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The ferro-, ferri- and antiferro-electric properties of a series of novel 2- or 3-substituted-alkyl 4-(4′-dodecyloxybiphenyl-4-carbonyloxy)-benzoate esters

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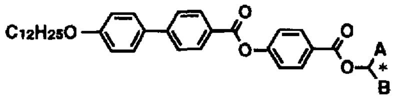
This paper reports the synthesis of six chiral liquid crystalline 2- or 3-substituted-alkyl 4-(4′-dodecyloxybiphenyl-4-carbonyloxy)benzoates, their mesophase assignments and the phase transition temperatures. All six materials display S_A^* followed by S_C^* phases on cooling from their isotropic liquids. The magnitudes of switched tilt angle, spontaneous polarization, helical twist sense (L.H.) and direction of polarization ($P_s(-)$) are given for the S_C^* phases. Close inspection of the S_C^* phases revealed that for the six compounds, two showed a ferrielectric ($S_{C_\gamma}^*$) and an antiferroelectric ($S_{C_A}^*$) subphase, two showed only a ferrielectric subphase and one showed only an antiferroelectric subphase. The field-dependent behaviour of the switched tilt angle of the ferrielectric and antiferroelectric phases of some of the compounds is also presented.

1. Introduction

In recent years the phenomena of ferri- and antiferroelectricity in liquid crystalline materials have generated a great deal of interest in academic and industrial research laboratories [1–13]. A direct consequence of this surge of interest has been the synthesis and characterization of a large number of novel materials which possess one or both of the phases concerned. Most of these materials contain a chiral unit [4, 14, 15] and they have often provided a useful insight into the influence of molecular chirality on physical properties. Furthermore, the nature of the chiral group (often a branching group) has been demonstrated to influence strongly the nature of the smectic C* subphase formed. For example, certain bulky chiral centres lead to a complete eclipse of ferroelectric (S_C^*) and ferrielectric ($S_{C_\gamma}^*$) phases in favour of an antiferroelectric ($S_{C_A}^*$) subphase [5].

We present here the synthesis and characterization of a series of materials based on the 4-(4′-dodecyloxybiphenyl-4-ylcarbonyloxy)benzoate liquid crystalline core, the general structure of which is represented by compound **I**. These materials show a variety of phases, notably S_C^*, $S_{C_\gamma}^*$ and $S_{C_A}^*$, and their properties were investigated by a combination of techniques including optical microscopy and differential scanning calorimetry; their behaviour was also studied on the application of electric fields of various strengths.



I

A = alkyl or fluoroalkyl;
B = alkyl or methyleneoxyalkyl;
* = (*R*)- or (*S*)-.

2. Synthetic discussion

The 2- or 3-substituted-alkyl 4-(4′-dodecyloxybiphenyl-4-carbonyloxy)benzoates were prepared as shown in the scheme. The first step involves the protection of 4-hydroxybenzoic acid (**1**) with methyl chloroformate to give compound **2** in good yield [16]. The protected benzoic acid (**2**) was then esterified with the appropriate (*R*)- or (*S*)-2- or 3-substituted alcohol to give the (*S*)- or (*R*)-2- or 3-substituted-alkyl 4-methoxy-

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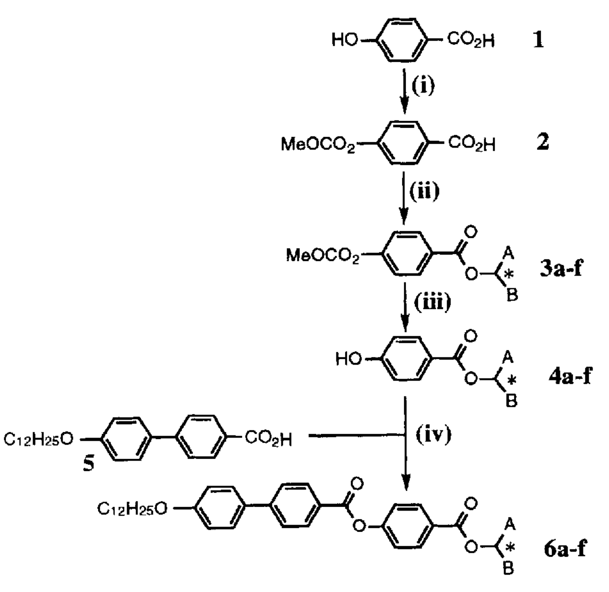


a..[A = CH_3, B = C_8H_{17}, * = (*R*)-]; b..[A = CH_3, B = $C_{10}H_{21}$, * = (*R*)-];
c..[A = C_2H_5, B = C_8H_{17}, * = (*R*)-]; d..[A = C_2H_5, B = $C_{10}H_{21}$, * = (*R*)-];
e..[A = CH_2F, B = C_6H_{13}, * = (*S*)-]; f..[A = CH_2F, B = $CH_2OC_6H_{13}$, * = (*S*)-].

(i)...MeOCOCl, NaOH, H_2O, 0 °C.

(ii)...(*R*)- or (*S*)-HOCH(A)(B), PPh_3, DEAD, THF, N_2, RT.

(iii)...$NH_{3\,(aq)}$, EtOH, RT.

(iv)...DCC, DMAP, CH_2Cl_2 or THF, RT.

