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Novel antiferroelectric liquid crystals with a phenylpiperazine moiety in the mesogenic core structure

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A novel series of antiferroelectric liquid crystalline compounds having a phenylpiperazine unit and a biphenyl or a phenyl moiety in the core structure was synthesized using the optically active alcohols 2-methyl octanol and 1,1,1-trifluoromethyl octanol. Most of the compounds exhibited enantiotropic SmC_A^*, SmC* and SmA mesophases. The phase transition temperatures, response times, spontaneous polarizations and the field-transmittance hysteresis loops were monitored. These data were compared with those of the MHPOBC compounds, which represent the most conventional core structure of the biphenyl/phenyl combination. The replacement of the biphenyl moiety, with the phenylpiperazine unit, reduced the isotropization temperature as well as the SmC_A^*–SmC transition point. It was found that some of the new compounds, which consisted of an octyl or a nonyl terminal chain with a 2-methyloctyl 2-fluorophenylcaboxylate group in the core structure, could have a potential application in display devices. Some work on blends of these compounds is also described.

1. Introduction

Following the discovery of tristable switching [1] and antiferroelectricity [2] in chiral smectic liquid crystals, considerable efforts have been directed to explore their application potential, in particular in the field of display technology. In contrast to conventional nematic liquid crystals, ferroelectric (SmC*) and anti-ferroelectric (SmC_A^*) liquid crystals offer the possibility of producing flat panel displays with such promising characteristics as: wide screen, high resolution and excellent image quality [3–5]. At the same time, shock resistance and well defined electric field threshold for switching can be considered as some salient features of the SmC_A^* phase as compared with the SmC* phase [1].

As a consequence of research in this field, a prototype full colour display device with a high contrast ratio has been developed [6]. However, so far, display manufacturers have been unable to commercialize AFLC display devices despite continuous efforts. It seems that there are still several material requirements to be optimized. To be highly utilizable in display devices, an AFLC material should possesses such vital requirements as: a broad SmC_A^* phase near room temperature, a fast response time, low rotational viscosity, large spontaneous polarization and a well defined electric field threshold. However, the structural requirements for the appearance of the SmC_A^* phase, as well as the structure–property relationship of AFLC materials are not yet understood well enough to optimize the material parameters.

In an AFLC molecule, it is believed that electrical properties such as spontaneous polarization and response time depend on the polar group neighbouring the chiral centre, whereas other properties such as rotational viscosity and molecular alignments largely depend on the core structure of the molecule. During the last few years much research has been carried out to clarify the structure–property relationship of AFLC materials, where in many cases the core structure has consisted of the biphenyl/phenyl combination. Major drawbacks of the biphenyl/phenyl system are that (1) in many of these compounds the SmC*–SmC_A^* transition temperatures seem to be far above room temperature and (2) the appearance of the highly ordered SmI_A^* phase in the low temperature region. When the biphenyl moiety is replaced by a phenyl ring, to give compounds with a phenyl/phenyl combination, the melting points are very low and the SmC*–SmC_A^* transition points are well below room temperature. In addition, only a few AFLC compounds with other core structures, especially with heterocyclic [7–12] and alicyclic [13, 14] units have been reported. Therefore, it is clearly useful to focus more attention on the synthesis of new AFLCs having core structures different from the conventional biphenyl/phenyl system, in order to generate broad range room temperature SmC_A^* phases. Herein, we describe the synthesis and mesomorphic properties of a new homologous series of AFLC compounds having a phenylpiperazine moiety in the core structure.

