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The synthesis and electro-optic properties of liquid crystalline 2-(2,3-difluorobiphenyl-4′-yl)-1,3-dioxanes

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Fifty-six novel alkyl and/or alkoxy disubstituted 2-(2,3-difluorobiphenyl-4′-yl)-1,3-dioxanes (DFBPD) were prepared. Smectic C and nematic mesophases were exhibited by most of the alkyl–alkoxy homologues. Conversely, most of the dialkyl compounds exhibited smectic C, smectic A and nematic phases. The birefringence (Δn), dielectric anisotropy ($\Delta\varepsilon$), spontaneous polarisation and response times of two ferroelectric mixtures formulated from the dioxanyl systems were determined. The birefringence results were compared with eight other groups of mixtures where the materials were based on different core systems. The overall electro-optic properties of the DFBPDs were found to be comparable to the best of the eight most commonly used materials in ferroelectric display devices.

Introduction

High performance ferroelectric liquid crystal (FLC) flat-panel electro-optic displays require ferroelectric mixtures that have low birefringences (Δn), low viscosities (η) and low spontaneous polarisations (Ps).[1] In addition, the materials need to align well on the internal surfaces of the electro-optic cell. High quality alignment is usually achieved by using a ferroelectric liquid crystal mixture that possesses an Iso–N*–SmA*–SmC* phase sequence, where alignment is achieved in the chiral nematic phase. The chiral smectic C* phase should also have a wide temperature range (over all foreseeable conditions of use) and should not exhibit ordered, lower temperature anisotropic plastic crystal (crystal smectic) phases. Device properties are optimised by the formulation of multi-component mixtures, however, the need for new pure component materials to fulfil the above criteria is of great importance.

Previous research has shown that the inclusion of a laterally difluorinated phenyl ring into a mesogenic core produces liquid crystals with negative dielectric anisotropies and biaxialities, and also leads to the suppression of the more ordered smectic phases and to the formation of tilted smectic phases.[2–7] In addition to laterally difluorinated biphenyls and terphenyls, a variety of other related liquid crystals with negative dielectric anisotropies are known that possess cyclohexyl or heterocyclic rings linked to a fluorophenyl ring.[3,8–12] Aromatic rings, be they homo- or heterocyclic, possess conjugated π-electrons, and this generally results in higher viscosities and birefringences than analogous non-conjugated, saturated alicyclic systems. Compounds containing a cyclohexyl ring usually possess relatively low viscosities and birefringences, however the inclusion of cyclohexyl rings in the core usually suppresses the formation of smectic C phases. Conversely the dioxane ring is also a saturated alicycle but is more polar than a cyclohexyl ring and therefore it tolerates the formation of smectic C phases to a greater extent. Therefore, it was decided to investigate a number of systems based on the very successful difluoroterphenyl three-ring core, but where one of the aromatic rings was replaced by a dioxanyl unit, and therefore the (difluorobiphenylyl)dioxane (DFBPD) systems were targeted for synthesis.

In this paper, we report the synthesis of some new heteroalicyclic liquid-crystalline materials, and the thermal properties of the pure materials and two ferroelectric liquid crystal mixtures derived from them. A number of electro-optic studies were carried out in order to evaluate the performance of the mixtures relative to state of the art materials.

Experimental

Analysis of materials

Confirmation of the structures of the intermediates and products was obtained by ^{1}H NMR spectroscopy (JEOL JNM-GX270 FT spectrometer operating at 270 MHz), infrared spectroscopy (Perkin-Elmer 783 or 983 spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 automated GC/MS). The progress of the reactions and the purity of a number of products were checked using a Perkin-Elmer 8320 capillary gas chromatograph equipped with a BP1 capillary column (12 m). The purity of all final compounds and a number of intermediates was checked by HPLC [Dynamax Microsorb C18 Reverse Phase Column (25 cm)]. The transition temperatures of all mesogens were determined using an Olympus BH-2 polarising light microscope in conjunction with a Mettler FP52 heating stage and a Mettler FP5 temperature control unit. The transition temperatures were verified and the transition enthalpies were determined by thermal analysis using a Perkin-Elmer DSC7-PC differential scanning calorimeter. Diethyl ether was dried and stored over sodium wire. THF was dried by distillation from sodium wire and benzophenone and stored over 4 Å molecular sieves. Ethanol was dried by distillation from magnesium and stored over 4 Å molecular sieves. Toluene was dried by distillation from and stored over 4 Å molecular sieves.

Synthesis

Fifty-six novel products were prepared according to the procedures detailed in Scheme 1. The results are summarised in Tables 1 and 2. All homologues were prepared using the same methods and therefore the general experimental procedures are illustrated using 2-(4-pentoxy-2,3-difluorobiphenyl-4′-yl)-5-pentyl-1,3-dioxane as an example.

Diethyl 2-pentylpropanedicarboxylate ($\mathbf{2_5}$). Alcoholic sodium ethoxide, prepared from sodium (7.8 g, 0.34 mol) in super-dry ethanol (200 cm^3) was cooled to *ca.* 50 °C and diethyl malonate

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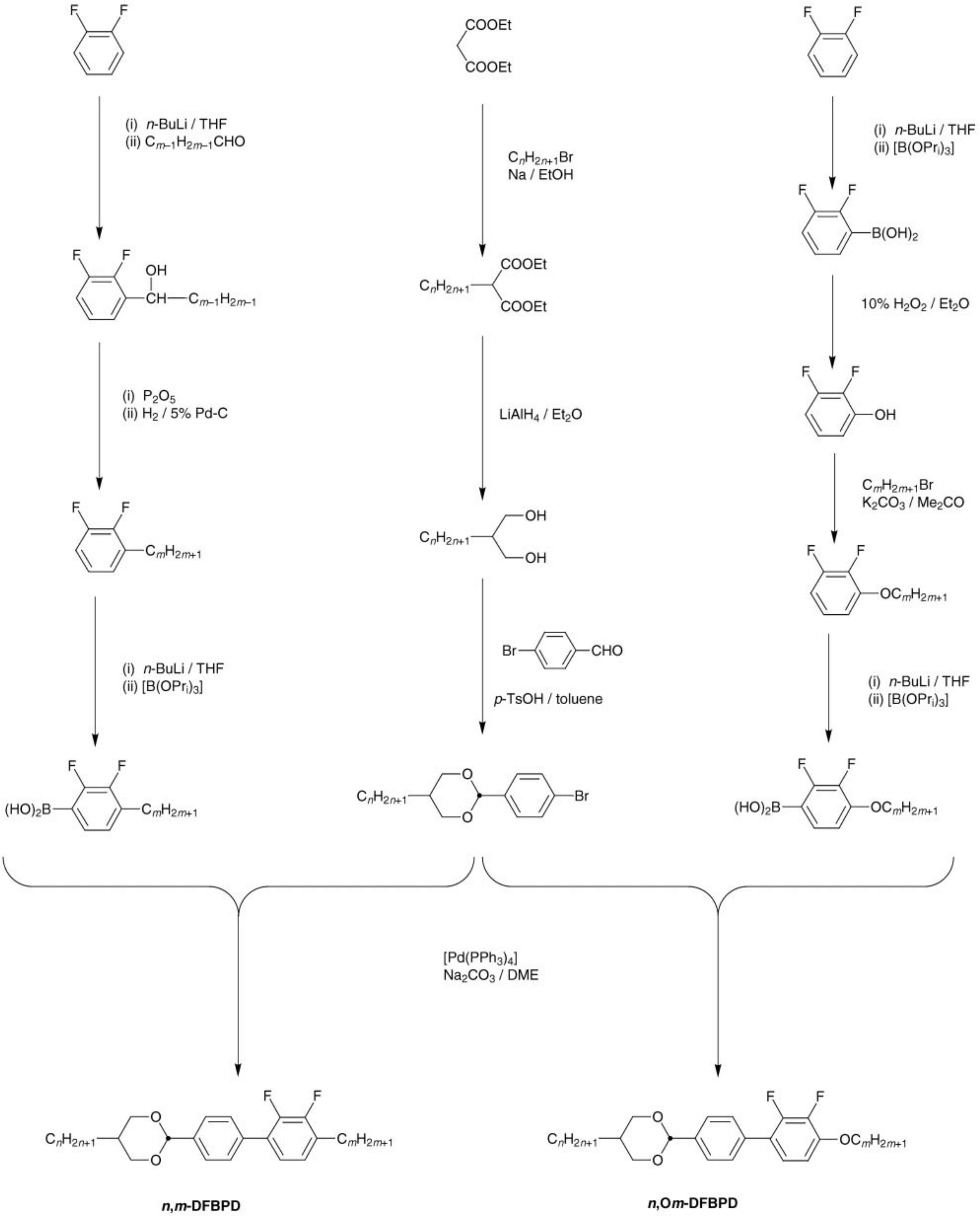


Scheme 1 Synthetic pathway to the target dioxane-containing materials.