Scheme. Synthetic route to the chiral 2- or 3-substituted-alkyl 4-(4′-dodecyloxybiphenyl-4-carbonyloxy)benzoates (**6a–f**).

carbonyloxybenzoates (**3a–f**) as viscous liquids in excellent yield [17]. Compounds **3a–f** were then deprotected [16] and the resulting phenols **4a–f** were esterified with 4′-dodecyloxybiphenyl-4-carboxylic acid (**5**) using dicyclohexylcarbodiimide and 4-*N*,*N*-dimethylaminopyridine to give the required products **6a–f** [18].

3. Experimental

3.1. *General*

The chemical structures of all intermediates and final products were confirmed by a combination of the following techniques: ^{1}H nuclear magnetic resonance spectroscopy (JEOL GX NM270 FT-NMR spectrometer using tetramethylsilane as the internal standard), infrared spectroscopy (Perkin Elmer 783 spectrometer) and mass spectrometry (Finnigan 1020 GC-MS spectrometer). Specific optical rotations were measured using an Optical Activity Ltd AA-10 Automatic Polarimeter with chloroform (Spectrosol) as the solvent.

The products of each reaction stage were purified by flash chromatography (May & Baker Sorbsil® C60 40–60H micron silica gel) as described by Clark Still [19]. The purity of all intermediates and final compounds was checked by thin layer chromatography (using Merck 60 F254 preformed aluminium-backed plates) and by normal- and reverse-phase HPLC (Merck-Hitachi; L-6200A Intelligent Ternary Gradient Pump and L-4000 UV Detector set at 254 nm) using Microsorb C18 or Si columns and acetonitrile (May & Baker Chromanorm™) as the mobile phase. Each of the final products was found to have a chemical purity in excess of 99·5%. All solvents used in reactions were dried, distilled and stored as described in Perrin and Armarego [20]. The optical purity of all chiral compounds was checked by NMR using chiral shift reagents. This revealed that no racemization had occurred and confirmed literature findings that the Mitsunobu reaction proceeds with inversion at the stereocentre.

The initial phase assignments and transition temperatures were determined by thermal polarized light microscopy using a polarizing microscope (Zeiss Universal) in conjunction with a hot stage and controller (Mettler FP82 microfurnace and FP80 control unit). Differential scanning calorimetry (Perkin Elmer DSC7 calorimeter, TAC7/PC controller and IBM system/2model 50Z computer) was used to determine both the transition temperatures and the heats of transitions. The instrument was calibrated against an indium standard (measured $\Delta H = 28{\cdot}35\,\mathrm{J\,g^{-1}}$, literature value $28{\cdot}45\,\mathrm{J\,g^{-1}}$) [21] and all enthalpies are quoted in kJ mol^{-1}.

Tilt angle and ferroelectric polarization measurements were performed using planar aligned cells (Electronics Chemicals High Technology Group, Japan) with an active area of 0·25 cm^2 indium–tin oxide electrodes, previously treated with unidirectionally buffed polyimide alignment layers; electrical contacts were made directly to the internal surfaces. The cells were filled by capillary action with the materials in their isotropic liquid states. Reasonably good alignment for optical and polarization studies was achieved by slowly cooling each material from the isotropic liquid into their respective smectic states; cooling rates were $\leqslant 0{\cdot}2^\circ\mathrm{C\,min^{-1}}$. Once filled, the cell was connected to an a.c. frequency generator (6 or 15 V peak to peak, 60 Hz), a dual trace oscilloscope and a Diamant Bridge [22]. Tilt angles (θ) in the smectic C* phase were obtained by measuring the angle (2θ) between the optical extinction positions for the ferroelectrically switched states observed with the polarizing microscope [23]. The ferroelectric polarization (P_s) was measured using the Diamant Bridge, while observing a characteristic hysteresis loop for switching at 60 Hz; polarization values are quoted in nC cm^{-2}.

3.2. *4-Methoxycarbonyloxybenzoic acid (2)*

Methyl chloroformate (19·0 g, 201 mmol) was added to a stirred mixture of 4-hydroxybenzoic acid (17·0 g, 123 mmol), ground sodium hydroxide (14·8 g, 370 mmol) and water (300 ml) at such a rate as to maintain the temperature between 0 and 2°C. The resulting turbid solution was left to stir at ~0°C for a further 4 h, before being acidified with a 1 : 1 solution of conc. hydrochloric acid–water. The voluminous white precipitate was then collected by filtration; it was washed thoroughly with a large volume of cold water before being dried in a vacuum oven, recrystallized (ethanol), and dried *in vacuo* (P_2O_5, 0·1 mmHg, 40°C, 5 h). Yield = 17·6 g (73%); m.p. = 177–179°C (lit. 185°C [16]); δ_H (270 MHz; $CDCl_3$; TMS): 3·95 (3H,s), 7·31 (2H,d), 8·16 (2H,d), no carboxyl proton detected; ν_{max} (KBr disc): 3420, 2960, 1770, 1755, 1680, 1430, 1260, 1220, 1165, 1070, 940, 770, 725, 660 cm^{-1}; *m/z* 196 (M^+, 38%), 179 (5%), 152 (39%), 135 (100%), 121 (7%), 107 (28%).

