The effect of the octan-3-yloxy and the octan-2-yloxy chiral part in ferroelectric liquid crystals on their mesomorphic properties

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1 Preparative procedures

The purity of intermediates and the main compounds were determined by thin layer chromatography (TLC), GC-MS(EI) (Agilent 6890N, Santa Clara, CA, USA) and HPLC-PDAMS(API-ESI) (Shimadzu Prominence LC20) chromatography systems. The structures of the final compounds were confirmed by mass spectra registered on HPLC chromatography system with a diode array detector (SPD-M20A) and mass detector (LCMS-85 2010EV) and by \(^1\)H and \(^1\)C NMR spectroscopy (Bruker, Avance III HD, 500 Hz; CDCl\(_3\), Billerica, MA, USA).

Synthetic details are described for an exemplary compound 3FO5C2.

1.1 Ethyl (R)-(−)-4-(octan-3-yloxy)benzoate (4a)

A mixture of ethyl 4-hydroxybenzoate (44.1 g, 0.28 mol), (S)-(−)-3-octanol (3a) (Fluka, GC>99.0%, ee: 99.99%, \([\alpha]_{D}^{25}= +10.0^\circ \pm 0.5; 22.1 g, 0.17 mol), triphenylphosphine (PPh\(_3\), 65.6 g, 0.25 mol) and dry toluene (400 ml), obtained by distillation over diphosphorus pentaoxide, was cooled to −10°C on a acetone/dry ice bath, and then diisopropyl azodicarboxylate (DIAD, 50.6 g, 0.25 mol) was added dropwise. The mixture was stirred at room temperature until the reaction was completed (TLC). Then toluene was removed on vacuum evaporator and hexane (900 ml) was added. The mixture was passed through an alumina pad. The solvent was evaporated. A colorless oil was obtained. Yield: 48.5 g (68.9%); purity (HPLC): >99.9%; ee: 99.99%. MS: 279 [M+H]\(^+\), 301 [M+Na]\(^+\).

1.2 (R)-(−)-4-(octan-3-yloxy)benzoic acid (5a)
A mixture of ethyl (R)-(−)-4-(octan-3-yloxy) benzoate (4a) (39.4 g; 0.14 mol), potassium hydroxide (31.8 g; 0.57 mol) solved in water (50 ml) and ethanol (400 ml) was refluxed for 6 h. Then the reaction mixture was acidified with 10% hydrochloric acid to pH=0 (300 ml) and the colorless oil layer was separated. The product was extracted with hexane (3×200 ml) and collected organic layer were dried over MgSO$_4$, filtered off and the solvent was evaporated. The product was purified by column chromatography (SiO$_2$/CH$_2$Cl$_2$). A yellowish oil was obtained. Yield: 26.4 g (74.7%); purity (HPLC): >99.9%; [α]$^{25}_D$ = −9.0°; c=10.4 in 100 cm$^3$ CHCl$_3$; MS: 250 [M+H]$^+$, 272 [M+Na]$^+$.

1.3 (R)-(−)-4-(octan-3-yloxy)benzoyl chloride (6a)

To the solution of (R)-(−)-4-(octan-3-yloxy) benzoic acid (5a) (10.4 g; 0.04 mol) in dry toluene (100 ml) oxalyl chloride (12.4 ml; 0.07 mol) and one drop of N,N-dimethylformamide were added. The reaction mixture was stirred at room temperature for a one day and then the excess of oxalyl chloride with toluene was distilled off (50 ml).

1.4 (R)-(−)-4’-benzyloxybiphenyl-4-yl 4-(octan-3-yloxy)benzoate (7a)

To the solution of (R)-(−)-4-(octan-3-yloxy)benzoic acid (6a) in dry toluene (50 ml) 4’-benzyloxy-4-hydroxybiphenyl 7 (11.9 g; 0.04 mol) was added and then dried pyridine (10.4 ml; 0.13 mol) was dropped. The reaction mixture was refluxed for two days, and after cooling to room temperature, it was filtered through Fullers earth off. The filtrate was poured into diluted hydrochloric acid (5M) and organic phase was separated. The water phase was extracted with toluene (3×100 ml). The combined toluene solutions were washed with diluted hydrochloric acid (5M, 3×100 ml) and water (3×100 ml), dried over MgSO$_4$, filtered off and the toluene was evaporated on a vacuum evaporator. The crude product was purified on a chromatography column (SiO$_2$/CH$_2$Cl$_2$) and then crystallized from ethanol/acetone solution (300 ml, 2:1). A white solid was obtained. Yield: 6.9 g (32.3%); purity (HPLC): 98.7%; MS: 510 [M+H]$^+$, 532 [M+Na]$^+$; mp 147.3°C.