(55 g, 0.34 mol) was added slowly with vigorous stirring. 1-Bromopentane (49.5 g, 0.33 mol) was added gradually and the mixture was heated under reflux until neutral to moist litmus (*ca.* 2 h). The solvent was removed *in vacuo* and water (200 cm^3) was added. The aqueous layer was partitioned into diethyl ether (2 × 100 cm^3) and the combined ethereal layers were dried (Na_2SO_4). The solvent was removed *in vacuo* and the pure product was isolated by distillation under reduced pressure. Yield = 71 g (78%); bp 82–87 °C/0.2 mmHg.

δ_H (270 MHz; $CDCl_3$; Me_4Si): 0.88 (3H, t, *J* 7.0, $CH_3C_3H_6$–), 1.28 [12H, m, –C_3H_6–, –$(CO_2CH_2CH_3)_2$], 1.88 (2H, q, *J* 8.0, –$C_3H_6CH_2CH$–), 3.31 (1H, t, *J* 8.5, –CH_2CHCO_2–), 4.20 [4H, q, *J* 8.0, –$(CO_2CH_2\,CH_3)_2$]. ν_{max} (film)/cm^{-1}: 2968 (CH_3–, C–H asym str), 2935 (–CH_2–, C–H asym str), 2884 (CH_3–, C–H sym str), 2870 (–CH_2–, C–H sym str), 1735 (C=O str), 1468 (CH_3– asym, –CH_2– sci, C–H def), 1372 (CH_3–, C–H sym def), 1156 (C–O str), 1120, 1035. *m*/*z*: 230 $[M]^+$, 185, 173, 160, 143.

Pentylpropane-1,3-diol ($\mathbf{3_5}$). A solution of compound $\mathbf{2_5}$ (59.2 g, 0.26 mol) in sodium-dried diethyl ether (50 cm^3) was added dropwise to a mixture of lithium aluminium hydride (19.5 g, 0.52 mol) in dry diethyl ether (450 cm^3) with vigorous stirring and the mixture heated under gentle reflux. During this period, 4×50 cm^3 portions of dry diethyl ether were added. After further heating (1 h), water (75 cm^3) was added carefully followed by sulfuric acid (20%, 350 cm^3) in order to decompose the lithium aluminium complex. The aqueous layer was partitioned with diethyl ether (2×100 cm^3) and the combined ether extracts were washed with water (2×100 cm^3) and dried ($MgSO_4$). The solvent was removed *in vacuo* to give the product as a colourless oil. Yield = 31 g (83%).

δ_H (270 MHz; $CDCl_3$; Me_4Si): 0.90 (3H, t, *J* 6.5, CH_3–), 1.30 (8H, m, $CH_3C_4H_8$), 1.77 (1H, m, *J* 4.0, –$C_4H_8CHCH_2$–), 2.74 (2H, s, –O*H*), 3.64 [2H, dd, *J* 10.5 and 7.5, –(CH_2OH)$_2$], 3.82 [2H, dd, *J* 10.5 and 4.0, –(CH_2OH)$_2$]. ν_{max} (film)/cm^{-1}: 3700–3040 (bonded O–H str), 2962 (CH_3–, C–H asym str), 2930 (–CH_2–, C–H asym str), 2882 (CH_3–, C–H sym str), 2866 (–CH_2–, C–H sym str), 1470 (CH_3– asym, -CH_2– sci, C–H def), 1381 (O–H in-plane def), 1035 (C–O str). *m*/*z*: 128 $[M - H_2O]^+$, 110, 98.

2-(4-Bromophenyl)-5-pentyl-1,3-dioxane ($\mathbf{4_5}$). A mixture of compound $\mathbf{3_5}$ (31 g, 0.21 mol), 4-bromobenzaldehyde (38.8 g, 0.21 mol) and toluene-4-sulfonic acid (0.11 g, 0.6 mmol) in dry toluene (200 cm^3) was heated under reflux (3 h) using a Dean and Stark trap to remove water as it was produced. On cooling to room temperature, the mixture was poured into aqueous sodium hydrogen carbonate solution (5%, 70 cm^3) and the separated organic layer was washed with aqueous sodium hydrogen carbonate solution (5%, 2×60 cm^3), water (2×60 cm^3) and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue purified by crystallisation from methanol to remove the *cis*-isomer. Yield = 33.1 g (50%); mp 76.5–77.0 °C.

δ_H (270 MHz; $CDCl_3$; Me_4Si): 0.89 (3H, t, *J* 6.5, CH_3–), 1.09 (2H, q, *J* 7.0, CH_3CH_2–), 1.29 (6H, m, –$CH_2C_3H_6$–), 2.11 (1H, m, 5-*H*), 3.52 (2H, dd, *J* 11.5 and 11.5, Ha), 4.22 (2H, dd, *J* 11.5 and 4.5, He), 5.36 (1H, s, 2-*H*), 7.35 (2H, AA′BB′, –C_6H_4–), 7.49 (2H, AA′BB′, –C_6H_4–). ν_{max} (KBr disc)/cm^{-1}: 2964 (CH_3–, C–H asym str), 2936 (–CH_2–, C–H asym str), 2868 (CH_3–, –CH_2–, C–H sym str), 1600 and 1490 (C=C str), 1470 (CH_3– asym, –CH_2– sci, C–H def), 1387 (CH_3–, C–H sym def), 1168, 1132, 1088, 1073, 1026 and 1014 (C–O str), 982, 805 (1,4-disub, C–H o.o.p.d.). *m*/*z*: 314 $[M]^+$, 312 $[M]^+$, 185, 183, 157, 155.

2,3-Difluorophenylboronic acid (6). *n*-Butyllithium (30 cm^3, 10.0 M in hexanes, 0.3 mol) was added dropwise to a stirred, cooled (−78 °C) solution of 1,2-difluorobenzene (34.5 g, 0.3 mol) in dry THF (350 cm^3) under an atmosphere of dry nitrogen. The reaction mixture was stirred (2.5 h), then a previously cooled (−78 °C) solution of triisopropyl borate (113 g, 0.6 mol) in dry THF (200 cm^3) was added dropwise at −78 °C. The reaction mixture was allowed to warm to room temperature overnight then stirred (1 h) with hydrochloric acid (10%, 300 cm^3). The product was partitioned into diethyl ether (2×300 cm^3), and the combined ether extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield colourless crystals. Yield = 47 g (100%).

δ_H (270 MHz; $CDCl_3$; Me_4Si): 5.10 [2H, d, *J* 5.5, –B(O*H*)$_2$], 7.15 (1H, ABCXY, –$C_6H_3F_2$), 7.27 (1H, ABCXY, –$C_6H_3F_2$), 7.57 (1H, ABCXY, –$C_6H_3F_2$). ν_{max} (KCl disc)/cm^{-1}: 3700–3000 (bonded O–H str), 1628, 1588 and 1472 (C=C str), 1360 (B–O str), 1270, 1048, 908, 796 and 734 (1,2,3-trisub, C–H o.o.p.d.). *m*/*z*: 158 $[M]^+$, 140, 114.