3.3. *(R)-1-Methylnonyl 4-methoxycarbonyloxybenzoate (**3a**)*

A solution of triphenylphosphine (0·86 g, 3·2 mmol) and (*S*)-decan-2-ol (0·73 g, 4·6 mmol) in dry tetrahydrofuran (10 ml) was added dropwise to a stirred solution of compound **2** (0·62 g, 3·2 mmol) and diethyl azodicarboxylate (0·55 g, 3·2 mmol) in dry tetrahydrofuran (10 ml) at room temperature under a nitrogen atmosphere. The reaction mixture was then stirred for 20 h, before it was diluted with diethyl ether (100 ml) and filtered through a pad of 'Hyflosupercel'; the filtrate was then washed with brine (50 ml), dried ($MgSO_4$), filtered and evaporated to give a colourless liquid. The product was purified by flash chromatography (fine mesh silica gel; 4% (v/v) ethyl acetate in petrol (b.p. 40–60°C); the resulting colourless oil was dried *in vacuo* (P_2O_5, 0·1 mmHg, RT, 18 h). Yield = 1·07 g (99%); $[\alpha]_D^{22} = -11·5°$ ($c = 0·0348$ g ml^{-1}; $CHCl_3$); δ_H (270 MHz; $CDCl_3$; TMS): 0·85 (3H,t), 1·30 (15H,m), 1·65 (2H,m), 3·90 (3H,s), 5·15 (1H, sextet), 7·25 (2H,d), 8·10 (2H,d); ν_{max} (film): 2960, 2930, 2860, 1770, 1715, 1605, 1440, 1255, 1220, 1165, 1110, 1015, 940, 775 cm^{-1}; *m/z* 336 (M^+, trace), 316 (5%), 204 (100%), 197 (82%), 152 (40%), 135 (57%).

3.4. *(R)-1-Methylundecyl 4-methoxycarbonyloxybenzoate (**3b**)*

This compound together with **3c–f** was prepared using a similar procedure to that described for compound **3a**. The NMR data are given only for **3a**, **e** and **f**, as the data for **3a** differ from **3b**, **c** and **d** only in the number of protons in one multiplet (*c.* 1·25–1·30 ppm). Yield = 1·38 g (100%); $[\alpha]_D^{22} = -12·3°$ ($c = 0·0325$ g ml^{-1}; $CHCl_3$); ν_{max} (film): 2960, 2930, 2850, 1770, 1715, 1605, 1440, 1265, 1220, 1115, 1015, 940, 860, 775, 720 cm^{-1}; *m/z* 365 ($M^+ + 1$, trace), 197 (60%), 186 (28%), 152 (32%), 135 (30%).

3.5. *(R)-1-Ethylnonyl 4-methoxycarbonyloxybenzoate (**3c**)*

Yield = 0·75 g (85%); $[\alpha]_D^{22} = -7·9°$ ($c = 0·0254$ g ml^{-1}; ν_{max} (film): 2960, 2920, 2850, 1765, 1710, 1600, 1505, 1485, 1255, 1220, 1160, 1110, 1015, 940, 770 cm^{-1}; *m/z* 350 (M^+, trace), 196 (54%), 179 (99%), 154 (44%), 135 (53%).

3.6. *(R)-1-Ethylundecyl 4-methoxycarbonyloxybenzoate (**3d**)*

Yield = 0·88 g (92%); $[\alpha]_D^{22} = -16·1°$ ($c = 0·0124$ g ml^{-1}; $CHCl_3$); ν_{max} (film): 2960, 2920, 2850, 1765, 1710, 1440, 1255, 1220, 1160, 1110, 1015, 940, 755 cm^{-1}; *m/z* 378 (M^+, trace), 197 (94%), 152 (30%), 135 (47%).

3.7. *(S)-1-(Fluoromethyl)heptyl 4-methoxycarbonyloxybenzoate (**3e**)*

Yield = 1·34 g (100%); $[\alpha]_D^{22} = -20·7°$ ($c = 0·0483$ g ml^{-1}; $CHCl_3$); δ_H (270 MHz; $CDCl_3$; TMS): 0·90 (3H,t), 1·30 (8H,m), 1·75 (2H,m), 3·90 (3H,s), 4·45 (1H,m), 4·65 (1H,m), 5·30 (1H,2xm), 7·30 (2H,d), 8·10 (2H,d); ν_{max} (film): 2950, 2920, 2860, 1765, 1715, 1600, 1440, 1255, 1160, 1110, 1010, 940, 770 cm^{-1}; *m/z* 326 (M^+, 4%), 196 (94%), 179 (57%), 152 (100%), 135 (91%).

3.8. *(S)-1-(Fluoromethyl)-2-hexyloxyethyl 4-methoxycarbonyloxybenzoate (**3f**)*

Yield = 1·46 g (100%); $[\alpha]_D^{22} = -3·8°$ ($c = 0·0525$ g ml^{-1}); δ_H (270 MHz; $CDCl_3$; TMS): 0·85 (3H,t), 1·25 (6H,m), 1·55 (2H,m), 3·49 (3H,m), 3·73 (2H,m), 3·93 (3H,s), 4·60 (1H,m), 4·80 (1H,m), 5·40 (1H,2xm), 7·25 (2H,d), 8·10 (2H,d); ν_{max} (film): 2960, 2920, 1765, 1740, 1600, 1260, 1220, 1110, 940 cm^{-1}; *m/z* 357 ($M^+ + 1$, trace), 179 (29%), 135 (27%), 113 (44%), 92 (45%), 84 (100%).