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2. Experimental

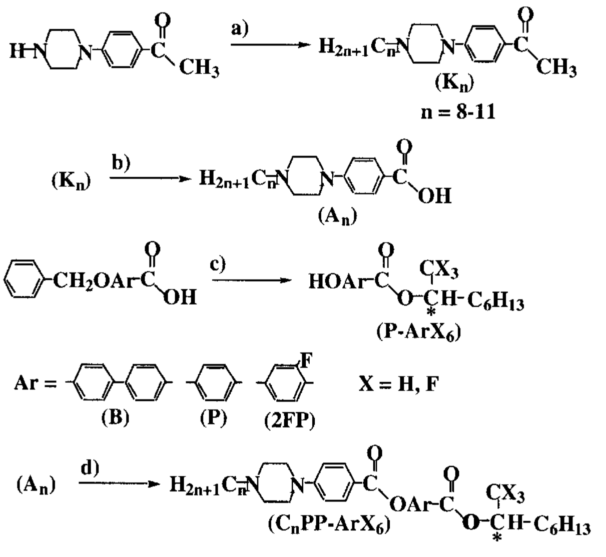
2.1. *Measurements*

^{1}H NMR spectra were recorded on a JEOL JNM-GX 270 spectrometer; obvious multiplicity and routine coupling constants are normally not listed here. High performance liquid chromatography (HPLC) was performed with a Shimadzu LC-10AD instrument with a Wakosil 5C18 stationary phase using acetonitrile and tetrahydrofuran (96:4) as the eluent. DSC was carried out with a Rigaku DSC-8240D instrument with a TAS 200 data analysis system, at a heating and cooling rate of 0.1 °C min^{-1} under a N_2 atmosphere in both heating and cooling modes. The phase transition temperatures and mesophase identification of the final products were determined by DSC, polarized optical microscopy (using an Olympus BH2 microscope equipped with a Mettler FP2 temperature controller) and electro-optical measurements, which were made in liquid nitrogen cooling systems. Homogeneously aligned cells were prepared as reported by Negi *et al.* [15]. The spontaneous polarization was measured by the triangular wave voltage method (± 100 V, 30 Hz). The response time was determined by applying a rectangular wave voltage of ± 40 V or ± 50 V at 1 Hz.

2.2. *Synthesis*

The reaction procedure for the preparation of these liquid crystal materials is given in the scheme. Detailed procedures for the preparation of starting chiral alcohols, (*R*)-(+)-2-octanol and (*R*)-(+)-1,1,1-trifluoro-2-octanol as well as phenols, P-ArX$_6$, are given in the literature [16].

Reaction Scheme



a) $CHCl_3$ and EtOH (1:1) / diisopropylamine / $C_nH_{2n+1}Br$ / refluxed 16h. b) i. Dioxane and H_2O (10:4) / NaOBr / 10° C 1h / r. t. 2h. ii. Na_2SO_3 in H_2O / 5% HCl c) i. $SOCl_2$ / refluxed 2h ii. CH_2Cl_2 / HO-CH(CX_3)C_6H_{13} iii. EtOH / Pd-C (10%) / H_2 d) i. SOCl2 / DMSO (few drops) / refluxed 2h ii. P-ArX$_6$ / CH_2Cl_2

2.2.1. *4-(N-decylpiperazino)acetophenone (K_{10})*

1.02 g (5 mmol) of 4-piperazinoacetophenone was dissolved in 5 ml of a mixture of $CHCl_3$ and ethanol (1:1) and to this was added 1.105 g (5 mmol) of decylbromide and 0.505 g (5.5 mmol) of diisopropylamine; the mixture was heated under reflux for 16 h. The mixture was then cooled and solid matter filtered off. The pale yellow solid mass obtained from the filtrate after solvent evaporation was purified by column chromatography on alumina with a mixture of hexane and ethylacetate (10:4); $R_f = 0.75$, yield 80%. ^{1}H NMR ($CDCl_3$, δ, ppm) 7.89 (2H, d, ArH), 6.86 (2H, d, ArH), 3.40 (4H, t, NCH_2), 2.60 (4H, t, NCH_2), 2.55 (3H, s, $COCH_3$), 2.40 (2H, dd, NCH_2), 1.63–1.44 (2H, m, CH_2CH_2N), 1.40–1.20 (14H, m, $7CH_2$), 0.92 (3H, t, CH_3).

2.2.2. *4-(N-decylpiperazino)benzoic acid (A_{10})*

1.38 g (4 mmol) of compound K_{10} was dissolved in a mixture of dioxane (100 ml) and distilled water (40 ml), and the solution was cooled below 8°C. Then, 35.5 ml (35.5 mmol) of NaOBr, previously prepared from NaOH and Br_2 in dioxane/water mixture, was added as a steady stream. The mixture was stirred for 1 h below 10°C and then for 2 h at room temperature. At the end of the reaction, 0.30 g of Na_2SO_3 in 20 ml of water was added, and the mixture boiled for 1 h. Finally, the mixture was neutralized with 5% HCl, and poured into an excess of cold water. The resulting pale yellow solid mass was filtered off and purified by column chromatography on silica gel with a mixture of hexane and ethylacetate (1:1); $R_f = 0.15$, yield 55%, m.p. 33–34°C. Other carboxylic acids A_8, A_9, and A_{11} were prepared by the same procedure. ^{1}H NMR of all four carboxylic acids were identical: ($CDCl_3$, δ, ppm) 7.94 (2H, d, ArH), 7.43–7.00 (1H, bs, COOH), 6.86 (2H, d, ArH), 3.40 (4H, t, NCH_2), 2.76 (4H, t, NCH_2), 2.50 (2H, dd, NCH_2), 1.70–1.46 (2H, m, CH_2), 1.40–1.13 (2(n-3)H, m, $7CH_2$), 0.90 (3H, t, CH_3).