2,3-Difluorophenol (7). Hydrogen peroxide (10%, 340 cm^3, 1 mol) was added dropwise to a stirred solution of compound **6** (47 g, 0.3 mol) in diethyl ether (350 cm^3) and heated under reflux. The stirred mixture was heated under reflux for a further 2.5 h, and then cooled. The ethereal layer was separated and the aqueous layer partitioned into diethyl ether (2×200 cm^3). The combined ether extracts were washed with aqueous sodium hydroxide (10%, 4×100 cm^3) and the separated aqueous layers were acidified with 36% hydrochloric acid. The product was partitioned from the aqueous layer into diethyl ether (3×100 cm^3) and the combined ether extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to give an off white solid. Yield = 39 g (100%); mp 30–32 °C.

δ_H (270 MHz; $CDCl_3$; Me_4Si): 5.15 (1H, d, O*H*), 6.67–6.82 (2H, ABCXY, –$C_6H_3F_2$), 6.90–7.00 (1H, ABCXY, –$C_6H_3F_2$). ν_{max} ($CDCl_3$ film)/cm^{-1}: 3700–3000 (bonded O–H str), 1630, 1535, 1513, 1492 and 1482 (C=C str), 1310 (O–H in-plane def), 1255, 1182 (C–O str), 1025, 910, 736 and 700 (1,2,3-trisub, o.o.p.d.). *m*/*z*: 130 $[M]^+$.

2,3-Difluoro-1-pentoxybenzene ($\mathbf{8_5}$). A solution of 1-bromopentane (30.5 g, 0.2 mol) in acetone (50 cm^3) was added dropwise to a stirred mixture of compound **7** (26 g, 0.2 mol) and potassium carbonate (55.5 g, 0.4 mol) in acetone (200 cm^3) at room temperature. The stirred mixture was heated under reflux (48 h) (*i.e.* until GLC analysis revealed complete reaction) and the crude product was extracted into diethyl ether (2×200 cm^3) and dried (Na_2SO_4). The solvent was removed *in vacuo* and the pure product obtained by distillation under reduced pressure as a colourless liquid. Yield = 37 g (92%); bp 75–78 °C/0.6 mmHg.

δ_H (270 MHz; $CDCl_3$; Me_4Si): 0.93 (3H, t, *J* 7.0, CH_3–), 1.43 (4H, m, $CH_3C_2H_4$–), 1.83 (2H, qn, *J* 7.0, –CH_2CH_2O–), 4.03 (2H, t, *J* 6.5, –CH_2O–), 6.74 (2H, ABCXY, –$C_6H_3F_2$), 6.96 (1H, ABCXY, –$C_6H_3F_2$). ν_{max} (KCl disc)/cm^{-1}: 2968 (CH_3–, C–H asym str), 2942 (–CH_2–, C–H asym str), 2882 (CH_3–, C–H sym str), 2872 (–CH_2–, C-H sym str), 1624, 1517 and 1487 (C=C str), 1473 (CH_3– asym, –CH_2– sci, C–H def), 1322, 1294, 1257 (aryl–O str), 1076 (alkyl–O str), 768 and 710 (1,2,3-trisub, C–H o.o.p.d.). *m*/*z*: 200 $[M]^+$, 130.

2,3-Difluoro-4-pentoxyphenylboronic acid ($\mathbf{9_5}$). *Quantities*. *n*-Butyllithium (20 cm^3, 10.0 M in hexanes, 0.2 mol), compound $\mathbf{8_5}$ (37 g, 0.19 mol) and triisopropyl borate (70 g, 0.38 mol). The experimental procedure was as described previously for the preparation of compound **6**. Yield = 45 g (100%).

δ_H (270 MHz; $CDCl_3$; Me_4Si): 0.94 (3H, t, *J* 6.5, CH_3–), 1.42 (4H, m, –C_2H_4–), 1.84 (2H, qn, *J* 7.0, –CH_2CH_2O–), 3.15 [2H, br, –B(O*H*)$_2$], 4.07 (2H, t, *J* 6.5, –CH_2O–), 6.77 (1H, ABXY, –$C_6H_2F_2$–), 7.44 (1H, ABXY, –$C_6H_2F_2$–). ν_{max} (KBr disc)/cm^{-1}: 3700–3000 (bonded O–H str), 2960 (CH_3–, C–H asym str), 2940 (–CH_2–, C–H asym str), 2880 (CH_3–, C–H sym str), 2868 (–CH_2–, C–H sym str), 1630 and 1520 (C=C str), 1470 (CH_3– asym, –CH_2– sci, C–H def), 1365 (B–O str), 1306, 1222 (aryl–O str), 1084 and 1030 (alkyl–O str), 908, 820 (1,4-disub, C–H o.o.p.d.), 790, 747. *m*/*z*: (180 °C): 678 $[M]^+$–trimer, 468, (120 °C): 244 $[M]^+$, 174, 130.

1-(2,3-Difluorophenyl)pentan-1-ol ($\mathbf{10_5}$). *n*-Butyllithium (50 cm^3, 10.0 M in hexanes, 0.5 mol) was added dropwise to a stirred and cooled (−78 °C) solution of 1,2-difluorobenzene (57 g, 0.5 mol) in dry THF (600 cm^3) under an atmosphere of dry nitrogen. The mixture was maintained under these conditions (3 h), then a solution of pentanal (43.1 g, 0.5 mol) in dry THF (50 cm^3) was added dropwise at −78 °C. The temperature of the reaction mixture was allowed to reach room temperature overnight. An aqueous solution of ammonium chloride (27 g in 160 cm^3 water) was added and the product was extracted into diethyl ether (2×150 cm^3).

The combined extracts were washed with water (2 × 150 cm^3) and dried ($MgSO_4$). The solvent was removed *in vacuo* to give the product as a colourless oil which was purified by distillation under reduced pressure. Yield = 55.5 g (55%); bp 94–98 °C/1.0 mmHg.

δ_H (270 MHz; $CDCl_3$; Me_4Si): 0.90 (3H, t, *J* 6.5, $\mathrm{C}H_3$–), 1.35 (4H, m, –C_2H_4–), 1.77 [2H, m, –$\mathrm{C}H_2\mathrm{CH(OH)}$–], 1.92 (1H, s, –$\mathrm{O}H$), 5.03 [1H, t, *J* 6.5, –$\mathrm{CH_2C}H\mathrm{(OH)}$–], 7.07 (2H, ABCXY, –$\mathrm{C}_6H_3\mathrm{F}_2$), 7.22 (1H, ABCXY, –$\mathrm{C}_6H_3\mathrm{F}_2$). ν_{max} (film)/cm^{-1}: 3600–3100 (bonded O–H str), 2964 (CH_3–, C–H asym str), 2938 (–CH_2–, C–H asym str), 2882 (CH_3–, C–H sym str), 2870 (–CH_2–, C–H sym str), 1631 and 1601 (C=C str), 1487 (br, C=C str, CH_3– asym, –CH_2– sci, C–H def), 1278 (O–H in-plane def), 1205, 1060 (C–O str), 826, 787 and 730 (1,2,3-trisub, C–H o.o.p.d.). *m*/*z*: 200 [M]$^+$, 142.

2,3-Difluoro-1-pentylbenzene (11_5). A solution of compound 10_5 (55.5 g, 0.28 mol) in light petrol (100 cm^3) was added dropwise to a stirred mixture of phosphorus pentoxide (127 g, 0.9 mol) in light petrol (300 cm^3). The mixture was stirred overnight at room temperature (GLC analysis revealed complete reaction) and then filtered. 5% Palladium-on-charcoal (7 g) was added to the filtrate and the mixture was stirred under an atmosphere of hydrogen (12 h) at room temperature and pressure (GLC analysis revealed complete reaction). The catalyst was removed by filtration and the solvent was removed *in vacuo* to give the product as a colourless oil which was purified by distillation under reduced pressure. Yield = 29.2 g (57%); bp 50–52 °C/0.85 mmHg.

