benzoyl chloride (previously prepared by the treatment of 4-(4-alkoxyphenyl)benzoic acid with oxalyl chloride) to obtain the target materials.

2.1.1. *N,N-Dipropyl-(S)-2-(6-methoxy-2-naphthyl)-propionamide*

Oxalyl chloride (9.5 ml, 108.67 mmol) was added slowly to (*S*)-(6-methoxy-2-naphthyl)propionic acid (10 g, 43.43 mmol), and the resulting solution heated under reflux with stirring for 2 h. Excess oxalyl chloride was removed by evaporation under reduced pressure. The crude (*S*)-2-(6-methoxy-2-naphthyl)propionic acid chloride in dichloromethane (10 ml) was added to a solution of dipropylamine (22.33 ml, 126.85 mmol) and triethylamine (10 ml) in anhydrous dichloromethane (30 ml) with stirring in an ice bath. After some solids had been produced, the mixture was placed in a refrigerator overnight. The mixture was evaporated to dryness under reduced pressure and the residue purified by column chromatography over silica gel (70–230 mesh ASTM) using dichloromethane/ethyl acetate (v/v = 8/2) as eluent. The product was obtained in about 70% yield. Chemical shifts by ^{1}H NMR: δ (ppm, $CDCl_3$) 0.9–1.1 (m, 6H, $N(CH_2CH_2C\mathbf{H_3})_2$), 1.4–1.5 (m, 4H, $N(CH_2C\mathbf{H_2}CH_3)_2$), 1.6 (d, 3H, $C^*H(C\mathbf{H_3})$), 3.0–3.6 (m, 4H, $N(C\mathbf{H_2}CH_2CH_3)_2$), 3.9 (s, 3H, $C\mathbf{H_3}O$) 3.9–4.0 (m, 1H, ArC*$\mathbf{H}$), 7.1–7.7 (m, 6H, Ar$\mathbf{H}$).

2.1.2. *N,N-Dipropyl-(S)-2-(6-hydroxy-2-naphthyl)-propionamide*

N,*N*-dipropyl-(*S*)-2-(6-methoxy-2-naphthyl)propionamide (8 g, 26.76 mmol) dissolved in dry dichloromethane (52.36 ml) was mixed with boron tribromide (5.24 ml) at −20°C. The mixture was stirred at −20°C for 5 min, and at 0°C for 40 min. After diluting with dry dichloromethane (104 ml), the solution was poured into a mixture of saturated ammonium chloride (104 ml) and crushed ice (100 g). The organic layer was separated and washed with brine–ice, dried over anhydrous sodium sulfate, and concentrated in vacuum. The pure product was collected in about 51% yield after recrystalization from acetonitrile. Chemical shifts by ^{1}H NMR: δ (ppm, $CDCl_3$) 0.9–1.2 (m, 6H, $N(CH_2CH_2C\mathbf{H_3})_2$), 1.4–1.5 (m, 4H, $N(CH_2C\mathbf{H_2}CH_3)_2$), 1.6 (d, 3H, $C^*H(C\mathbf{H_3})$), 3.0–3.7 (m, 4H, $N(C\mathbf{H_2}CH_2CH_3)_2$), 3.9–4.0 (m, 1H, ArC*$\mathbf{H}$), 5.7–5.8 (s, 1H, O$\mathbf{H}$), 7.0–7.8 (m, 6H, Ar$\mathbf{H}$).

2.1.3. *N,N-Dipropyl-(S)-2-{6-[4-(4-alkoxyphenyl)-benzoyloxy]-2-naphthyl}propionamides, DPmPBNPA (m = 9–13)*

Oxalyl chloride (0.35 ml, 1.58 mmol) was added slowly to the 4-(4-alkoxyphenyl)benzoic acid (1.05 mmol) and the resulting solution heated under reflux with stirring for 2 h. Excess oxalyl chloride was removed by evaporation under reduced pressure. The crude acid chloride in dichloromethane (3 ml) was added to a mixture of *N*,*N*-dipropyl-(S)-2-(6-hydroxy-2-naphthyl)-propionamide (0.3 g, 1.05 mmol) and pyridine (5 ml) in dichloromethane (5 ml) with stirring in an ice bath. When precipitation began the mixture was placed in a refrigerator overnight. The solution was evaporated to dryness under reduced pressure and the residue purified by column chromatography over silica gel (70–230 mesh ASTM) using dichloromethane/ethyl acetate (v/v = 8/2) as eluent. A yield of about 60% of white product was obtained. Chemical shifts by ^{1}H NMR for a sample of $C_{41}H_{51}O_4N$: δ (ppm, $CDCl_3$) 0.96 (t, 3H, $RCH_2C\mathbf{H_3}$), 1.00–1.15 (t, 6H, $N(CH_2CH_2C\mathbf{H_3})_2$), 1.24–1.64 (m, 12H, $(C\mathbf{H_2})_6$), 1.33–1.44 (m, 4H, $N(CH_2C\mathbf{H_2}CH_3)_2$), 1.55(d, 3H, $C^*H(C\mathbf{H_3})$), 1.82–1.91 (q, 2H, $ArOCH_2C\mathbf{H_2}$), 2.90–3.60 (m, 4H, $N(C\mathbf{H_2}CH_2CH_3)_2$), 3.9–4.0 (m, 1H, ArC*$\mathbf{H}$), 3.99–4.10 (m, 2H, $ArOC\mathbf{H_2}$), 7.00–8.30 (m, 14H, Ar$\mathbf{H}$). Elemental analysis data are summarized in table 1.