2.2.3. *4-[(R)-(+)-1-methylheptyloxycarbonyl]phenyl 4-(N-decylpiperazino)benzoate ($C_{10}PP$-PH_6)*

In a flask, 0.70 g (2 mmol) of A_{10} was reacted with an excess of $(COCl)_2$ in 1,1-dichloroethane at 60°C for 3 h. Excess $(COCl)_2$ and the solvent were removed by evaporation. The product was dissolved in 5 ml of CH_2Cl_2 and the solution added dropwise to a mixture of 0.50 g of 1-methylheptyl 4-hydroxybenzoate and 0.22 g (2.2 mmol) of triethylamine in 4 ml of CH_2Cl_2. After the reaction mixture was stirred for 24 h at 30°C under a N_2 atmosphere, it was washed with water and then dried over anhydrous Mg_2SO_4. The product was purified by column chromatography on alumina with a mixture of hexane and ethylacetate (10:1); $R_f = 0.43$, yield 78%.

Ten liquid crystal compounds were prepared by the same procedure. ^{1}H NMR ($CDCl_3$, δ, ppm) data of some representative compounds are given below.

C_{10}PP-PH$_6$: 8.17–8.00 (4H, m, ArH), 7.33–7.23 (2H, d, ArH), 6.93–6.83 (2H, d, ArH), 5.23–5.09 (1H, m, CH), 3.40 (4H, t, NCH_2), 2.60 (4H, t, NCH_2), 2.50 (2H, dd, NCH_2), 1.80–1.20 (29H, m, $CH_3 + 13(CH_2)$), 0.97–0.80 (6H, m, $2CH_3$).

C_{10}PP-PF$_6$: 8.23–7.97 (4H, m, ArH), 7.32 (2H, d, ArH), 6.89 (2H, d, ArH), 5.46–5.26 (1H, m, CH), 3.40 (4H, t, NCH_2), 2.60 (4H, t, NCH_2), 2.40 (2H, dd, NCH_2), 1.97–1.83 (2H, m, CH_2), 1.63–1.14 (24H, m, $14CH_2$), 1.00–0.80 (6H, m, $2CH_3$).

C_{10}PP-BH$_6$: 8.20–8.00 (4H, dd, ArH), 7.75–7.60 (4H, m, ArH), 7.31 (2H, d, ArH), 6.91 (2H, d, ArH), 5.31–5.11 (1H, m, CH), 3.44 (4H, t, NCH_2), 2.64 (4H, t, NCH_2), 2.42 (2H, dd, NCH_2), 1.91–1.18 (29H, m, $CH_3 + 13CH_2$), 1.00–0.80 (6H, m, $2CH_3$).

C_{10}PP-BF$_6$: 8.20–8.00 (4H, dd, ArH), 7.75–7.60 (4H, m, ArH), 7.31 (2H, d, ArH), 6.93 (2H, d, ArH), 5.67–5.49 (1H, m, $CHCF_3$), 3.40 (4H, t, NCH_2), 2.60 (4H, t, NCH_2), 2.40 (2H, dd, NCH_2), 2.00–1.12 (26H, m, $13CH_2$), 0.97–0.80 (6H, m, $2CH_3$).

C_{10}PP-2FPH$_6$: 8.09 (2H, d, ArH), 7.92 (1H, m, ArH), 7.12–7.00 (2H, m, ArH), 6.91 (2H, d, ArH), 5.17 (1H, m, CH), 3.40 (4H, t, NCH_2), 2.60 (4H, t, NCH_2), 2.40 (2H, dd, NCH_2), 1.80–1.20 (29H, m, $CH_3 + 13CH_2$), 0.96–0.80 (6H, m, $2CH_3$).

3. Results and discussion

3.1. *Synthesis*

The synthetic procedure for the new AFLC compounds is outlined in the reaction scheme. The starting chiral alcohols (*R*)-(+)-1,1,1-trifluoro-2-octanol and (*R*)-(+)-2-octanol were prepared by the method of Suzuki *et al.* [16]. The enantiomeric excess of the compounds was found to be 90–95%. Optically active phenols, P-ArX$_6$, were prepared starting from 4-benzyloxybenzoic acid or 4-benzyloxy 2-fluorobenzoic acid by the following sequence of procedures: protection of the hydroxyl group, conversion to acid chloride, esterification with chiral alcohol and finally deprotection of the hydroxyl function.