δ_H (270 MHz; $CDCl_3$; Me_4Si): 0.90 (3H, t, *J* 6.5, $\mathrm{C}H_3$–), 1.35 (4H, m, –C_2H_4–), 1.62 (2H, qn, *J* 7.5, –$\mathrm{C}H_2\mathrm{CH_2}$–), 2.67 (2H, dt, *J* 1.5 and 7.5, –$\mathrm{C}H_2\mathrm{C_6H_3F_2}$), 6.96 (3H, ABCXY, –$\mathrm{C}_6H_3\mathrm{F}_2$). ν_{max} (film)/cm^{-1}: 2964 (CH_3–, C–H asym str), 2938 (–CH_2–, C–H asym str), 2880 (CH_3–, C–H sym str), 2868 (–CH_2, C–H sym str), 1630 and 1600 (C=C str), 1489 (br, C=C str, CH_3– asym, –CH_2– sci, C–H def), 1286, 1210, 1109, 1058, 827, 782 and 728 (1,2,3-trisub, C–H o.o.p.d.). *m*/*z*: 184 [M]$^+$, 127.

4-Pentyl-2,3-difluorophenylboronic acid (12_5). *Quantities.* Compound 11_5 (17.3 g, 94 mmol), *n*-butyllithium (10 cm^3, 10.0 M in hexanes, 0.1 mol) and triisopropyl borate (35.7 g, 0.19 mol). The experimental procedure was as described previously for the preparation of compound 9_5. Yield = 21 g (98%).

δ_H (270 MHz; $CDCl_3$; Me_4Si): 0.90 (3H, t, *J* 7.0, $\mathrm{C}H_3$–), 1.33 (4H, m, –C_2H_4–), 1.62 (2H, qn, *J* 7.5, –$\mathrm{C_2H_4C}H_2\mathrm{CH_2}$–), 2.68 (2H, dt, *J* 1.2 and 7.5, –$\mathrm{C}H_2\mathrm{C_6H_2F_2}$–), 4.97 [2H, br, –$\mathrm{B(O}H)_2$], 7.00 (1H, ABXY, –$\mathrm{C}_6H_2\mathrm{F}_2$), 7.46 (1H, ABXY, –$\mathrm{C}_6H_2\mathrm{F}_2$–). ν_{max} (KBr disc)/cm^{-1}: 3600–3000 (bonded O–H str), 2962 (CH_3–, C–H asym str), 2940 (–CH_2–, C–H asym str), 2880 (CH_3–, C–H sym str), 2870 (–CH_2–, C–H sym str), 1636 and 1497 (C=C str), 1455 (CH_3– asym, –CH_2– sci, C–H def), 1355 (B–O str), 1220, 1133, 1056, 996, 905, 815 (1,4-disub, C–H o.o.p.d.). *m*/*z*: 630 [M]$^{+-}$trimer, 574, 505, 448, 391, 378, 322, 228 [M]$^+$.

2-(4-Pentoxy-2,3-difluorobiphenyl-4′-yl)-5-pentyl-1,3-dioxane (5,O5-DFBPD). A mixture of compound 12_5 (1.34 g, 5.5 mmol), compound 4_5 (1.57 g, 5.0 mmol), tetrakis(triphenylphosphine)palladium(0) (173 mg, 0.15 mmol), aqueous sodium carbonate (2 mol dm^{-3}, 5 cm^3) and 1,2-dimethoxyethane (20 cm^3) was heated under reflux (24 h) then cooled to room temperature. The excess boronic acid was oxidised using 27% hydrogen peroxide (0.5 cm^3) over a period of 1 h. The mixture was partitioned into diethyl ether (2 × 50 cm^3) and the ethereal extracts were washed with saturated aqueous sodium chloride (2 × 50 cm^3) and dried (Na_2SO_4). The solvent was removed *in vacuo* and the product purified by flash column chromatography (dichloromethane–light petrol: 1 : 1) and recrystallisation from methanol–light petrol (1 : 1). Yield = 1.6 g (74%); Purity (HPLC, MeCN): 99.84%; Elemental analysis: Calculated (Found) for $C_{26}H_{34}F_2O_3$: C 72.20 (72.43); H 7.92 (7.92)%. Mesomorphism (*T*/°C): Cryst 65 SmC 81.4 N 140.4 Iso.

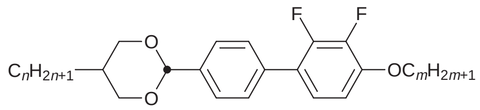
δ_H (270 MHz; $CDCl_3$; Me_4Si): 0.90 (3H, t, *J* 6.5, $\mathrm{C}H_3$–), 0.95 (3H, t, *J* 6.5, $\mathrm{C}H_3$–), 1.11 (2H, q, *J* 6.5, $\mathrm{CH_3C}H_2\mathrm{C_3H_6}$–), 1.29 (8H, m, $\mathrm{CH_3C}H_2$–, $\mathrm{CH_3CH_2C_3}H_6$–), 1.45 (2H, m, –$\mathrm{CH_2C}H_2\mathrm{CH_2CH_2O}$–), 1.85 (2H, qn, *J* 7.0, –$\mathrm{CH_2C}H_2\mathrm{CH_2O}$–), 2.14 (1H, m, 5-*H*), 3.55 (2H, dd, *J* 11.5 and 11.5, Ha), 4.07 (2H, t, *J* 6.5, –$\mathrm{C}H_2\mathrm{O}$–), 4.25 (2H, dd, *J* 11.5 and 4.5, He), 5.46 (1H, s, 2-*H*), 6.78 (1H, ABXY, –$\mathrm{C}_6H_2\mathrm{F}_2$–), 7.07 (1H, ABXY, –$\mathrm{C}_6H_2\mathrm{F}_2$–), 7.53 (4H, AA′BB′, –$\mathrm{C}_6H_4$–). ν_{max} (KBr disc)/cm^{-1}: 2966 (CH_3–, C–H asym str), 2932 (–CH_2–, C–H asym str), 2876 (CH_3–, C–H sym str), 2864 (–CH_2–, C–H sym str), 1630 and 1510 (C=C str), 1472 (CH_3– asym, –CH_2– sci, C–H def), 1388 (CH_3–, C–H sym def), 1320, 1303 and 1294 (aryl–O str), 1128, 1081 and 1021 (alkyl–O str), 800 (1,4-disub, C–H o.o.p.d.). *m*/*z*: 432 [M]$^+$, 361, 234.

Results and discussion

Mesomorphism

The mesomorphic phase behaviour was determined over a range of alkyl chain lengths (C_5–C_{10}) for the two series of substituted (difluorobiphenylyl)dioxanes defined as follows: (i) the alkyl–alkoxy (*n*,O*m*-DFBPD) and (ii) the alkyl–alkyl (*n*,*m*-DFBPD) (difluorobiphenylyl)dioxanes. By defining the properties of homologous series of these materials, we were able to select from a wide base of materials for mixture formulation studies. Surprisingly, the two different series of materials gave quite different results in terms of phase sequence and stability.

(i) Alkyl–alkoxy (2,3-difluorobiphenylyl)dioxane series.



