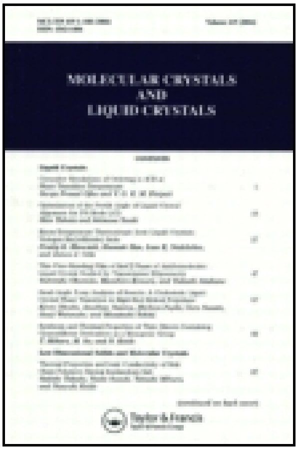

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Synthesis, Mesomorphic Properties and Physical Measurements of a Series of Fluorinated Antiferroelectric Liquid Crystals

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Synthesis, Mesomorphic Properties and Physical Measurements of a Series of Fluorinated Antiferroelectric Liquid Crystals

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We report the synthesis and mesomorphic properties of a series of fluorinated antiferroelectric liquid crystalline materials. The materials form the homologous series of "12F1M7"[1] and were derived from (R)-2-octanol. The physical properties (tilt angles and spontaneous polarisation at 20Hz and 50Hz) were measured and compared with those of the related compounds (S)-12F1M7 and (S)-MHPOBC. The effect of varying the unbranched terminal chain from 8 [(S)-8F1M7] to 12 on the mesomorphic and physical properties is discussed.

Keywords: Antiferroelectric; homologous series; switching studies

INTRODUCTION

Antiferroelectric liquid crystalline smectic C* materials exhibit a number of desirable properties which make them suitable for high information-content displays devices[2];

- Fast response times
- Matrix addressable
- Low driving voltages
- High contrast ratios
- High multiplexability
- Wide viewing angles

It has been suggested that display devices utilising antiferroelectric materials (AFLCDs) possess the additional advantage over standard ferroelectric display devices (FLCDs), of decreased sensitivity to external shock, as the averaged optical axis of the molecules in the bulk material lies parallel to the direction of alignment[3]. Both monochrome and full-colour prototype displays with video frame-rate, good "viewability" (viewing angles and contrast ratios), and VGA resolution have already been demonstrated by various groups[4]. Continual improvements in the liquid crystalline mixtures, switching characteristics and device construction, have widened the potential applications of AFLCDs[5,6]. Optimising the mixtures used in devices, in order to extend operating temperature ranges and further improve contrast ratios and switching times (for higher-resolution displays), relies on the optimum combination of individual components with the most suitable properties.

The overall aim of this work was to identify the best components from an homologous series of liquid crystals, shown in Figure 1, for use in antiferroelectric mixtures for fast-switching applications. This was principally carried out by investigating the effect of varying the size of the unbranched chain, C_nH_{2n+1}, (compounds **1** - **5**; n = 8-12) on the following parameters;-

1. occurrence and stability of the SmC_A* phase;
2. size of the spontaneous polarisation;
3. tilt angles, switching speeds and contrast ratios.

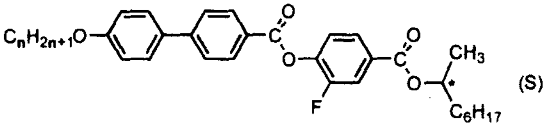
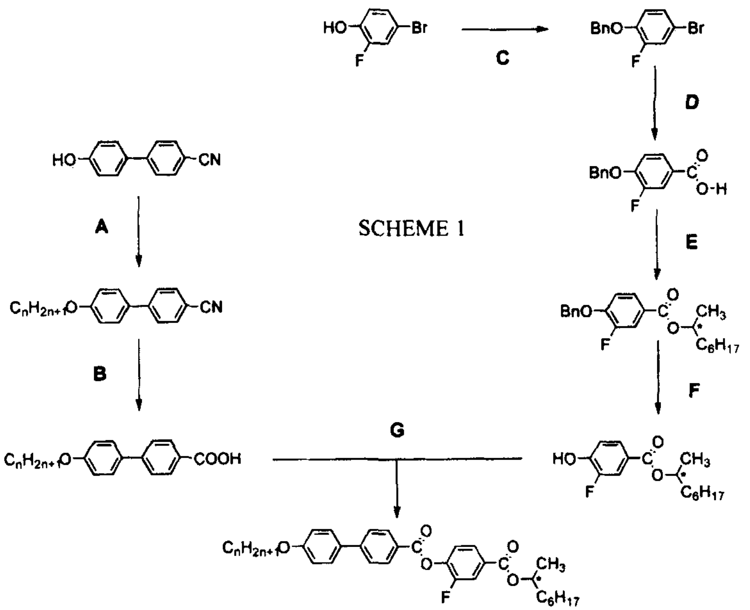