3.9. *(R)-1-Methylnonyl 4-hydroxybenzoate (**4a**)*

Compound **3a** (1·07 g, 3·2 mmol) in ethanol (12 ml) was added dropwise to a stirred mixture of ammonia (16 ml; sp. gr. 0·88) and ethanol (13 ml) at RT. The reaction mixture was stirred for a further 72 h and then poured into water (150 ml) with stirring. The product was extracted using diethyl ether (3 x 50 ml) and the combined ethereal extracts were washed with brine (50 ml), dried ($MgSO_4$), filtered and evaporated to give a colourless oil. The oil was purified by flash chromatography (fine mesh silica gel; 9 : 1 dichloromethane–petrol (b.p. 40–60°C)); the resulting oil was then dried *in vacuo* (P_2O_5, 0·2 mmHg, RT, 19 h). Yield = 0·36 g (44%); δ_H (270 MHz; $CDCl_3$; TMS): 0·85 (3H,t), 1·30 (15H,m), 1·65 (2H,m), 5·10 (1H,sextet), 5·95 (1H,s,broad), 6·85 (2H,d), 7·95 (2H,d); ν_{max} (film): 3340, 2920, 2860, 1675, 1605, 1590, 1510, 1440, 1280, 1165, 1115, 850, 775, 700, 620 cm^{-1}; *m/z* 278 (M^+, trace), 138 (59%), 121 (100%).

3.10. *(R)-1-Methylundecyl 4-hydroxybenzoate (***4b***)*

This compound together with **4c–f** was prepared using a similar procedure to that described for compound **4a**. The NMR data are given only for **4a**, **e** and **f**, as the data for **4a** differ from **4b**, **c** and **d** only in the number of protons in one multiplet (*c.* 1·25–1·30 ppm). Yield = 0·19 g (18%); ν_{max} (film): 3340, 2920, 2850, 1670, 1600, 1585, 1510, 1440, 1280, 1160, 1110, 850, 770 cm^{-1}; *m/z* 306 (M^+, 3%), 168 (16%), 139 (60%), 121 (100%).

3.11. *(R)-1-Ethylnonyl 4-hydroxybenzoate (***4c***)*

Yield = 0·40 g (72%); ν_{max} (film): 3360, 2930, 2860, 1677, 1603, 1590, 1510, 1280, 1165, 1110, 850, 775 cm^{-1}; *m/z* 292 (M^+, trace), 155 (11%), 139 (71%), 101 (100%).

3.12. *(R)-1-Ethylundecyl 4-hydroxybenzoate (***4d***)*

Yield = 0·42 g (63%); ν_{max} (film): 3340, 2920, 2855, 1680, 1605, 1590, 1460, 1280, 1165, 1110, 1100, 850, 775 cm^{-1}; *m/z* 182 (9%), 139 (68%), 121 (100%).

3.13. *(S)-1-(Fluoromethyl)heptyl 4-hydroxybenzoate (***4e***)*

Yield = 0·80 g (81%); $[\alpha]_D^{22} = -29{\cdot}3°$ ($c = 0{\cdot}0239\ g\ ml^{-1}$; $CHCl_3$); δ_H (270 MHz; $CDCl_3$; TMS): 0·87 (3H,t), 1·33 (8H,m), 1·75 (2H,m), 4·47 (1H,m), 4·65 (1H,m), 5·26 (1H,m), 6·23 (1H,s,broad), 6·88 (2H,d), 7·80 (2H,d); ν_{max} (film): 3360, 2950, 2920, 2860, 1680, 1600, 1590, 1510, 1450, 1280, 1165, 1100, 850, 770 cm^{-1}; *m/z* 268 (M^+, 9%), 138 (100%), 121 (95%).

3.14. *(S)-1-(Fluoromethyl)-2-hexyloxyethyl 4-hydroxybenzoate (***4f***)*

Yield = 0·97 g (84%); $[\alpha]_D^{22} = -8{\cdot}6°$ ($c = 0{\cdot}0232\ g\ ml^{-1}$; $CHCl_3$); δ_H (270 MHz; $CDCl_3$; TMS): 0·87 (3H,t), 1·37 (6H,m), 1·56 (2H,quintet), 3·51 (2H,m), 3·73 (2H,q), 4·60 (1H,m), 4·78 (1H,m), 5·38 (1H,m), 6·48 (1H,s,broad), 6·84 (2H,d), 7·94 (2H,d); ν_{max} (film): 3360, 2950, 2930, 2860, 1705, 1600, 1510, 1450, 1270, 850, 770 cm^{-1}; *m/z* 299 ($M^+ + 1$,10%), 197 (10%), 160 (39%), 138 (49%), 121 (93%), 113 (56%).

3.15. *(R)-1-Methylnonyl 4-(4′-dodecyloxybiphenyl-4-carbonyloxy)benzoate (***6a***)*