The basic synthesis product, 4-(*N*-alkylpiperazino)-benzoic acid (A), could be obtained by a two step procedure starting from commercially available 4-piperazinoacetophenone. In the first step, *n*-alkylation was carried out with alkylbromide to yield 80% 4-(*N*-alkylpiperazino)-acetophenone. Secondly, the ketone group was oxidized with NaOBr, followed by acidification which gave a 50% yield of the corresponding acid. Finally, 4-(*N*-alkylpiperazino)benzoic acid was converted to the acid chloride and this was then coupled with optically active phenol (P-ArX$_6$) to give the final AFLC ester compound (C_nPP-ArX$_6$). The final product was purified by column chromatography on alumina using a mixture of hexane and EtOAc (10:1) as the eluent and recrystallized from EtOH.

3.2. *Liquid crystalline properties*

The phase behaviour of the compounds prepared was assessed by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and electro-optical measurements. The phase sequences and transition temperatures of all the liquid crystal homologues are summarized in table 1. As can be seen, most of the compounds exhibited enantiotropic SmC* and SmC_A^* mesophases over a wide range of temperatures. In addition, these compounds exhibited the SmA phase, which is an important feature for preparing well-aligned homogenous samples.

In this series of compounds, if there is a biphenyl moiety adjacent to the chiral centre (compounds C_{10}PP-BH$_6$ and C_{10}PP-BF$_6$), the melting points (T_m) and isotropization points (T_I) are noticeably high. As it is well known, stronger electron conjugation along the liquid

Table 1. Liquid crystalline properties of the new AFLC compounds.

Compound	Phase transition temperatures/°C	
	Heating	Cooling
C_8PP-PF$_6$	Cr 39.8 SmC$_A$ 57.0 SmA 69.0 I	Cr – 2.4 SmC$_A$ 55.0 SmA 68.2 I
C_8PP-2FPF$_6$	Cr 43.7 SmC$_A$ 57.4 SmA 59.6 I	Cr 7.9 SmC$_A$ 56.9 SmA 59.1 I
C_8PP-2FPH$_6$	Cr 41.1 SmC$_A$ 78.4 SmC 80.9 SmA 103.6 I	Cr – 0.8 SmC$_A$ 77.1 SmC 80.6 SmA 103.0 I
C_9PP-2FPH$_6$	Cr 38.8 SmC$_A$ 78.7 SmC 84.7 SmA 101.9 I	Cr – SmI$_A$ 40.0 SmC$_A$ 77.6 SmC 83.8 SmA 101.9 I
C_{10}PP-2FPH$_6$	Cr 44.8 SmC$_A$ 81.8 SmC 84.9 SmA 100.0 I	Cr – 50 SmI$_A$ 45.0 SmC$_A$ 81.5 SmC 84.8 SmA 99.5 I
C_{10}PP-PF$_6$	– SmC$_A$ 55.6 SmC 56.8 SmA 63.9 I	< – 50 SmC$_A$ 54.5 SmC 56.6 SmA 68.2 I
C_{10}PP-PH$_6$	Cr 72.4 SmC$_A$ 85.8 SmC 89.9 SmA 106.3 I	Cr 67.5 SmC$_A$ 85.0 SmC 89.3 SmA 68.2 I
C_{10}PP-BH$_6$	Cr 89.5 SmI$_A$ 116.8 SmC 159.9 SmA 211 I	Cr 21.4 SmI$_A$ 116.1 SmC 159.2 SmA 210.1 I
C_{10}PP-BF$_6$	Cr 100.8 SmC$_A$ 126 SmC 166.6 SmA 208 I	Cr 84.7 SmC$_A$ 122.9 SmC 165.8 SmA 208 I
C_{11}PP-2FPH$_6$	Cr 42.7 SmC$_A$ 83.3 SmC 86.1 SmA 98.5 I	Cr – SmI$_A$ 48.0 SmC$_A$ 82.2 SmC 85.0 SmA 98.4 I

crystalline molecule, as well as the higher molecular weight, may be related to higher T_m and T_I values as compared with those of phenyl counterparts. Compound C$_{10}$PP-BH$_6$, which contains a CH$_3$ group at the chiral centre, did not exhibit a SmC$_A^*$ mesophase while its CF$_3$ homologue (C$_{10}$PP-BF$_6$) did. However, as the SmC$_A^*$ temperature range lies well above room temperature (84.7–122.9°C), we believe that there is little possibility to use these compounds in display devices. Therefore, in order to bring down the T_m and T_I, as well as to get a room temperature SmC$_A^*$ phase, the biphenyl moiety of these compounds was replaced with a phenyl ring. This change led to a drastic decrease in T_m and T_I; for most of the compounds these temperatures were found to be around 40 and 100°C, respectively. Moreover, during the cooling process the SmC$_A^*$ phase persisted below room temperature, i.e. SmC$_A^*$–Cr transition temperatures for compounds C$_{10}$PP-PF$_6$, C$_8$PP-PF$_6$ and C$_8$PP-2FPF$_6$ were found to be < -50, 2.4 and -0.8°C, respectively.