FIGURE 1 (S)-8F1M7 – (S)-12F1M7 (**1** – **5**; n = 8 – 12)

RESULTS AND DISCUSSION

Synthesis

The fluorinated materials ["(S)-8F1M7" to "(S)-12F1M7"] (Compounds **1** - **5**), structurally related to MHPOBC (the first reported antiferroelectric liquid crystal)[7], were prepared according to the synthesis outlined in Scheme 1.

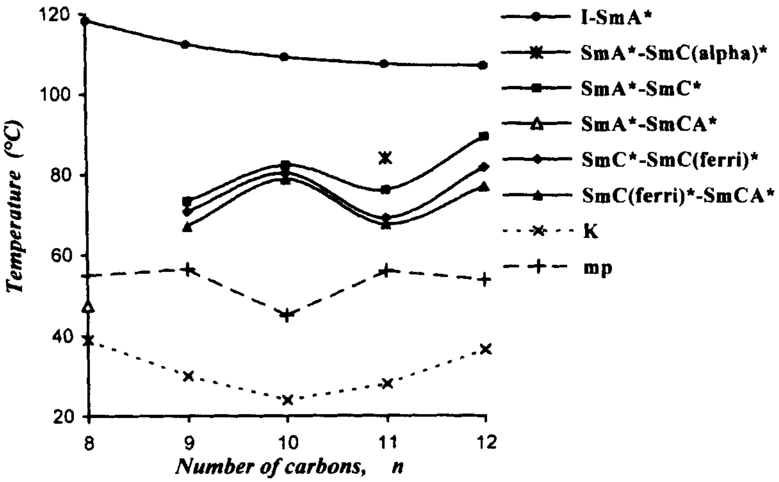


SCHEME 1

A $C_nH_{2n+1}Br$, K_2CO_3, *butanone, reflux*
B c.H_2SO_4, H_2O, *CH_3CO_2H, reflux*
C BnBr, K_2CO_3, *butanone, reflux*
D i) Mg, *THF* ii) CO_2(s) iii) HCl
E $CHCH_3(C_nH_{2n+1})OH$, DEAD, PPh_3, *THF*
F Pd/C, H_2, *ethanol*
G DEAD, PPh_3, *THF* or DCC, DMAP, *DCM*

Mesomorphic Properties

Graph 1 shows the phases and transition temperatures of the chiral materials (compounds **1** – **5**) determined by optical microscopy and verified by DSC. The presence of the fluorine substituent in the molecules inhibited the formation of any ordered smectic phases. All the compounds exhibit a SmA* phase. Only compound **1** (n = 8) shows a direct SmA* - SmC_A* transition whereas in compounds **2** and **3** the SmC_A* phase arises via a SmC* phase. A SmC_α* phase, thought to be formed due to a combination of competing factors responsible for the formation of SmC* and SmC_A* phases on cooling from the SmA* phase, and a reduced ability of the materials to form tilted phases[8], is