Dicyclohexylcarbodiimde (0·33 g, 1·6 mmol) was added to a stirred solution of compound **4a** (0·34 g, 1·2 mmol), 4′-dodecyloxybiphenyl-4-carboxylic acid (**5**) (0·50 g, 1·3 mmol), 4-*N*,*N*-dimethylaminopyridine (0·05 g, 0·4 mmol) in dry dichloromethane (15 ml). This was stirred for a further 20 h at RT, before being diluted with dichloromethane (100 ml) and filtered through a pad of 'Hyflosupercel'; the filtrate was washed with water (50 ml), 5% (v/v) acetic acid (2 × 50 ml) and water (50 ml) before being dried ($MgSO_4$), filtered and evaporated to give a colourless solid. This was purified by flash chromatography (fine mesh silica gel; 4% (v/v) ethyl acetate in petrol (b.p. 40–60°C)); the resulting colourless solid was recrystallized (cyclohexane × 3) and dried *in vacuo* (P_2O_5, 0·20 mmHg, 45°C, 5 h). Yield = 0·25 g (32%); m.p. = 61·7°C; transition temperatures: I 124·0 S_A^* 113·9 S_C^* 93·5 $S_{C_\gamma}^*$ 43·1 $S_{C_A}^*$ 35·9 recryst. (°C); $[\alpha]_D^{22} = -19{\cdot}3°$ ($c = 0{\cdot}0207\ g\ ml^{-1}$; $CHCl_3$); δ_H (270 MHz; $CDCl_3$; TMS): 0·89 (6H,m), 1·31 (33H,m), 1·82 (4H,m), 4·02 (2H,t), 5·16 (1H, sextet), 7·01 (2H,d), 7·32 (2H,d), 7·60 (2H,d), 7·70 (2H,d), 8·13 (2H,d), 8·24 (2H,d); ν_{max} (KBr disc): 2950, 2920, 2850, 1730, 1710, 1600, 1270, 1160, 1080, 830, 765, 640 cm^{-1}; *m/z* 642 (M^+, trace), 365 (100%), 197 (15%).

3.16. *(R)-1-Methylundecyl 4-(4′-dodecyloxybiphenyl-4-carbonyloxy)benzoate (***6b***)*

This compound together with **6c–f** was prepared using a similar procedure to that described for compound **6a**. Again the NMR data for **6b**, **c**, and **d** are not presented as they differ from **3a** only in the number of protons in one multiplet (*c.* 1·25–1·30 ppm). Yield = 0·04 g (10%); m.p. = 66·3°C; transition temperatures; I 120·0 S_A^* 111·3 S_C^* 89·9 $S_{C_\gamma}^*$ 41·3 recryst. (°C); $[\alpha]_D^{22} = -9{\cdot}9°$ ($c = 0{\cdot}0217\ g\ ml^{-1}$; $CHCl_3$); ν_{max} (KBr disc): 2950, 2910, 2850, 1725, 1595, 1290, 1200, 890, 830, 760 cm^{-1}; *m/z* 365 (100%), 197 (16%).

3.17. *(R)-1-Ethylnonyl 4-(4′-dodecyloxybiphenyl-4-carbonyloxy)benzoate (***6c***)*

Yield = 0·44 g (61%); m.p. = 56·2°C; transition temperatures: I 93·8 S_A^* 84·0 S_C^* 83·9 $S_{C_\gamma}^*$ 38·9 recryst. (°C); $[\alpha]_D^{22} = -4{\cdot}8°$ ($c = 0{\cdot}0210\ g\ ml^{-1}$; $CHCl_3$); ν_{max} (KBr disc): 2920, 2850, 1730, 1715, 1600, 1495, 1465, 1270, 1215, 1200, 1160, 1080, 830, 765, 690 cm^{-1}; *m/z* 656 (M^+, trace), 365 (100%), 197 (21%), 91 (78%).

3.18. *(R)-1-Ethylundecyl 4-(4′-dodecyloxybiphenyl-4-carbonyloxy)benzoate (***6d***)*

Yield = 0·36 g (40%); m.p. = 52·0°C; transition temperatures: I 89·5 S_A^* 77·0 S_C^* 75·4 $S_{C_A}^*$ 42·6 recryst. (°C); $[\alpha]_D^{22} = -5{\cdot}4°$ ($c = 0{\cdot}0184\ g\ ml^{-1}$; $CHCl_3$); ν_{max} (KBr disc): 2920, 2850, 1730, 1720, 1600, 1465, 1270, 1215, 1195, 1160, 1080, 830, 765 cm^{-1}; *m/z* 684 (M^+, trace), 365 (100%), 197 (27%).

3.19. *(S)-1-(Fluoromethyl)heptyl 4-(4′-dodecyloxybiphenyl-4-carbonyloxy)benzoate (***6e***)*

Yield = 0·77 g (47%); m.p. = 80·5°C; transition temperatures: I 120·6 S_A^* 112·5 S_C^* 68·0 $S_{C_\gamma}^*$ 56·1 $S_{C_A}^*$ 55·5 recryst. (°C); $[\alpha]_D^{22} = -16{\cdot}9°$ ($c = 0{\cdot}0236\ g\ ml^{-1}$); δ_H (270 MHz; $CDCl_3$; TMS): 0·88 (6H,2xt), 1·28 (26H,m), 1·82 (4H,m), 4·02 (2H,t), 4·49 (1H,m), 4·67 (1H,m), 5·31 (1H,m), 7·01 (2H,d), 7·33 (2H,d), 7·60 (2H,d), 7·70 (2H,d), 8·16 (2H,d), 8·23 (2H,d); ν_{max} (KBr disc): 2950, 2910, 2840, 1730, 1720, 1600, 1270, 1160, 1070, 830, 765 cm^{-1}; *m/z* 365 (43%), 197 (26%), 169 (15%), 141 (20%), 69 (25%), 55 (100%).