Table 1. Elemental analysis for compounds DP*m*PBNPA ($m = 9$–13).

	Theoretical/%			Experimental/%		
m	C	N	H	C	N	H
9	79.23	2.25	8.21	79.29	2.23	8.29
10	79.37	2.20	8.35	79.19	2.18	8.40
11	79.51	2.16	8.47	79.39	2.15	8.52
12	79.64	2.11	8.60	79.58	2.12	8.68
13	79.76	2.07	8.71	79.59	2.07	8.78

2.2. *Characterization*

The purity of the target materials was determined by elemental analysis using a Perkin-Elmer 2400 spectrometer. The chemical structure was identified by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy using a Bruker WP100SY FTNMR spectrometer. Transition temperatures and enthalpies of transition for the liquid crystals were determined by differential scanning calorimetry using a Perkin-Elmer DSC7 calorimeter at a rate of 2°C min^{-1}. Mesophases were identified by the observation of textures using a Nikon Microphot-FXA optical microscope under crossed polarizers with an INSTEC HS1 hot stage in connection with a RTC heating controller. Sample cells were purchased from E. H. C. Co. Japan. Cells of 5 and 25 μm thickness with 1 and 0.25 cm^2 conducting area, respectively, were fabricated by coating with unidirectionally buffed polyimide film. Switching behaviour and electro-optical response of the antiferroelectric smectic phase were investigated by the triangular wave method [14].

3. Results and discussion

The mesophases, transition temperatures, and enthalpies of transition for the materials are listed in table 2. The SmA* phase was characterized by the appearance of focal-conic and pseudo-homeotropic textures. The SmC$_A$* phase appeared as a striated focal-conic texture and was further characterized by the appearance of the two-brush defect [15–17] in the schlieren texture. Three materials (DP*m*PBNPA; $m = 9$–11) exhibited monotropic SmA* and SmC$_A$* mesophases. The thermal stability of the SmC$_A$* phases increased as *m* increased. However, with $m \geqq 12$, the chiral materials became non-mesogenic.

The switching behaviors of the materials in the SmC$_A$* phase were measured and representative results for DP11PBNPA are presented in figure 1. Two switching current peaks appeared, similar to the normal SmC$_A$* phase [18], supporting the existence of an antiferroelectric SmC$_A$* phase.

Table 2. Transition temperatures T(°C) and enthalpies ΔH(J g^{-1}) (in square brackets) of the transitions for materials DP*m*PBNPA ($m = 9$–13) measured by DSC at 2°C min^{-1} scanning rate during cooling.

m	Iso		SmA		SmC$_A$*		Cr	m.p.^{b}
9	●	(83.58)^a [−2.81]	●	(73.96) [−0.26]	●	(70.01) [−31.01]	●	101.91 [75.89]
10	●	(80.68) [−2.93]	●	(72.44) [−0.38]	●	(54.92) [−31.34]	●	83.79 [43.03]
11	●	(95.70) [−3.61]	●	(86.63) [−0.62]	●	(58.70) [−37.47]	●	105.00 [67.78]
12	●		—		—	(68.26) [60.64]	●	90.92 [77.19]
13	●		—		—	(69.45) [61.70]	●	91.04 [66.95]

[a] The parentheses denote a monotropic phase transition.

[b] m.p. refers to the melting point taken from DSC thermograms recorded at heating rates of 2°C min^{-1}.