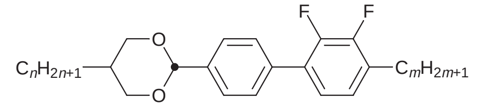
The transition temperatures are shown in Table 1 and

Table 1 Transition temperatures (°C) for the alkyl–alkoxy series (*n*,O*m*-DFBPD)

n	*m*	Cryst–SmC	SmC–SmA	N–Iso
5	5	65	81.4	140.4
5	6	62	81.1	139.9
5	7	63	85.1	134.6
5	8	62	85.8	133.9
5	9	63	86.9	129.3
6	5	66	94.2	135.5
6	6	65	95.6	135.1
6	7	57	99.0	130.9
6	8	53	97.7	129.4
6	9	58	97.5	126.3
7	5	59	104.5	138.4
7	6	55	107.8	139.9
7	7	59	110.6	135.1
7	8	58	108.2	133.4
7	9	57	110.7	130.5
8	5	56	112.5	134.1
8	6	52	113.0	134.7
8	7	59	117.3	133.0
8	8	54	116.1	131.5
8	9	67	115.4	128.4
9	5	58	119.7	135.7
9	6	54	121.1	136.0
9	7	54	121.7	132.3
9	8	48	120.8	131.4
9	9	61	122.3	129.7

represented graphically in Fig. 1. It is clear that the phase behaviour is similar for all homologues of n,Om-DFBPD where $n = 5$–9 and $m = 5$–9. Increasing the length of the terminal alkoxy chain (m) across a series gives rise to little change in the temperature of the melting (Cryst–SmC) transition although a slight odd–even effect was observed. The transition between the smectic C and the nematic phase varied little with changes in the value of m but increased significantly with an increase in the length of the terminal alkyl substituent on the dioxane ring (n). The transition between the nematic phase and the isotropic liquid on the other hand varied little with the value of n, but decreased slightly with increasing the value of m. The overall effect of increasing either n alone or n and m together is generally to increase the smectic C phase range and stability at the expense of the nematic phase. It is interesting to note that orthogonal smectic A (SmA) phases are absent for all homologues, irrespective of terminal chain lengths. This may be explained in both steric and electronic terms. The three-ring core has a geometry that is reasonably fixed due to steric and electronic repulsions, with the dioxane ring being flattened slightly relative to a cyclohexane ring as a consequence of the two sp^3 hybridised oxygen heteroatoms. However, the alkyl substituents are free to move relative to the core. X-Ray crystallography experiments and computer simulations[13] have revealed that an alkoxy chain substituent located at the 4-position on a benzene ring will give a dihedral angle with the ring (C_{AR}–O–C_1–C_2) of approximately 0°. In the case of alkyl substituents, the same dihedral angle (C_{AR}–C_1–C_2–C_3) is approximately 90°. This automatically constrains some degrees of freedom for the alkyl or alkoxy chains. Additionally, NMR evidence shows that when an alkoxy substituent has an *ortho*-fluoro substituent on the aromatic ring, the conformation is biased so that the dipoles associated with the fluorine and oxygen lone pairs are co-operatively aligned[14] (Fig. 2). Consequently another degree of freedom is removed. If we assume therefore, that the alkoxy chain adopts this preferred conformation, and then include a cone to define the precessional motion of the chain away from the fixed dihedral, we obtain an average molecular shape that is bent. This is conducive to the formation of a smectic C phase but not necessarily a smectic A phase. In terms of the electronic properties, the molecule possesses two sites of high electron density as a consequence of the alkoxy and difluoro substituents located on the aromatic portion of the core, and the other one due to the two oxygen heteroatoms in the dioxane ring. Two dipoles, one at either end of the molecular core, are predicted by McMillan to be conducive to the formation of smectic phases and the smectic C phase in particular.[15] Thus, increasing the chain length of the terminal aliphatic chain (n) on the dioxane ring increases the overall molecular bend and therefore both the smectic C phase stability and phase range are increased.

(ii) Alkyl–alkyl (difluorobiphenylyl)dioxane series.



The transition temperatures are shown in Table 2 and represented graphically in Fig. 3. The phase behaviour is far more complex than for the alkyl–alkoxy series, however a number of general trends can be distilled from the results. The melting points (Cryst–SmC) increase steadily with increasing aliphatic chain length (m) across each series. There is a small variation in the Cryst–SmC transition with n, the temperature decreasing for increasing odd members but increasing with increasing even members. When $n = 5$, a short temperature range smectic C phase was observed for aliphatic chain lengths of $m = 6$–8 and 10, however the SmC phase was monotropic for $m = 5$ and 9. Increasing the aliphatic chain length n on the terminal dioxane ring increases the smectic phase stability, which is reflected in the increased temperature range and phase stability of the smectic C phase and the introduction of an orthogonal smectic A phase. As the value of m is increased across each series, so too is the temperature stability of the smectic C phase. However, for higher values of m, the smectic C phase stability begins to decrease again. As the smectic C range decreases, the smectic A to nematic transition temperature increases and hence so does the smectic A phase range. This can be rationalised in terms of changes in the length to width ratio as m and n are varied. At short chain lengths, the length to width ratio is small and the molecules tend to have a rod-like shape [Fig. 4(a)]. As the chain length increases, so the molecules become zig-zag shaped which favours the formation of tilted phases.[16] However, at long chain lengths the molecules again tend to become more linear and rod-like and so orthogonal phases again become stabilised in preference to

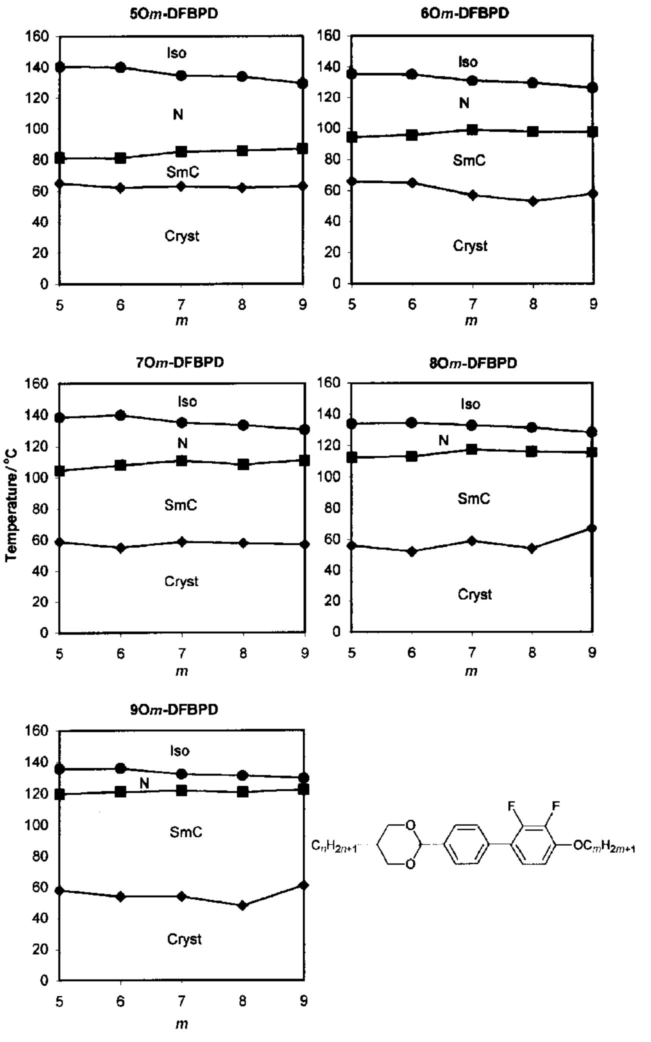


Fig. 1 Plots of transition temperatures (°C) for the alkyl–alkoxy series (n,Om-DFBPD).

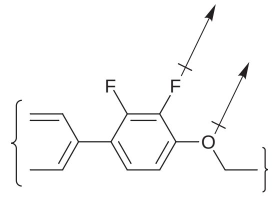


Fig. 2 Schematic representation of co-operative dipole alignment in laterally fluorinated phenyl ethers.