3.20. *(S)-1-(Fluoromethyl)-2-hexyloxyethyl 4-(4'-dodecyloxybiphenyl-4-carbonyloxy)benzoate (6f)*

Yield = 1·29 g (63%); m.p. = 78·1°C; transition temperatures: I 132·4 S_A^* 114·5 S_C^* 60·9 recryst. (°C); $[\alpha]_D^{22} = -4·9°$ ($c = 0·0289\,g\,ml^{-1}$; CHCl$_3$); δ_H (270 MHz; CDCl$_3$; TMS): 0·88 (6H,2xt), 1·26 (26H,m), 1·82 (2H,m), 3·50 (2H,td), 3·73 (2H,q), 4·02 (2H,t), 4·63 (1H,d), 4·80 (1H,d), 5·41 (1H,m), 7·01 (2H,d), 7·33 (2H,d), 7·60 (2H,d), 7·70 (2H,d), 8·17 (2H,d), 8·23 (2H,d); ν_{max} (KBr disc): 2950, 2910, 2840, 1730, 1600, 1270, 1125, 1080, 830, 765 cm^{-1}; *m/z* 366 (100%), 197 (80%), 169 (35%), 141 (28%).

4. Optical microscopy and differential scanning calorimetry

The phase assignments, transition temperatures and associated enthalpies of compounds **6a–f** are listed in table 1; optical microscopic observations were made at a heating and cooling rate of 2 deg min^{-1}, and enthalpy data obtained at a cooling rate of 5 deg min^{-1}.

Slow cooling of all compounds **6a–f** from the isotropic liquid results in the formation of focal-conic fans interspersed with regions of dark homeotropically aligned texture; this is consistent with the formation of a smectic A* phase. Further cooling of these materials results in the appearance of *pseudo*-planar, iridescent (blue–green) smectic C* textures. The blue–green colour of selectively reflected light indicates that all the compounds have a relatively short pitch length in their respective S_C^* phases (*c.* 0·4–0·5 μm). Furthermore, polarimetry by microscopy reveals that all the compounds have left-handed helices; this is completely in accordance with the accepted selection rules relating absolute configuration, parity, electronic factors, etc. to helical twist sense [12]. However, the compounds may be divided into two groups because of the opposing electronic nature of the substituents ((+I) ... alkyl and (−I) ... fluoroalkyl) and absolute configuration at the chiral centres ((*R*)- and (*S*)-); these may be summarized as follows:

6a–d (*R*)-. o. (+I). *d* ... Left-handed helices.

6e and **f** (*S*)-. o. (−I). *d* ... Left-handed helices.

Cooling the smectic C* phase of compound **6f**, resulted only in the crystallization of the sample; this compound proved to have the most straightforward S_C^* phase behaviour of the series. In the cases of compounds **6a**, **b**, **c** and **e**, slow cooling of the ferroelectric S_C^* phases resulted in the sudden loss of the blue–green colour as well as the appearance of grey, mobile 'fluid-like' domains within the microscope's field of view; continuing the cooling process resulted in the crystallization of compounds **6b** and **c**. Rotation of the upper polarizer revealed that the phases had left-handed helices indicating no twist inversion processes had occurred during this transformation. This behaviour is characteristic of the transition from a ferroelectric S* phase to a ferrielectric modification ($S_{C_\gamma}^*$). This is further supported by the fact that on cooling the 'ferrielectric' phases of compounds **6a** and **6e**, the violent 'fluid-like' motion of the domains suddenly stops and the texture becomes a marbled yellow–grey colour which is thought to arise from an antiferroelectric phase ($S_{C_A}^*$). DSC calorimetry confirms the presence of both the ferrielectric and antiferroelectric phases in compound **6a**, but only the ferrielectric phase in compound **6e**. Again no twist inversion processes were observed to mediate these transitions in compound **6a** and **b**. In contrast to any of the phase behaviour observed in compounds **6a**, **b**, **c**, **e** and **f**, compound **6d** appears to show both a ferroelectric (S_C^*) and either a ferrielectric ($S_{C_\gamma}^*$) or antiferroelectric ($S_{C_A}^*$) phase; on cooling through the short S_C^* phase towards the transition, the sample's colour suddently disappears; rotation of the microscope's upper polarizer indicates not only that the phase is helical, but has a left-handed helix (as had the preceding S_C^* phase). The DSC thermogram shows a first-order event occurring after the S_A^*–S_C^* transition ($\Delta H = 0·03$ kJ mol^{-1}), and in the light of such an observation the phase is tentatively assigned as being an antiferroelectric phase ($S_{C_A}^*$).

5. Switching studies

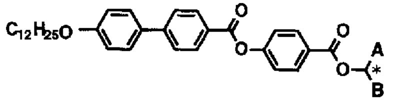
The magnitude of spontaneous polarization, direction of polarization and switched tilt angles of compounds **6a–f** (compound **6b** excluded) are listed in table 2.

It is evident from table 2 that a definite order of magnitude of polarization may be written and the decreasing order of the magnitude of spontaneous polarization is

6c > **6d** > **6f** > **6e**.

It should be noted that although compound **6d** is believed to have an antiferroelectric phase, measurement of spontaneous polarization was possible, presumably because the measurements were made at a field strength (7·14 MV m^{-1}) greater than the threshold field (E_{th}) required to effect switching between the antiferroelectric and ferroelectric states. (This was actually proved to be the case—see section on ferroelectric–antiferroelectric switching of compound **6d**).

Table 1. Transition temperatures and enthalpy data for the chiral 2- or 3-substituted-alkyl 4-(4′-dodecyloxybiphenyl-4-carbonyloxy)benzoate esters.