1.5 (R)-(−)-4’-hydroxybiphenyl-4-yl 4-(octan-3-yloxy)benzoate (8a)

To the solution of (R)-(−)-4’-(benzyloxy)biphenyl-4-yl 4-(octan-3-yloxy)benzoate (7a) (6.9 g; 0.01 mol) in THF (50 ml) 10% palladium on charcoal (1.0 g) was added. The reaction mixture was flushed with nitrogen and connected to a gas burette filled with hydrogen. The mixture was then stirred until the reaction was completed (TLC). After that, the reaction mixture was flushed with nitrogen. Catalyst was filtered off and rinsed with tetrahydrofuran (THF). THF was evaporated and
the dry residue was crystallized from heptane/toluene solution (1:1, 400 ml). A white solid was obtained. Yield: 4.6 g (81.2%); purity (GC): 99.1%; MS: 418 [M]+; mp 170.8°C.

1.6 (R)-(−)-4′-[2-(2,2,3,3,4,4,4-heptafluorobutoxy)ethoxy]biphenyl-4-yl 4-(octan-3-yl)benzoate (3FO2C2)
A mixture of (R)-(−)-4′-hydroxybiphenyl-4-yl 4-(octan-3-yl)benzoate (8a) (0.7 g; 0.0017 mol), 2-(2,2,3,3,4,4,4-heptafluorobutoxy) ethanol (0.44 g; 0.0018 mol), triphenylphosphine (0.46 g; 0.0018 mol), diisopropyl azodicarboxylate (0.36 g; 0.0018 mol) and dry THF (20 ml) was stirred at room temperature until the reaction was completed (TLC). Then the solvent was evaporated to dryness and the residue was purified on chromatography column (SiO\textsubscript{2}/CH\textsubscript{2}Cl\textsubscript{2}). The product was crystallized from ethanol twice (2×40 ml). A white solid was obtained. Yield: 0.23 g (41.4%); purity (HPLC): 99.6%; MS: 645 [M+H]\textsuperscript{+}, 667 [M+Na]\textsuperscript{+}.

In similar way were obtained:

1.7 (R)-(−)-4′-[3-(2,2,3,3,4,4,4-heptafluorobutoxy)propoxy]biphenyl-4-yl 4-(octan-3-yl)benzoate (3FO3C2)
Yield: 0.46 g (41.8%); purity (HPLC): 99.4%; MS: 659 [M+H]\textsuperscript{+}, 681 [M+Na]\textsuperscript{+}.

1.8 (R)-(−)-4′-[5-(2,2,3,3,4,4,4-heptafluorobutoxy)pentyloxy]biphenyl-4-yl 4-(octan-3-yl)benzoate (3FO5C2)
Yield: 0.48 g (41.7%); purity (HPLC): >99.9%; MS: 687 [M+H]\textsuperscript{+}, 709 [M+Na]\textsuperscript{+};

$\text{^1}H$ NMR (CDCl\textsubscript{3}) \(\delta/\text{ppm:} \ 0.92 \ (t, \ 3H, \ -CH\textsubscript{3}, \ 30) , \ 1.00 \ (t, \ 3H, \ -CH\textsubscript{3}; \ 25) , \ 1.28-1.89 \ (m, \ 16H, \ -CH\textsubscript{2}--; \ 6, \ 7, \ 8, \ 24, \ 26, \ 27, \ 28, \ 29) , \ 3.67 \ (t, \ 2H, \ -CH\textsubscript{2}--; \ 5) , \ 3.95 \ (t, \ 2H, \ -CH\textsubscript{2}--; \ 9) , \ 4.04 \ (t, \ 2H, \ -CH\textsubscript{2}--; \ 4) , \ 4.34 \ (m, \ 1H, \ -CH--; \ 23) , \ 6.99 \ (d, \ 4H, \ Ar-H; \ 16, \ 21) , \ 7.28 \ (d, \ 2H, \ Ar-H; \ 11) , \ 7.53 \ (d, \ 2H, \ Ar-H; \ 12) , \ 7.60 \ (d, \ 2H, \ Ar-H; \ 15) , \ 8.17 \ (d, \ 2H, \ Ar-H; \ 20) ; \ \text{^1}C \ NMR \ (CDCl\textsubscript{3}) \ \delta/\text{ppm:} \ 9.5 \ (25) , \ 14.0 \ (30) , \ 22.5 \ (29) , \ 22.6 \ (7) , \ 25.0 \ (27) , \ 26.6 \ (6) , \ 29.0 \ (8) , \ 29.2 \ (24) , \ 31.9 \ (28) , \ 33.3 \ (26) , \ 65.4 \ 1$
1.9 (R)-(−)-4′-[7-(2,2,3,3,4,4,4-heptafluorobutoxy)heptyloxy]biphenyl-4-yl 4-(octan-3-yloxy)benzoate (3FO7C2)
Yield: 0.46 g (38.7%); purity (HPLC): 99.7%; MS: 715 [M+H]+, 737 [M+Na]+.