If we compare the mesophase properties of compounds C$_8$PP-2FPH$_6$ and C$_8$PP-2FPF$_6$, which contain a CH$_3$ group and a CF$_3$ group at the chiral centre, respectively, a drastic decrease of T_I can be seen in the latter compound. In addition, in this compound and also in compound C$_8$PP-PF$_6$, a direct SmA–SmC$_A^*$ transition without a SmC* phase could be observed. This suggests that the highly polar CF$_3$ group stabilizes the antiferroelectric ordering. Furthermore, comparison of compounds C$_{10}$PP-PF$_6$ with C$_{10}$PP-PH$_6$ and C$_{10}$PP-2FPH$_6$ and C$_{10}$PP-BF$_6$ with C$_{10}$PP-BH$_6$ revealed that the compounds with a CH$_3$ group exhibited a highly ordered SmI$_A^*$ phase (except in C$_{10}$PP-PH$_6$ which gave a narrow SmC$_A^*$ phase) narrowing the SmC$_A^*$ temperature range. On the contrary, the compound with a CF$_3$ group exhibited a very broad SmC$_A^*$. This antiferroelectricity stabilization due to the CF$_3$ substitution has been reported by Suzuki *et al.* [17]. When we consider the effect of terminal chain length on the LC properties by comparing compounds C$_n$PP-2FPH$_6$; $n = 8 \sim 11$, the broadest SmC$_A^*$ phase can be seen with the octyl tail. When the terminal chain is longer than the octyl group, compounds exhibited the SmI$_A^*$ phase, narrowing the SmC$_A^*$ phase. However, it was observed that the terminal chain length had little effect on the isotropization temperatures of the AFLC materials.

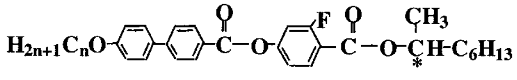


Figure 1. Chemical structure of some F-substituted MHPOBC compounds.

Let us now compare the liquid crystalline properties of these new compounds, in particular, C$_n$PP-2FPH$_6$; $n = 8 \sim 11$, with those of the AFLCs having the most conventional core structure of biphenyl/phenyl combination: MHPOBC [18, 19] (figure 1). Tables 1 and 2 show that the introduction of the phenylpiperazine system, replacing the biphenyl moiety, notably depresses

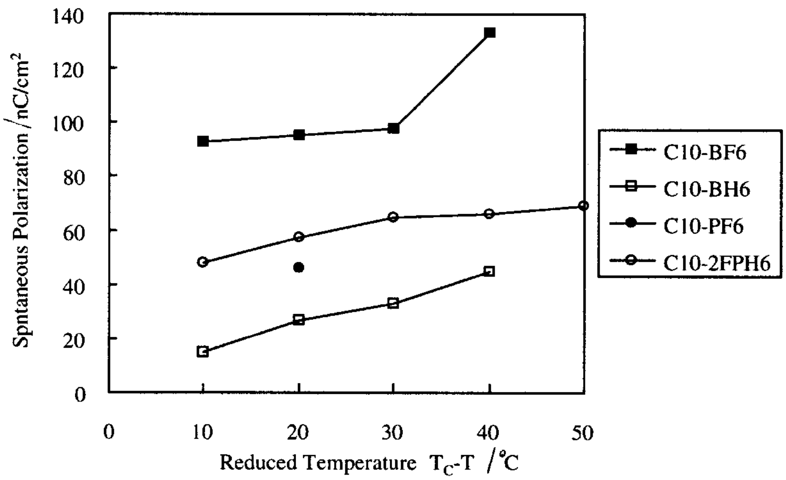


Figure 2. Effect of temperature on spontaneous polarization of the new AFLC compounds with the decyl terminal chain.

Table 2. Phase transition temperatures (°C) of some F-substituted MHPOBC compounds [18, 19].

n	Heating	Cooling
8	Cr 39.3 SmC$_A$ 122.8 SmC 123.6 SmA 141.6 I	Cr -14 SmC$_A$ 122.3 SmC 123.1 SmA 141.2 I
9	Cr 41.9 SmC$_A$ 118.6 SmC 122.2 SmA 134.7 I	Cr -23 SmI$_A$ 40.0 SmC$_A$ 117.4 SmC 121.6 SmA 134.1 I
10	Cr 31 SmC$_A$ 118.6 SmC 122.3 SmA 132.6 I	
11	Cr 36.2 SmC$_A$ 112.3 SmC 120.3 SmA 128.3 I	Cr -3.2 SmI$_A$ 30.0 SmC$_A$ 109.2 SmC 119.8 SmA 127.9 I

the isotropization point. Although this structural change would have little influence on the crystallization temperature, a marked decrease of the SmC$_A^*$ temperature range can be seen.