Table 2 Transition temperatures (°C) for the alkyl–alkyl series (*n*,*m*-DFBPD)

n	*m*	Cryst–SmC	SmC–SmA	SmA–N	N–Iso
5	5	65			119.6
5	6	63	74.9		114.8
5	7	68	71.8		111.5
5	8	68	73.5		110.1
5	9	75			110.1
5	10	67	70.5		105.0
6	5	53	71.0	91.5	114.6
6	6	61	85.0	93.0	111.2
6	7	58	84.5	91.8	108.8
6	8	64	84.6	93.4	108.5
6	9	65	81.5	91.6	107.7
6	10	69	79.8	89.8	103.2
7	5	62	93.6	108.1	122.3
7	6	63	96.6	107.8	113.2
7	7	72	91.4	107.9	116.5
7	8	65	86.2	108.0	113.6
7	9	71	86.7	106.2	113.2
7	10	66	74.4	105.3	109.0
8	5	60	96.0	111.2	118.3
8	6	61	97.2	110.9	113.5
8	7	66	98.3	109.5	113.7
8	8	67	95.6	109.9	111.4
8	9	67	96.1	109.2	111.4
8	10	68	90.1	106.8	107.5
9	5	58	84.7	114.3	115.8
9	6	60	99.3		114.1
9	7	66	103.2	115.3	116.2
9	8	67	101.5		113.9
9	9	70	101.9		113.6
9	10	68	95.1		111.1

the tilted smectic C phase [Fig. 4(c)]. The smectic A phase stability is found to increase with the value of *n* but decrease slightly with *m*. The clearing temperature varies little with changes in the value of *n*, but decreases slightly with *m*.

The phase behaviour of the *n*,*m*-DFBPD homologues may also be explained in terms of the steric and electronic properties of the materials. As stated previously, the conformation of the alkyl substituents relative to the phenyl ring presents a dihedral angle (C_{AR}–C_1–C_2–C_3) of 90°. If the overall shape of the molecule is now considered, it will on average present a more linear shape which will favour orthogonal phase formation, although there is some tendency to form tilted layers because of the lateral polar groups in the molecular structure of the materials.[17] However, the stability of the smectic C phase in the *n*,*m*-DFBPD materials is decreased relative to the analogous *n*,O*m*-DFBPD compounds. This can be explained in terms of the reduced dipole moment on the aromatic end of the molecule and therefore the subsequent loss of dipolar coupling with the *ortho*-fluorine substituent.

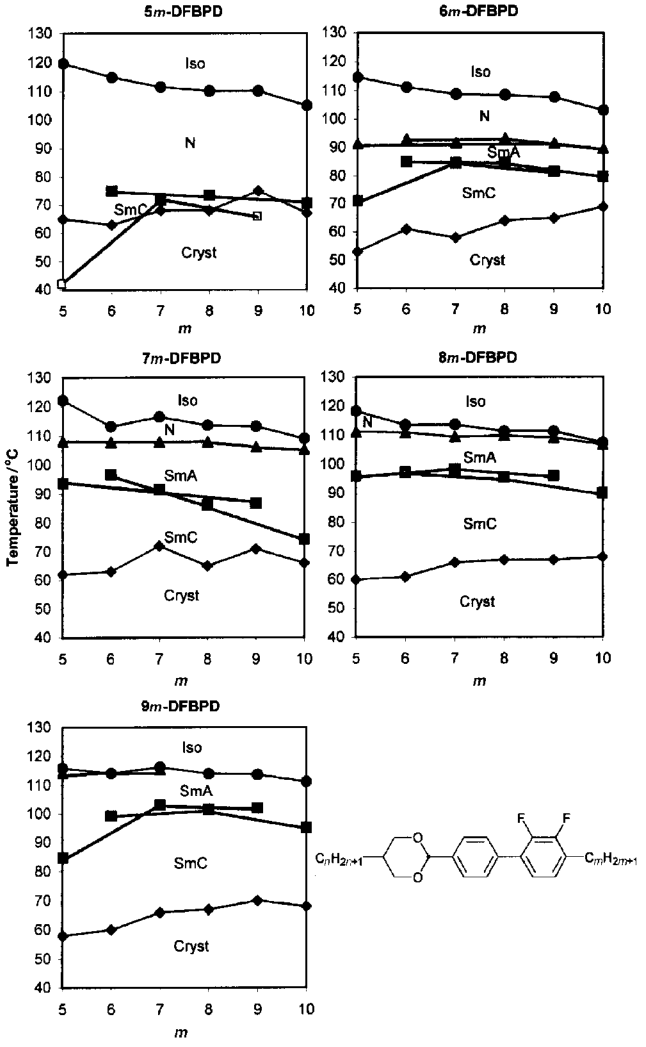


Fig. 3 Plots of transition temperatures (°C) for the alkyl–alkyl series (*n*,*m*-DFBPD).

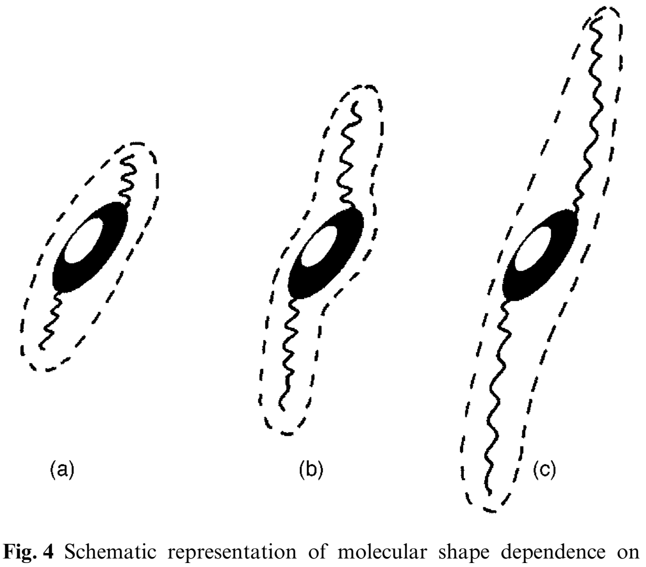


Fig. 4 Schematic representation of molecular shape dependence on the length of terminal alkyl chains.

Comparisons with other single component literature FLC host materials

We have compared the transition temperatures and mesophase stability of the two dioxanyl series with those of similar liquid crystalline ferroelectric host materials described in the literature (Fig. 5). In all cases materials with equivalent alkyl/alkoxy chains and substitution patterns were compared. If we compare the dialkyl (*n*,*m*-DFBPD) materials with the analogous non-fluorinated derivatives[18,19] (A) it is obvious that the introduction of the two lateral fluoro substituents in the 2- and 3-positions changes the mesomorphism considerably (Table 3). The strong dipole moment generated by the difluoro substituents combines with the dipole from the dioxane ring to give a high tendency to form tilted phases. Surprisingly, for equivalent chain lengths the inclusion of the lateral fluorines does not produce any reduction in the melting temperatures, however the clearing temperatures are depressed by around 40–45 K as expected. Nevertheless, unlike the non-fluorinated materials A, fluorination has the advantageous effect of suppressing the formation of anisotropic crystal B phases and stabilises the formation of the desired smectic C phase, while retaining the smectic A and nematic phases.

The 2,3-difluorinated alkyl–alkoxy homologues show lower

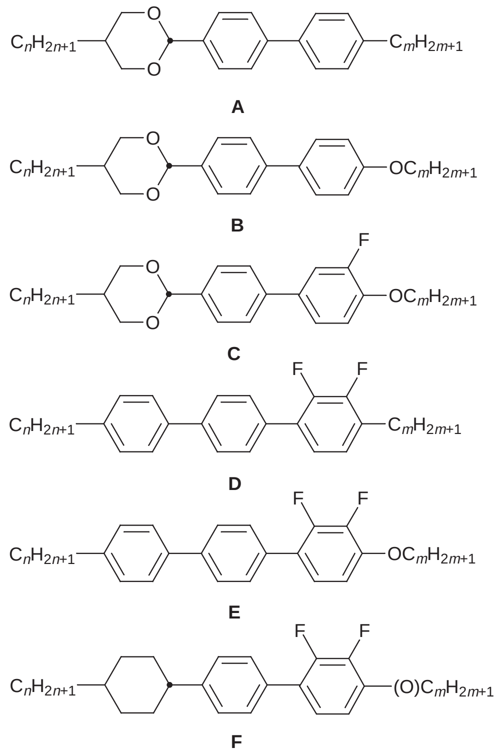


Fig. 5 Structures of the literature materials used in comparative thermal studies.