1.10 (R)-(−)-4’-(3-butoxypropoxy)biphenyl-4-yl 4-(octan-3-yloxy)benzoate (3HO3C2)
Yield: 0.32 g (31.1%); purity (HPLC): 99.4%; MS: 533 [M+H]+, 555 [M+Na]+

1.11 (S)-(+)–4′-[2-(2,2,3,3,4,4,4-heptafluorobutoxy)etoxy]biphenyl-4-yl 4-(octan-2-yloxy)benzoate (3FO2C1)
A mixture of (S)-(+)–4’-hydroxybiphenyl-4-yl 4-(octan-2-yloxy)benzoate (8b) (0.9 g, 0.0022 mol), 2-(2,2,3,3,4,4,4-heptafluorobutoxy)-ethanol (0.68 g, 0.0028 mol), triphenylphosphine (0.73 g, 0.0028 mol), diisopropyl azodicarboxylate (0.56 g, 0.0028 mol) and dry THF (30 ml) was stirred at room temperature until the reaction was completed (TLC). Then the solvent was concentrated to the dryness, and the residue was purified on chromatography column (SiO2/CH2Cl2) and crystallised from ethanol twice (2×50 ml). A white solid was obtained. Yield: 0.92 g (66.4%); purity (HPLC): >99.9%; MS: 645 [M+H]+, 667 [M+Na]+;

1H NMR (CDCl3) δ/ppm: 0.89 (t, 3H, -CH3, 27), 1.27-1.47 (m, 10H, -CH2-, 22, 23, 24, 25, 26), 1.55 (m, 3H, -CH3, 21), 4.01 (t, 2H, -CH2-, 5), 4.12 (t, 2H, -CH2-, 4), 4.19 (d, 2H, -CH2-, 6), 4.48 (m, 1H, -CH-, 20), 6.96 (d, 2H, Ar-H, 13), 6.99 (d, 2H, Ar-H, 18), 7.25 (d, 2H, Ar-H, 8), 7.51 (d, 2H, Ar-H,
In similar way were obtained:

1.12 \((S)\)-(+)\- 4'-[3-(2,2,3,3,4,4,4-heptafluorobutoxy)propoxy]biphenyl-4-yl 4-(octan-2-yloxy)benzoate (3FO3C1)
Yield: 0.79 g (79.7 %); purity (HPLC): >99.9 %; MS: 659 [M+H]⁺, 681 [M+Na]⁺.

1.13 \((S)\)-(+)\- 4'-[4-(2,2,3,3,4,4,4-heptafluorobutoxy)butoxy]biphenyl-4-yl 4-(octan-2-yloxy)benzoate (3FO4C1)
Yield: 0.87 g (67.5 %); purity (HPLC): 99.8 %; MS: 673 [M+H]⁺, 695 [M+Na]⁺.

1.14 \((S)\)-(+)\- 4'-[5-(2,2,3,3,4,4,4-heptafluorobutoxy)pentyloxy]biphenyl-4-yl 4-(octan-2-yloxy)benzoate (3FO5C1)
Yield: 0.48 g (35.0 %); purity (HPLC): 99.2%, MS: 687 [M+H]⁺, 709 [M+Na]⁺.

1.15 \((S)\)-(+)\- 4'-[5-(2,2,3,3,4,4,4-heptafluorobutoxy)hexyloxy]biphenyl-4-yl 4-(octan-2-yloxy)benzoate (3FO6C1)
Yield: 0.91 g (80.5 %); purity (HPLC): 99.8 %; MS: 701 [M+H]⁺, 723 [M+Na]⁺.

1.16 \((S)\)-(+)\- 4'-[7-(2,2,3,3,4,4,4-heptafluorobutoxy)heptyloxy]biphenyl-4-yl 4-(octan-2-yloxy)benzoate (3FO7C1)
Yield: 0.93 g (65.1 %); purity (HPLC): 99.6%, MS: 715 [M+H]⁺, 737 [M+Na]⁺.

1.17 \((S)\)-(+)\- 4'-(3-butoxypropoxy)biphenyl-4-yl 4-(octan-2-yloxy)benzoate ()
Yield: 0.23 g (22.6 %); purity (HPLC): 99.4%; MS: 533[M+H]⁺, 555 [M+Na]⁺.
2 Additional textures

The observed texture for compounds: 3HO3C1: a) the N* phase at 81.0 °C, b) during N*-SmC* phase at 71.1 °C and c) the SmC* phase at 65.0 °C observed during cooling.

3 Additional dielectric measurements

![Figure A.](image)

**Figure A.** Real part of electric permittivity $\varepsilon'$ for 3FO5C2 for four temperatures (where SmC* phase is observed).
**Figure B.** Imaginary part of electric permittivity $\varepsilon''$ for 3FO5C2 for four temperatures (where SmC* phase is observed).

**Figure C.** Cole-Cole plots ($\varepsilon''$ versus $\varepsilon'$) for 3FO5C2 for four temperatures (where SmC* phase is observed).
Figure D. Real part of electric permittivity $\varepsilon'$ for 3HO3C1 for two temperatures (where SmC* phase is observed).

Figure E. Imaginary part of electric permittivity $\varepsilon''$ for 3HO3C1 for two temperatures (where SmC* phase is observed).
**Figure F.** Cole-Cole plots ($\varepsilon''$ versus $\varepsilon'$) for 3HO3C1 for two temperatures (where SmC* phase is observed).