3.3. *Electro-optical properties*

3.3.1. *Spontaneous polarization*

The temperature dependence of the spontaneous polarization of the newly prepared compounds with a decyl terminal chain, measured by a triangular wave voltage method (± 100 V, 30 Hz), is illustrated in figure 2. Among them, the largest P_s of 130 nC cm^{-2} at 80°C was seen in compound C_{10}PP-BF$_6$: the phenylpiperazine/biphenyl combination with a CF$_3$ group at the chiral centre. As is well accepted, a very strong π-electron conjugation along the molecular axis due to three phenyl rings, together with a very strong electron withdrawing group (CF$_3$) at the chiral centre, would induce a strong dipole moment in the molecule resulting in a large spontaneous polarization. However, in this compound when the CF$_3$ was replaced by a CH$_3$ group the SmC$_A^*$ phase disappears and the spontaneous polarization became significantly smaller (45 nC cm^{-2} at 119°C). When the biphenyl group was replaced with a phenyl ring, in compound C_{10}PP-PF$_6$, again P_s became very small (50 nC cm^{-2}). This suggests that the removal of one phenyl ring adversely affects the magnitude of the spontaneous polarization. Compound C_{10}PP-2FPH$_6$,

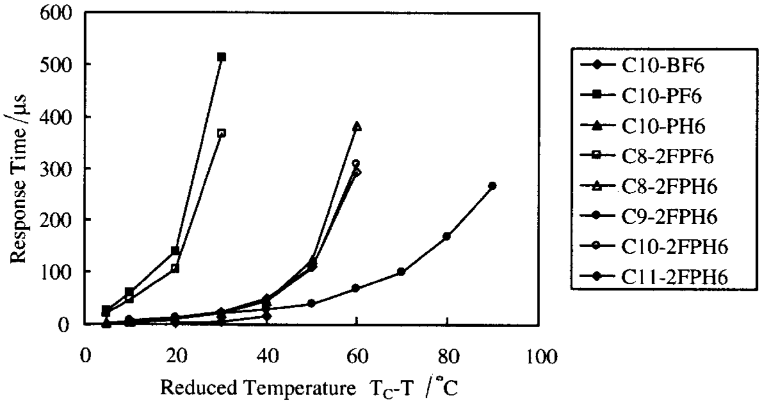


Figure 3. Effect of temperature on response times of the new AFLC compounds.

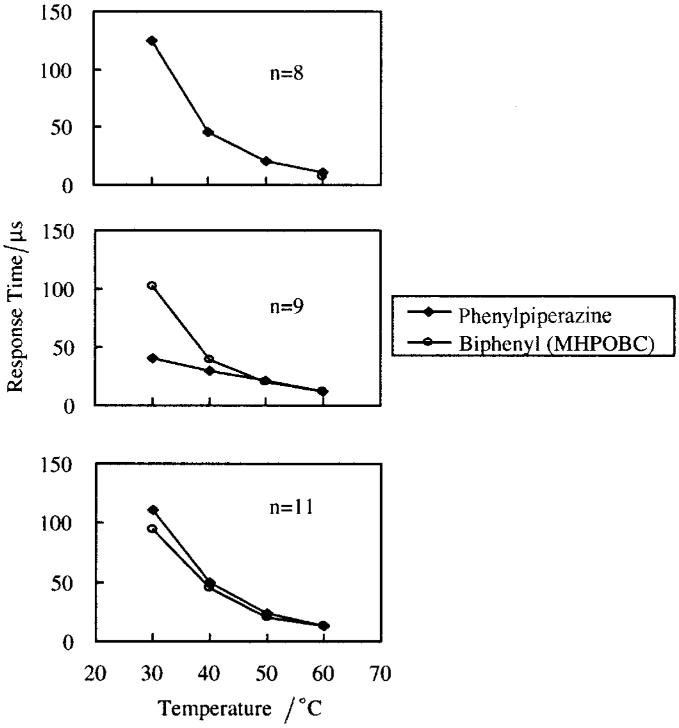


Figure 4. Comparison of the response times of the new 2FPH$_6$ homologues (◆) with those of F-substituted MHPOBC compounds (○) around room temperature (cell thickness = 2.0 μm, $E = \pm 25$ V μm^{-1}).

consisting of a 2-fluorophenyl moiety with a CH_3 group at the chiral centre, gave a moderate spontaneous polarization of 70 nC cm^{-2} at 32°C.