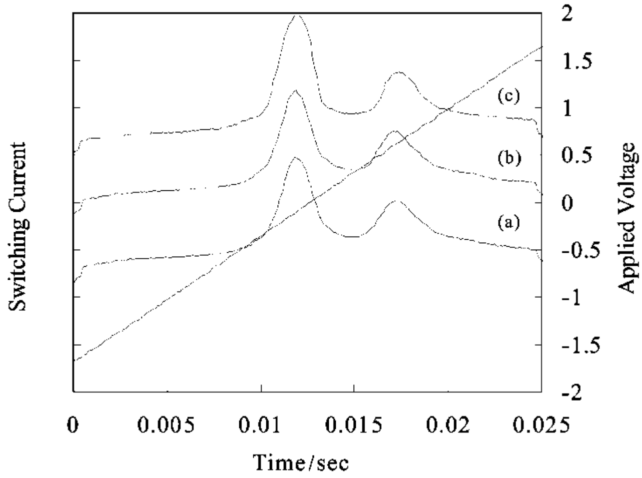


Figure 1. Switching behaviour of compound DP11PBNPA in the SmC$_A$* phase at (a) 65°C, (b) 64°C and (c) 63°C.

Further investigation of the characteristics of the SmC$_A$* phase was conducted by recording the electro-optical response of the material in a 5 μm homogeneously aligned cell at varying temperature and frequency. The response is critically dependent on temperature and frequency. The electro-optical response of DP11PBNPA showed an ideal double hysteresis at 62–67°C at 5 Hz in the SmC$_A$* phase, as shown in figure 2. This corresponds to tristable switching in the antiferroelectric state [5, 19], and is characteristic of a stable antiferroelectric phase.

Figure 3 shows the temperature dependence of the dielectric constant ε′ for the representative material DP11PBNPA. The ε′ in the SmA* phase is small and increases at the SmA* to SmC$_A$* phase transition. The characteristic point, corresponding to the SmA* to SmC$_A$* phase transition, is seen as a small peak at

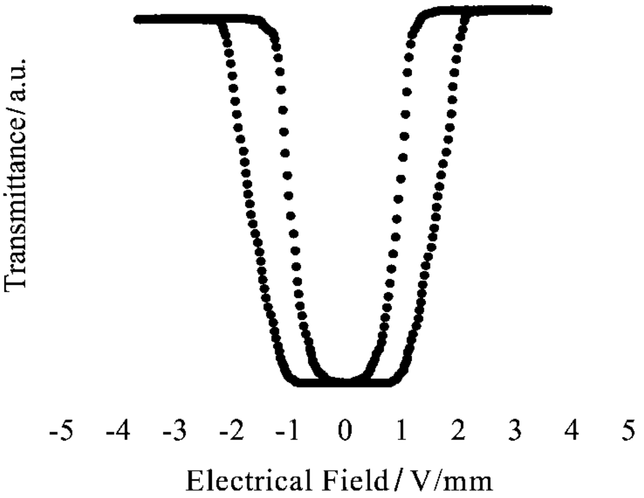


Figure 2. The electro-optical response of compound DP11PBNPA in the SmC$_A$* phase measured at a frequency of 5 Hz and a temperature of 65°C.

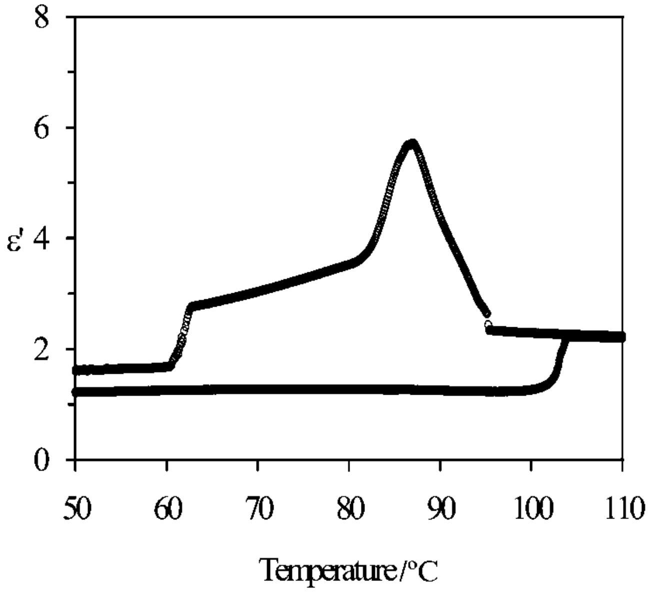


Figure 3. Temperature dependence of the dielectric constant ε′ measured in compound DP11PBNPA at 10 kHz.