Table 3 Transition temperatures (°C) for the literature materials used in comparative studies

Material	*n*	*m*	Transition temperatures/°C
A	5	5	Cryst 77 B 107.0 SmA 119.6 N 159.0 Iso
A	6	5	Cryst 69.1 B 122.5 SmA 136.6 N 160.5 Iso
A	7	5	Cryst 43 B 140.8 SmA 153.4 N 165.8 Iso
A	8	5	Cryst 47 B 139.9 SmA 153.1 N 159.5 Iso
A	9	5	Cryst 49.4 B 142.7 SmA 154.8 N 156.6 Iso
A	7	6	Cryst 46 B 137.3 SmA 149.0 N 153.5 Iso
A	7	8	Cryst 46 B 139.0 SmA 150.0 N 150.5 Iso
A	8	8	Cryst 50.5 B 140.5 SmA 148.8 Iso
B	7	7	Cryst 66.6 × 92.9 B 122 SmC 153 N 173 Iso
B	7	8	Cryst 62.5 × 96.7 B 123 SmC 155 N 177 Iso
B	9	8	Cryst 65.8 B 142 SmC 163 N 168.5 Iso
C	8	6	Cryst 48.4 SmB 91.5 SmC 126.5 SmA 155.5 Iso
C	8	7	Cryst 52.9 SmB 88.4 SmC 126.5 SmA 152.5 Iso
C	8	8	Cryst 52.6 Sm B 81.3 SmC 127.2 SmA 149.0 Iso
D	5	5	Cryst 81.0 SmC 115.5 SmA 131.5 N 142.0 Iso
D	5	7	Cryst 56.0 SmC 105.5 SmA 131.0 N 136.5 Iso
D	7	5	Cryst 65.5 SmI 74.5 SmC 118.5 SmA 135.0 N 137.0 Iso
D	7	9	Cryst 44.0 SmI 55.0 SmC 105.0 SmA 127.0 Iso
E	5	6	Cryst 97.5 SmC 145.5 SmA 166.0 Iso
E	5	8	Cryst 93.5 SmC 144.0 SmA 148.0 N 159.0 Iso
E	7	8	Cryst 89.5 SmC 148.0 SmA 151.5 N 154.0 Iso
F	5	5	Cryst 33.0 SmA 96.5 N 123.0 Iso
F	5	O8	Cryst 53.0 SmC 58.0 SmA 127.0 N 142.0 Iso
F	5	O10	Cryst 52.0 SmC 58.5 SmA 126.5 N 137.0 Iso

melting and clearing temperatures when compared to the non-fluorinated analogues[19] (B). Again, fluorination depresses the formation of the crystal B phase and promotes SmC–SmA–N phase sequences (the non-fluorinated analogues show a B–SmC–N phase sequence). In comparison to the non-fluorinated systems, fluorination has the effect of increasing the smectic C phase temperature range but destabilising the thermal stabilities of the smectic C and nematic phases by over 40 K. However, in comparison, a smectic A phase is introduced in the alkyl–alkoxy homologues for longer alkyl chain substituents on the dioxane ring.

In comparison to the mono-substituted alkyl–alkoxy analogues[20] (C), difluoro-substitution suppresses the formation of hexatic B (SmB) phases and induces the formation of nematic phases. Overall, disubstitution causes a small depression in the melting temperatures and a 25–30 K depression in the clearing temperatures. The thermal stability of the smectic C phase is decreased although the temperature range is increased significantly.

It is interesting to compare the dioxanyl compounds with the analogous difluoroterphenyl (DFTP) materials,[8] which are known to be excellent host materials in the formulation of FLC mixtures. Both sets of materials are three ring compounds although the polarisable core is shortened in the DFBPD materials by one terminal ring. In the case of the dialkyl materials, both series possess the desired SmC–SmA–N phase sequence, although the DFTP materials (D) have an additional, undesirable SmI phase. The inclusion of a dioxane ring has the beneficial effect of suppressing the SmI phase but it has no profound effect on the melting temperatures. Overall the stabilities of the smectic C, smectic A and nematic phases are depressed by the inclusion of a dioxane ring and the orthogonal smectic A phase has the widest existence range. In comparison to the alkyl–alkoxy materials (*n*,O*m*-DFBPD), the DFTP analogues (E) exhibit a SmC–SmA–N phase sequence. Inclusion of a dioxane ring has the effect of suppressing the melting point by over 30 K, suppressing the formation of a smectic A phase and stabilising the nematic phase. The nematic phase range is increased somewhat but the smectic C phase range is shortened by over 20 K.

In terms of the nature and the lengths of the polarisable cores, the (difluorobiphenylyl)cyclohexane derivatives[3,21] (F) are the closest to the dioxane materials. However, the additional dipole associated with the oxygens in the dioxanyl ring in the alkyl–alkyl derivatives results in an increase in the melting point relative to the comparative cyclohexyl materials but conversely it has very little effect on the clearing temperatures. The increase in structural curvature of the dioxane-containing materials results in a suppression of the smectic A phase and the introduction of a monotropic tilted smectic C phase, while the temperature range of the nematic phase is increased considerably. In the alkyl–alkoxy derivatives there is a slight increase in the melting temperature and a slight decrease in the clearing temperature on going from a cyclohexane to a dioxane ring system. Again the smectic A phase is suppressed and so surprisingly is the smectic C phase stability, by 40 K. This is as a result of the widening of the nematic phase range to approximately 50 K.

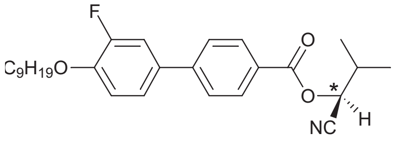
Mixture studies

Two mixtures were formulated based on alkyl–alkyl and alkyl–alkoxy DFBPD host materials, using an extremely low concentration of approximately 1% of a chiral dopant such as a cyanohydrin ester[22] (*S*-(−)-FIGS97) and the racemic form ((±)-FIGS97) as a pitch compensating agent. The resulting mixtures have spontaneous polarisations (Ps) of less than 3 nC cm^{-2}.

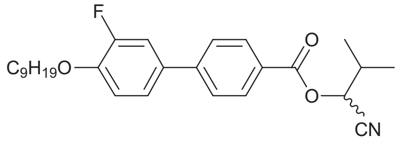
The first FLC mixture (DIOXFLC1) was based on alkyl–alkyl homologues alone and was composed of equal weight percentages (16.17%) of 5,6-DFBPD; 5,7-DFBPD; 5,8-DFBPD; 8,7-DFBPD; 8,8-DFBPD; 8,9-DFBPD, doped with S-(−)-FIGS97 (0.9%) and (±)-FIGS97 (2.1%). The phase sequence and transition temperatures for the mixture are given below:

Cryst <20 SmC* 69 SmA* 97* N 107 Iso (°C)

The second FLC mixture (DIOXFLC2) was based on alkyl–alkoxy homologues alone and was composed of 5,O7-DFBPD (18.25%); 7,O5-DFBPD (18.25%); 9,O7-DFBPD (18.25%); 9,O8-DFBPD (18.25%); 8,O6-DFBPD (8.0%); 8,O7-DFBPD



S-(-)-FIGS97



(±)-FIGS97

Table 4 Temperature dependence of the spontaneous polarisation in the mixture DIOXFLC1

Temperature/°C	25	35	45	55	60	65	70
Ps/nC cm^{-2}	2.97	2.81	2.23	1.65	0.94	0.58	0.21

(8.0%); 8,O8-DFBPD (8.0%), doped with *S*-(−)-FIGS97 (1.0%) and (±)-FIGS97 (2.0%). The phase sequence and transition temperatures for the mixture are given below:

Cryst <20 SmC* 92 SmA* 102* N 124 Iso (°C)

Both mixtures showed ideal phase sequences and SmC*–SmA* transition temperatures and gave good alignment in rubbed nylon cells. Wide-ranging electro-optic property evaluations were carried out for each mixture and the results of these are summarised below. Unless otherwise stated, all results were obtained at 25 °C.