Compound number	A	B	Absolute configuration	Transition temperatures/°C[a] and Associated Enthalpies[b]							Twist sense of S_C^*
				m.p.[c]	I	S_A^*	S_C^*	$S_{C_\gamma}^*$	$S_{C_A}^*$	Recryst.	
6a	CH_3	C_8H_{17}	(*R*)-	61·7	● 124·0 [4·70]	● 113·9 [0·42]	● 93·5 [0·02]	● 43·1 [—][e]	● 35·9 [22·76]	●	L.H.
6b	CH_3	$C_{10}H_{21}$	(*R*)-	66·3	● 120·0 [2·88]	● 111·3 [0·31]	●89·9 [—][e]	● —	● 41·3 [21·03]	●	L.H.
6c	C_2H_5	C_8H_{17}	(*R*)-	56·2	● 93·8 [2·10]	● 84·0 [—][d]	●83·9 [—][d]	● —	● 38·9 [30·72]	●	L.H.
6d	C_2H_5	$C_{10}H_{21}$	(*R*)-	52·0	● 89·5 [1·98]	● 77·0 [0·20]	● —	75·4 [0·03]	● 42·6 [28·37]	●	L.H.
6e	CH_2F	C_6H_{13}	(*S*)-	80·5	● 120·6 [4·88]	● 112·5 [0·64]	● 68·0 [—][e]	● 56·1 [—][e]	● 55·5 [28·19]	●	L.H.
6f	CH_2F	$CH_2OC_6H_{13}$	(*S*)-	78·1	● 132·4 [6·18]	● 114·5 [0·38]	● —	—	● 60·9 [30·49]	●	L.H.

[a] Recorded at a cooling rate of 2°C min^{-1}.
[b] Enthalpies of transitions given in square brackets (kJ mol^{-1}).
[c] Taken from DSC thermograms.
[d] Transition clearly observable by DSC, however peaks are too close to allow integration for enthalpy determination.
[e] Transition not observed in DSC thermogram.

Table 2. The spontaneous polarizations, switched tilt angles and polarization directions of compounds **6a**, **c**–**f**.

Compound number	P_s[a]/ nC cm^{-2}	Tilt angle[b]/°	Polarization direction[c] $P_s(\pm)$
6a	—[d]	28	$P_s(-)$
6c	64	29	$P_s(-)$
6d	43[d]	30[e]	$P_s(-)$
6e	19	29	$P_s(-)$
6f	30	25	$P_s(-)$

[a] Quoted at 5°C below the S_A^*–S_C^* transition (recorded in 2·6 μm spaced cell, at 10 V, 60 Hz).

[b] Quoted at 5°C below the S_A^*–S_C^* transition (recorded at an applied voltage of 20 V).

[c] As defined in references [12] and [23].

[d] P_s not recorded.

[e] Recorded at 5·4°C below S_C^*–$S_{C_A}^*$ transition with an applied field at 8·0 MV m^{-1}.

The electric field dependent properties of the ferrielectric and antiferroelectric phases of compounds **6a**, **6d** and **6e** were studied using rubbed, polyimide-coated test cells. The antiferroelectric phase of compound **6d** was found to exhibit the usual 'striped-domain' texture which has previously been observed when antiferroelectric phases have been constrained between polyimide aligned cells [4]. Compound **6d** also showed the classical switched tilt angle – applied field strength dependency as the phase undergoes electric switching. This is demonstrated in figure 1, the measurements being recorded at 5·4°C below the S_C^*–$S_{C_A}^*$ transition in a 2·4 μm spaced test cell.

At high applied fields, of say 7·5 MV m^{-1}, the ferroelectric phase is fully switchable and the measured switched tilt angle is of the order of 30°. However, as the applied field is lowered, a threshold point is reached at which the energetically preferred antiferroelectric structure becomes more dominant than the previously more favourable electrically-induced ferroelectric phase. At this point, the switched tilt angle collapses to a value of around 0°. The threshold field value (E_{th}) of compound **6d** corresponds to *c*. 5·0 MV m^{-1} under these particular test conditions; the ferroelectric–antiferroelectric switching characteristic shown in figure 1 is proof that compound **6d** displays an antiferroelectric phase ($S_{C_A}^*$) below the higher temperature ferroelectric phase (S_C^*). All efforts to measure a similar type of switched tilt angle – applied field dependence for the antiferroelectric phases of compounds **6a** and **6e** failed, as both samples proved prone to crystallization which rapidly curtailed any further tilt angle measurements. Presumably the presence of the polyimide alignment layers on the test cells, dust particles and the use of spacers encourages the growth of the crystal from suitable nucleation sites (test cells of a variety of thickness (2·6–4·6 μm) were employed).

The field dependent responses of the ferrielectric phases ($S_{C_\gamma}^*$) of compounds **6a** and **6e** were also measured in a similar manner to the threshold characteristics described previously for the antiferroelectric-induced ferroelectric response of compound **6d**. The characteristics are shown on the same axes in figure 2.

In the case of compound **6a** the switched tilt angle in the electrically-induced ferroelectric phase reaches an approximate value of 32° at field strengths between 1·0 and 5·5 MV m^{-1}. Below an applied field strength of 1·0 MV m^{-1}, the value of the switched tilt angle drops rapidly to zero, suggesting that the ferrielectric phase of

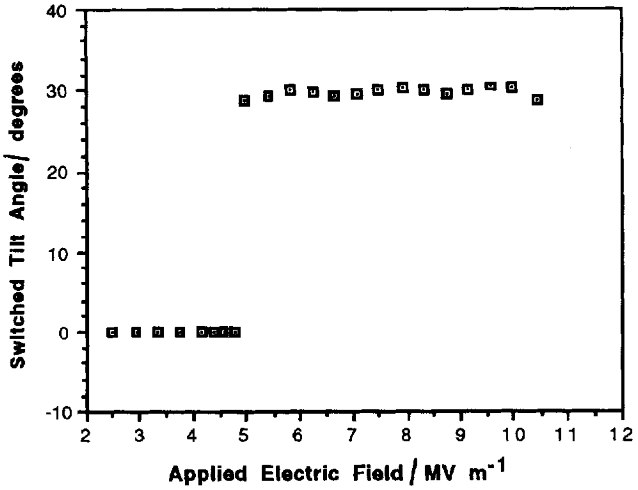


Figure 1. The field dependence of the switched tilt angle at 5·4°C below the S_C^*–S_A^* transition of compound **6d** (recorded in a 2·4 μm spaced PI cell).