3.3.2. *Response time*

The response time of an AFLC material is considered to be a very important feature as it affects the addressing speed of a display device. AFLC materials with a few tenths of microseconds response time around room temperature are currently in great demand in display technology. Figure 3 illustrates the effect of temperature on the response time of the new compounds. Compounds C_{10}PP-PF_6 and C_8PP-2FPF_6 gave comparatively slow responses. This is because at the low SmC^*–SmC_A^* transition points (54.5 and 56.9°C, respectively) of these compounds the viscosity increases resulting in slow responses as noted from the equation

$$\tau = \eta/\mathbf{P}_s\ \mathbf{E}$$

where τ = response time, η = viscosity, $\mathbf{P}_s$ = spontaneous polarization, and $\mathbf{E}$ = electric field. On the other hand, compound C_{10}PP-BF_6 gave the quickest response. This behaviour may be mainly attributed to the large spontaneous polarization (see figure 2) together with a comparatively high SmC^*–SmC_A^* transition temperature (121°C) which gives a low viscosity around this transition point. The other compounds, particularly 2FPH_6 homologues, possessed moderate SmC^*–SmC_A^* transition points and exhibited fast responses around room temperature.

If we compare the actual response times, as well as the response time measuring conditions of the new materials (2FPH_6 homologues), with those of the MHPOBC counterparts (figure 4), it may be noted that a weaker electric field is sufficient for the new compounds (± 40 V, 1 Hz), in contrast to MHPOBC materials which require ± 50 V or ± 60 V (1 Hz), particularly around room temperature. As it requires a strong electric field at low temperatures, the response time of the (MHPOBC) biphenyl member with an octyl terminal chain has not been reported. This suggests that these new compounds exhibit weaker antiferroelectric couplings than those of (MHPOBC) biphenyl compounds. Due to this weak antiferroelectric nature, the new compounds, especially those having an octyl or a nonyl tail, gave faster responses than those of the phenyl counterparts as depicted in figure 3.

3.3.3. *Electro-optical hysteresis*

The contrast ratio—light transmittance of the SmC_A^* phase (dark state) to the SmC* phase (bright state)—is considered to be one of the vital requirements which decide the quality of a display device. The magnitude of the contrast ratio reflects the extent of molecular alignment in a homogenous liquid crystal cell; it is considered that the molecular alignment in a cell is governed by the balance of molecular–molecular and molecular–substrate (alignment polymer layer) interactions. In other words, the nature of the LC molecule is a prime factor in deciding the contrast ratio. In practice, the contrast ratio is assessed by the electric field–light transmittance profile measured by a triangular wave voltage method. It is widely accepted that a wide hysteresis and steepness around the threshold voltage are sound indications for good electro-optical properties. The appropriate balance of steepness and the width of the hysteresis is described