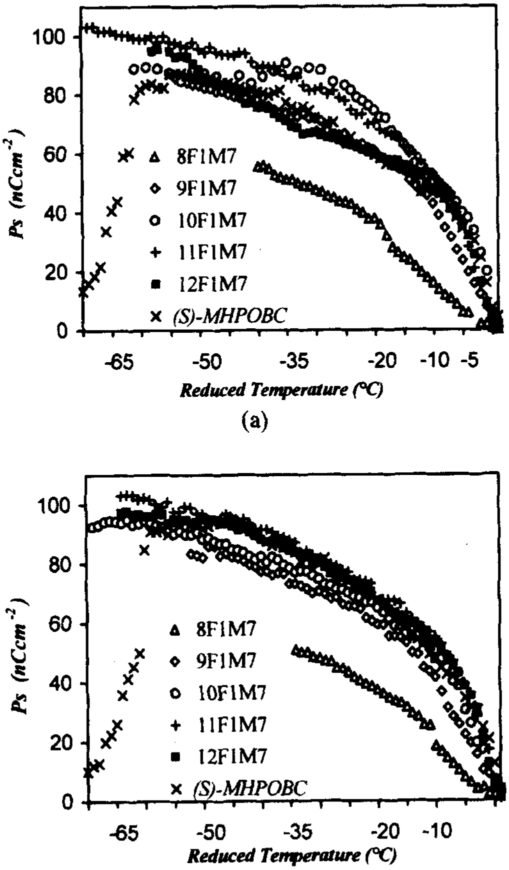
GRAPH 1

observed in compound **4**. There is a gradual decrease in the I – SmA* transition temperature as the value of n increases from 8 to 12. The material with the lowest melting point, lowest recrystallization temperature, and widest SmC_A* phase is compound **3** ((S)-10F1M7). An odd-even effect is clearly visible in the SmC*, SmCγ*, and SmC_A* transitions of compounds **2** – **5**.

Physical Measurements

Graphs 2(a) and 2(b) show the spontaneous polarization (P_s) of the new compounds as well as the standard antiferroelectric material, (S)-MHPOBC, measured at switching frequencies of 20Hz and 50Hz. A triangular-wave AC field of ±50V (±10Vμm^{-1}) (graphs 2(a) & 2(b)) was applied across standard Linkam cells (5μm thick, 0.81cm^2 area, ITO-coated, antiparallel-aligned). The observed tilt angles of the compounds, recorded from the temperature at which the P_s becomes measurable on cooling from the SmA* phase, are shown in Graph 3.

GRAPHS 2(a) & 2(b) P_s of compounds **1** - **5** and (S)-MHPOBC measured at 20Hz (a), and 50Hz (b).

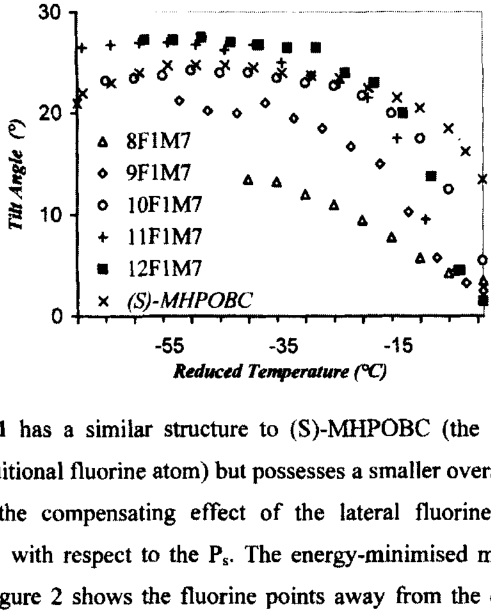


(a)

(b)

The material with the highest overall P_s, at both frequencies, is compound 4 (n = 11). Increasing the switching frequency from 20Hz to 50Hz improves the "profile" of the P_s trends for all the compounds. This may be due to an increase in saturated switching occurring at higher frequencies. An increase in the spontaneous polarization of the compounds is coupled with increases in tilt angle (on cooling); compounds with larger tilt angles have a higher P_s, and increasing the unbranched terminal chain from **n** = 8 (compound **1**) to **n** = 12 (compound **5**) increases the overall tilt angles. Compound **5** has a slightly lower P_s than compound **4** despite having slightly larger tilt angles. This may be due to the decrease in charge per unit volume of compound **5** (n = 12) in comparison to compound **4** (n = 11).