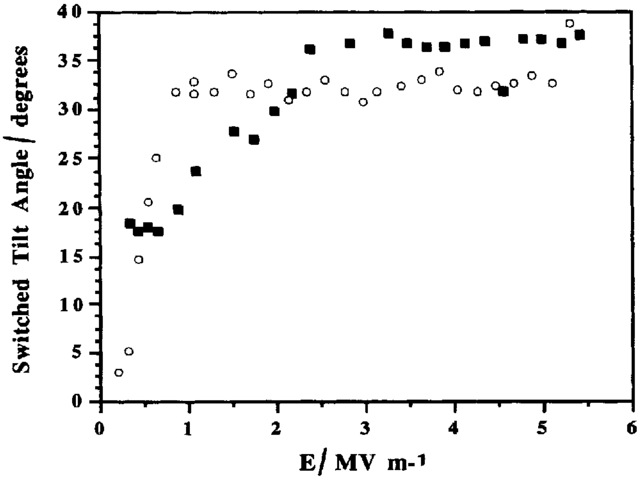


Figure 2. Applied field dependence of the switched tilt angle in the ferrielectric phases of compound **6a** (open circles) and **6e** (full squares). **6a** recorded at 91·5°C, in a 4·7 μm spaced cell; **6e** recorded at 65·0°C, in a 4·6 μm spaced cell.

compound **6a** is not especially stable. This behaviour contrasts sharply to that for compound **6e**; here the saturated ferroelectric tilt angle (θ_{FO}) corresponds to around 36° and as the applied field decreases below *c.* $3{\cdot}0\,\mathrm{MV\,m^{-1}}$, the observed tilt angle begins to drop until a small plateau at just below $1{\cdot}0\,\mathrm{MV\,m^{-1}}$ is reached. Here, the saturated ferrielectric tilt angle (θ_{FI}) is of the order of 18°, approximately half the magnitude of the induced tilt of the ferroelectric phase (θ_{FO}).

6. Discussion

Using table 1 it is possible to make a number of correlations between the prevalence of ferri- and antiferro-electric phases and the nature of the chiral terminal moiety in structure **I**. Broadly speaking, ferrielectric phases ($S^*_{C_\gamma}$) occur in materials in which group **A** contains one carbon atom (**A** = CH_3 or CH_2F); examples include compounds **6a**, **b** and **e**. The ethyl branched compound **6c** is one obvious exception to this rule of thumb, and the compound, unusually, shows only a ferrielectric phase. Compounds **6a** and **6e** also show a lower temperature antiferroelectric phase in addition to their ferrielectric phase. Interestingly, the effect of lengthening group **B** from C_8H_{17} to $C_{10}H_{21}$ (compounds **6c** and **6d**) results in the eclipse of the ferrielectric phase and gives the formation of a stable antiferroelectric phase (E_{th} **6d** $\approx 5{\cdot}0\,\mathrm{MV\,m^{-1}}$). The effect of lengthening the lateral chiral branch to give a stabilization of the antiferroelectric phase has been noted previously [5].

The use of polar terminal substituents has been cited as causing the destabilization of any antiferroelectric phase [24]; compounds **6e** and **6f** possess one and two polar terminal substituents respectively (**6e**, **A** = CH_2F; **6f**, **A** = CH_2F and **B** = $CH_2OC_6H_{13}$). Compound **6e** shows both ferri- and antiferro-electric phases, whereas, the more polar compound **6f** is only a normal smectic C* material. A consequence of the increased polarity of **6f** with respect to **6e** is seen in the $T_{I\text{-}S^*_A}$ and $T_{S^*_A\text{-}S^*_C}$ transitions of both compounds; the 'extra' methyleneoxy insert boosts the transition temperatures by 11·8 and 2·0°C, respectively. This result appears to suggest that polar substituents at the chiral point destabilize the formation of antiferroelectric phases.

7. Conclusions

The 2- or 3-substituted-alkyl 4-(4′-dodecyloxybiphenyl-4-carbonyloxy)benzoates discussed all displayed smectic A* and smectic C* phases. In addition some of the compounds also displayed ferrielectric ($S^*_{C_\gamma}$) and antiferroelectric ($S^*_{C_A}$) subphases of the ferroelectric smectic C* phases, but the occurrence of these phases depends on the nature of the branch at the chiral point. The compounds containing one carbon branch point showed ferrielectric and occasionally antiferroelectric phases. The field dependence of the switched tilt angle of the ferrielectric and antiferroelectric phases was determined for a number of the compounds, the antiferroelectric phases having higher thresholds than the ferrielectric phases. The helical twist sense and polarization direction of the ferroelectric phases of compounds **6a–f** could be accurately predicted from well known selection rules which consider the absolute configuration, parity, and electronic influence of the groups attached to the chiral centre of the molecules.

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