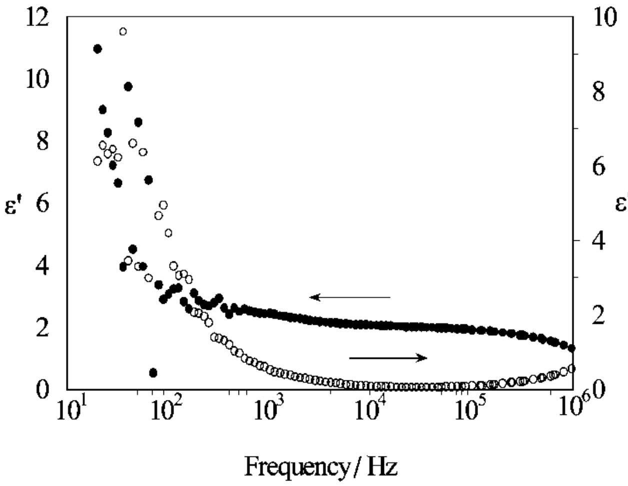


Figure 4. Dispersion and absorption curves of compound DP11PBNPA plotted as ε′ (●) and ε″ (○) versus frequency in the SmC$_A$* phase at 65°C.

approximately 87°C. The enhancement of dielectric constants in the antiferroelectric phase has been attributed to the vibration of the azimuthal molecular motion [20]. More detailed macro- and micro-molecular motions of molecules in the SmC$_A$* phase, investigated by the frequency dependence of dispersion and absorption curves, are represented in figure 4. The results show that both the real and imaginary parts of the dielectric constants are large but not quite stable at the frequencies <1 kHz due to effect of existing ions. It can also be seen that the real part of the dielectric constant shows a tendency to diverge, accompanied with a consistent increase of the imaginary loss, at higher frequencies, of 10^5–10^6 Hz. This feature is seen in the empty cell and is presumably due to the effect of the polyimide and/or ITO films. Thus, there is no significant occurrence of the relaxation process in the SmC$_A$* phase, as was detected in MHPOBC [21, 22].

Spontaneous polarization for the materials in the SmC$_A$* phase was measured as a function of temperature on cooling in 5 μm homogeneous cells, with results illustrated in figure 5. It is seen that the **P**$_s$ values of the three compounds illustrated increase as the temperature

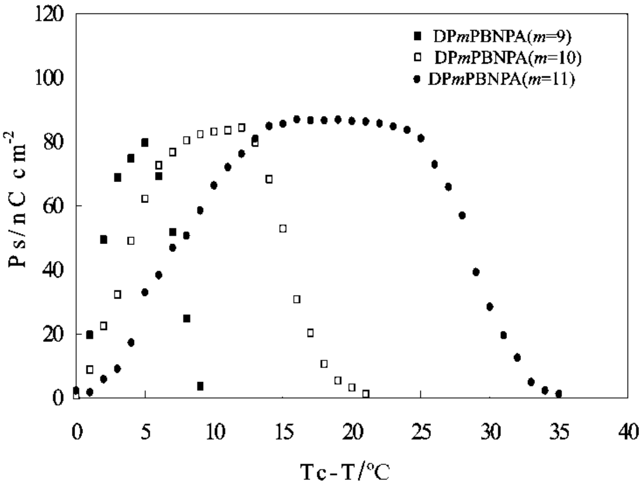


Figure 5. Spontaneous polarization plotted as a function of temperature for DP*m*PBNPA (m=9–11). T_c is the temperature of the SmA*–SmC$_A$* phase transition.

increases from T_c-$T = 0$ K, reaching a maximum of 80–87 nC cm^{-2}, then decrease gradually until the materials crystallize. The gradually decrease in $\mathbf{P}_s$ values is presumably because the antiferroelectric phase is monotropic and the gradual crystallization decreases the polarization. The $\mathbf{P}_s$ values of these chiral amide materials are about 2.6 times that of the structurally similar chiral ester material EP10PBNP [11, 12]. Model calculations using Hyperchem AM1 for the calculation of the dipole moments for the representatively simplified molecules: *N*,*N*-dimethylacetamide and methyl acetate, gave dipole moments of 3.175 B and 1.739 dB, respectively, suggesting that the amide linkage in the molecule gives the higher dipole moment. It can then be rationalized that higher $\mathbf{P}_s$ values for the chiral amide materials may be attributed to the stronger dipolar amide linkage group, generating stronger electrostatic interactions among the molecules in the smectic layer and/or between the interlayer molecules.

4. Conclusions

In summary, three novel chiral swallow-tailed amide materials, DP*m*PBNPA ($m = 9$–11), have been demonstrated to possess antiferroelectric SmC$_A$* phases. These materials provide high polarization and are feasible for use in antiferroelectric mixtures for the display devices. These materials also provide a new molecular design for antiferroelectric liquid crystals for future study.

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