GRAPH 3 – Observed tilt angles of compounds **1** – **5** (comparison with (S)-MHPOBC)



Compound **1** has a similar structure to (S)-MHPOBC (the only difference being an additional fluorine atom) but possesses a smaller overall P_s. This may be due to the compensating effect of the lateral fluorine substituent in compound **1** with respect to the P_s. The energy-minimised molecular model shown in Figure 2 shows the fluorine points away from the direction of the chiral methyl group, hence diminishing the observed value of the P_s.

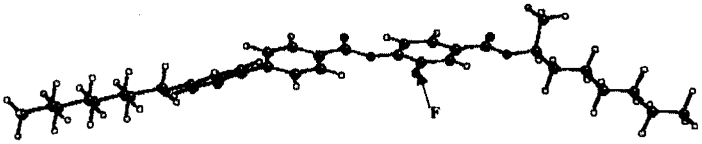


FIGURE 2 Energy-minimised molecular model of compound **8** ((S)-8F1M7) (Nemesis Interactive Modelling; Oxford Modelling Co.).

Although a SmC$_\alpha$* phase could not be observed in compound **3**, either by microscopy or DSC, the switching trends in Figure 3 clearly show the presence of a SmC$_\alpha$* phase above the SmC* phase of the material.

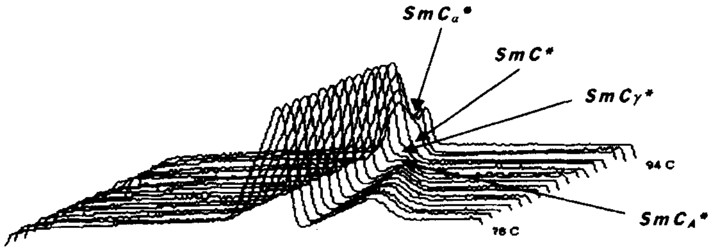


FIGURE 3 Switching trend of compound **3** ((S)-10F1M7) on cooling from 94°C to 78 °C [applied triangular-wave voltage of ±50V, 20Hz].

The contrast ratios and switching speeds of **1** - **5** were measured 15° above the recrystallization temperature (red laser λ = 634nm, photodetector) and are summarised in Table II. The contrast ratios increase with increasing chain length (**n**), together with an increase in tilt angle from **n** = 8 to 12, whereas the switching speeds become slower as the chain length increases (due to increasing viscosity). All the materials show faster switching times than those measured for the SmC$_A$* phase of (S)-MHPOBC under the same conditions.

TABLE II

Compound	n	Temp. (°C)	Contrast Ratio	Switching Speed
1	8	55	18 : 1	32 μs
2	9	55	26 : 1	34 μs
3	10	45	28 : 1	36 μs
4	11	50	28 : 1	37 μs
5	12	60	31 : 1	38 μs

CONCLUSIONS

An homologous series of liquid crystals possessing antiferroelectric smectic C$_A$* phases has been synthesized. The presence of the lateral fluorine atom gives rise to a slightly lower P_s value (than that observed for (S)-MHPOBC) which increases with tilt angle. Compounds with shorter chain lengths exhibit faster switching times despite lower P_s values. This is probably due to a lower effective viscosity and smaller switching angles. Liquid crystal cells containing these materials show relatively good contrast ratios and response times faster than those measured for (S)-MHPOBC. This suggests that they may be suitable as components for antiferroelectric mixtures for use in high information-content display devices. Compound **3** ((S-)10F1M7) shows the widest SmC_A^* range, and lowest melting point and compound **4** ((S)-11F1M7) possesses the highest overall P_s.

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