DIOXFLC1. Birefringence ($\lambda = 542$ nm): $\Delta n = 0.125$. Dielectric anisotropy (10 kHz, cell gap = 6.0 μm): $\varepsilon_{\perp} = 4.80$, $\varepsilon_{\parallel} = 3.79$, $\Delta\varepsilon = -1.01$. Electro-optic switching: Monostrobe pulse response[1] = 200 μs (at 16 V μm^{-1}); $\tau_{\min} = 75$ μs (at $V_{\min} =$ 35 V μm^{-1}); reorientational viscosity (25 °C), $\gamma_{\text{mono}} = 95$ mPa s at 16 V μm^{-1} and 78 mPa s at $V_{\min}$.

Multiplexing response[23] using the 2-slot JOERS-Alvey Scheme (Duty Cycle = 480 : 1): $V_s = 60$ V, Minimum Line Address Time (LAT$_{\min}$) = 150 μs; reorientational viscosity, $\gamma_{\text{mpx}} = 134$ mPa s. The temperature dependence of the spontaneous polarisation (Ps) is given in Table 4 below.

DIOXFLC2. Birefringence ($\lambda = 542$ nm): $\Delta n = 0.132$. Dielectric anisotropy (10 kHz, cell gap = 6.0 μm): $\varepsilon_{\perp} = 6.20$, $\varepsilon_{\parallel} = 4.78$, $\Delta\varepsilon = -1.42$. Electro-optic switching: Monostrobe pulse response[1] = 410 μs (at 16 V μm^{-1}); $\tau_{\min} = 260$ μs (at $V_{\min} = 27$ V μm^{-1}); reorientational viscosity (25 °C), $\gamma_{\text{mono}} =$ 195 mPa s at 16 V μm^{-1} and 208 mPa s at $V_{\min}$.

Multiplexing response[23] using the 2-slot JOERS-Alvey Scheme (Duty Cycle = 480 : 1): $V_s = 50$ V, Minimum Line Address Time (LAT$_{\min}$) = 420 μs; reorientational viscosity, $\gamma_{\text{mpx}} = 312$ mPa s. The temperature dependence of the spontaneous polarisation (Ps) is given in Table 5 below.

Table 5 Temperature dependence of the spontaneous polarisation in the mixture DIOXFLC2

Temperature/°C	25	35	45	55	65	75	85	95
Ps/nC cm^{-2}	2.97	2.83	2.53	2.31	1.91	1.68	1.16	0.52

One of the main objectives in the synthesis of DFBPD materials was to produce low birefringence materials for use in FLC mixture formulation. We have shown that such mixtures can be prepared and that these show good ferroelectric switching behaviour. We have measured the birefringence of the two mixtures and found these to be similar: alkyl–alkyl, $\Delta n = 0.125$; alkyl–alkoxy, $\Delta n = 0.132$. We have also compared these values with other FLC mixtures based on a wide variety of host materials (Fig. 6). The sequence of birefringence values is shown below:

Monofluoroterphenyls[20] (K) ($\Delta n = 0.132$) > fluorinated MBF esters[24] (J) ($\Delta n = 0.239$) ~ difluoroterphenyls[8] (L) ($\Delta n =$ 0.20) > cyclohexylcarbonitriles[25] (I) = 2-phenylpyrimidines[26] (G) ($\Delta n = 0.14$) > *n,m*O-DFBPD ($\Delta n = 0.132$) > *trans*[(4-alkylcyclohexyl)ethyl]-2,3-difluorobiphenyls[21] (M) = (difluorophenyl)pyrimidines[10] (N) ($\Delta n = 0.13$) > *n,m*-DFBPD ($\Delta n =$ 0.125) > 2-phenyl-1,3,4-thiadiazoles[27] (H) ($\Delta n = 0.12$).

Therefore, both series of dioxane materials possess low birefringence relative to the majority of other FLC systems and as such represent good candidates for further electro-optic investigations and mixture development.

Despite the fact that extremely low Ps mixtures (~3 nC cm^{-2} at 25 °C) were formulated for the present study, we were still able to achieve reasonable switching speed at room temperature. When these were tested under 480-ways simulated multiplexing conditions, which are compatible for a VGA display, both mixtures exhibit wide operating temperature ranges with very fast frame rates of up to 100 Hz at elevated temperatures. Furthermore, both mixtures exhibit good bistability, a property which is crucial for a flicker-free FLC display even when the display is operating at very low frame rates of <10 Hz.[28] We have determined that the dialkyl

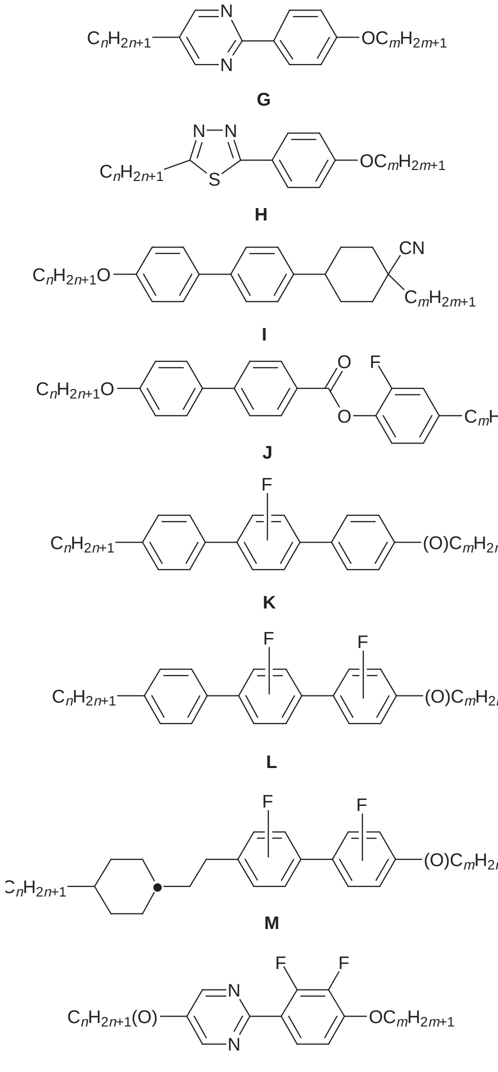


Fig. 6 General structures of the literature host materials used in the electro-optic comparative studies.

Table 6 FLC device characteristics of mixtures DIOXFLC1 and DIOXFLC2

Mixture	Temperature/ °C	Multiplexing speed/ μs	Frame rate[a]/ Hz
DIOXFLC1	20	200	10
DIOXFLC1	55	20.8	100
DIOXFLC2	35	200	10
DIOXFLC2	70	28	75

[a]For a VGA display.

system operates between 20 to 55 °C with a corresponding frame rate of 10 to 100 Hz, the lower frame frequency being at the lower temperature (Table 6). For the alkyl–alkoxy system with its higher viscosity, the mixture operates to a higher temperature than the dialkyl mixture but the overall temperature range remains unchanged (35 to 70 °C), with a frame rate between 10 and 75 Hz. By combining the dialkyl and alkyl–alkoxy systems together and adjusting the Ps value and dielectric properties, a much wider multiplexing temperature range with very fast frame rate is expected and work is continuing in this area.

Conclusions

Two new series of dioxanyl-based compounds were prepared and shown to exhibit smectic C phases with low viscosities and birefringences. Initial work on ferroelectric mixtures based on these (difluorobiphenylyl)dioxane materials shows that the compounds make excellent host materials for ferroelectric liquid crystal displays (FLCDs). Sub-millisecond response times have been achieved, thus making these materials excellent candidates for use in large, flat panel ferroelectric liquid crystal displays.

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