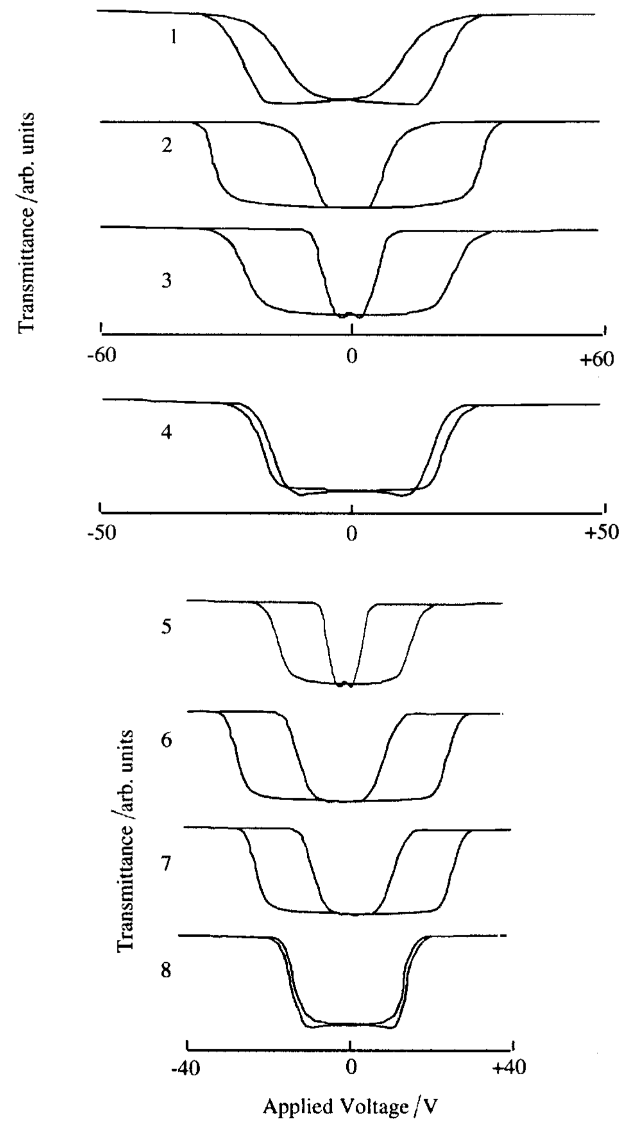


Figure 5. Electro-optic switching characteristics of the new AFLC compounds: (1) C_8PP-PF_6 at 30°C, (2) C_8PP-2FPF_6 at 30°C, (3) C_{10}PP-PF_6 at 20°C, (4) C_{10}PP-BF_6 at 81°C, (5) C_8PP-2FPH_6 at 47°C, (6) C_9PP-2FPH_6 at 40°C, (7) C_{10}PP-2FPH_6 at 50°C and (8) C_{10}PP-PH_6 at 65°C.

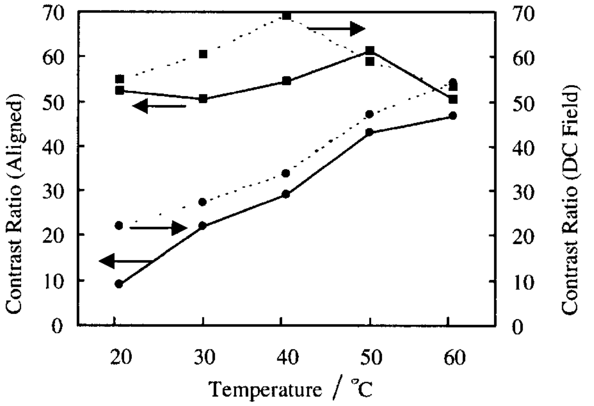


Figure 6. Contrast ratios of AFLC blend samples [● = AFLC blend 1, ■ = AFLC blend 1 (90%)+ C_8PP-2FPH$_6$ (10%)].

by another factor known as the driving margin (M). Definition of the driving margin is described elsewhere [15]. It is believed that in order to achieve a good contrast ratio the driving margin should be greater than one ($M > 1$).

All new compounds which showed the SmC$_A^*$ phase gave clear double hysteresis loops. However, in certain compounds, especially those with decyl and undecyl terminal chains, the hysteresis shape or the driving margin was found to be poor. As can be seen from figure 5, which gives hysteresis loops of some representative compounds, when the alkyl terminal chain is octyl or nonyl, well-defined hysteresis loops with good driving margins can be obtained. This suggests that irrespective of the core system, the terminal group greatly affects the molecular layer alignment and hence the contrast ratio.

Through careful analysis of parameters such as the SmC$_A^*$ temperature range, response time and hysteresis shape, we believe that compounds C_8PP-2FPH$_6$ and C_9PP-2FPH$_6$ have strong potential for use as materials in display devices. Furthermore, with these two compounds several AFLC blends were formulated, and their LC properties were evaluated. Among them, promising results were obtained when 10% C_8PP-2FPH$_6$ was added to the AFLC blend 1 [19], an AFLC mixture previously formulated in this laboratory. The phase sequence of the newly developed mixture is given below.

$$\mathrm{Cr} \longleftarrow \mathrm{SmC_A^*} \xleftarrow{76.1} \mathrm{SmC^*} \xleftarrow{83.7} \mathrm{SmA} \xleftarrow{94.1} \mathrm{I}$$

As compared with AFLC blend 1, the new blended sample exhibited great improvement in the contrast ratio, as depicted in figure 6.

4. Conclusion

A novel series of antiferroelectric liquid crystal compounds having a phenylpiperazine unit in the core structure was synthesized. Most of these compounds exhibited SmC* and SmC$_A^*$ mesophases and in some compounds the SmC$_A^*$ phase persisted well below room temperature. The spontaneous polarizations of the compounds in the SmC$_A^*$ phase ranged from 50–130 nC cm^{-2}. They possessed response times of 4–25 μs at temperatures 10°C below the SmC*–SmC$_A^*$ transition point. Compounds C_8PP-2FPH$_6$ and C_9PP-2FPH$_6$ gave well-defined hysteresis loops with good driving margins. When 10% C_8PP-2FPH$_6$ was added to a previous AFLC blend, a great improvement in the contrast ratio could be seen.

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