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Synthesis and mesomorphic properties of resorcyl di[4-(4-alkoxy-2,3-difluorophenyl)ethynyl]benzoate: a novel achiral antiferroelectric banana-shaped mesogen

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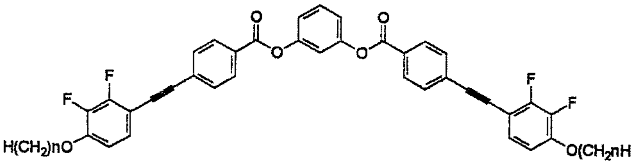
Two resorcyl di[4-(4-alkoxy-2,3-difluorophenyl)ethynyl]benzoate liquid crystals were prepared and their mesomorphic properties observed and measured. Achiral antiferroelectric phases were seen with increasing length of the hydrocarbon terminal chains.

1. Introduction

Since the discovery in 1996 of new 'Ferroelectric' phases formed by achiral banana-shaped compounds by Niori *et al.* [1, 2], considerable attention has been paid to these new interesting materials. Nevertheless, only a few achiral FLCs, with some slight modifications on the core or on the chain, have been reported to date [3–7]. The difficulty in finding new compounds indicates that the existence of banana mesophases depends not only on the shape of the molecules, but also on parameters such as local dipolar moments, the positions of different charges and the extent of conjugation [8]. A major shortcoming of these new compounds is their limited thermal, hydrolytic and photochemical stability; the design of novel, stable and low melting banana-shaped mesogens is therefore a topical subject in liquid crystal research.

Fluorination has a dramatic effect on mesomorphic behaviour and alters certain properties of liquid crystals, e.g. chemical and thermal stability and viscosity. Liquid crystals containing 2,3-difluorotolane have high negative dielectric anisotropy, low viscosity and high stabilities, and have been reported previously [9, 10]. In particular, some chiral liquid crystals with 2,3-difluorotolane exhibit twist grain boundary (TGB) and antiferroelectric smectic C* phases [11]. This paper reports the introduction of 4-alkoxy-2,3-difluorotolanes into banana-shaped compounds; two resorcyl di[4-(4-alkoxy-2,3-difluorophenyl)ethynyl]benzoate liquid crystal compounds have been prepared and their mesomorphic properties observed and measured.



n=4, 8.

2. Characterization

The structures of the final products and intermediates were elucidated by a variety of spectral methods. IR spectra were recorded on a PE-983G spectrophotometer, using KBr pellets of solids or films of liquids. ^{1}H NMR spectra with tetramethylsilane (TMS) as internal standard, and ^{19}F NMR spectra with trifluoroacetic acid (TFA) as external standard, were recorded on a Bruker300 spectrometer (300 MHz), a Varian EM360L spectrometer (60 MHz) or a FX-90Q spectrometer (90 MHz). For ^{19}F NMR spectra the high field was positive. MS spectra were measured with a Finnigan-4021 spectroscope using electrical ionization.

3. Synthesis

The paths to the target fluorinated mesogens are outlined in the scheme. The preparation of 4-*n*-alkoxy-2,3-difluoroacetylenes (**3a**, **b**) was reported previously [9]. We first thought that resorcinol would react with 4-iodobenzoic acid to produce resorcyl di(4-iodobenzoate) **4**

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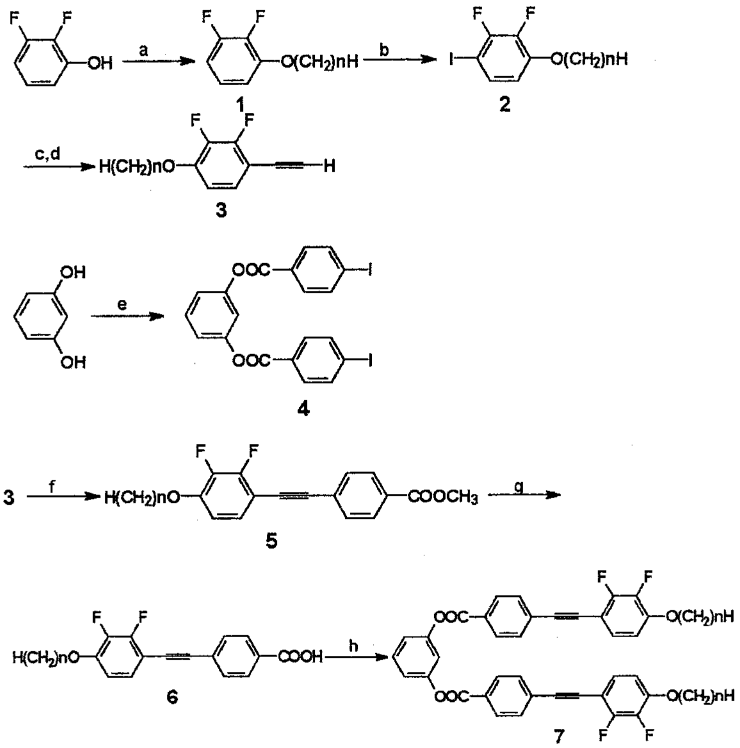

Scheme. $n=4$, compounds **2-7a**; $n=8$, compounds **2-7b**.
Reagents and conditions: (*a*) $H(CH_2)_nBr$, K_2CO_3, acetone; (*b*) n-BuLi, 78 C, then I_2/THF; (*c*) trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N; (*d*) NaOH, MeOH, acetone; (*e*) 4-iodobenzoic acid, DCC, cat. DMAP, THF; (*f*) methyl 4-iodobenzoate, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_2N; (*g*) NaOH, MeOH; (*h*) *m*-diphenol, DCC, cat. DMAP, THF.

to provide an intermediate for compound **7**, but the reaction was unsuccessful with the usual methods. We therefore coupled **3** with methyl 4-iodobenzoate, with bis(triphenylphosphine)palladium dichloride and copper(I) iodide as catalyst. Methyl 4-[(4-*n*-alkoxy-2,3-difluorophenyl)ethynyl]benzoates (**5a**, **b**) were obtained. Compounds **5** were then hydrolyzed in basic conditions to produce 4-[(4-*n*-alkoxy-2,3-difluorophenyl)ethynyl]benzoic acids (**6a**, **b**). Finally, the target compounds (**7a**, **b**) were prepared via a mild one-pot esterification procedure between **6** and resorcinol in the presence of dicyclohexylcarbodiimide (DCC) and DMAP as catalyst in THF.

3.1. *Methyl 4-[(4-n-butoxy-2,3-difluorophenyl)ethynyl]benzoate (5a)*

Compound **3a** (840 mg, 4.0 mmol), methyl 4-iodobenzoate (1048 mg, 4.0 mmol), bis(triphenylphosphine)palladium dichloride (60 mg), copper(I) iodide (100 mg), triphenylphosphine (160 mg) and anhydrous triethylamine (25 ml) were placed in a 50 ml flask; the mixture was stirred at 60 C for 48 h under nitrogen. After the reaction was complete, the precipitate formed was filtered off and washed with water; the filtrates were then dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90 C)/ethyl acetate (20/1) as the eluent. This gave pale yellow crystals which were recrystallized from methanol to yield white flaky crystals of compound **5a**; yield 1240 mg (90%). ^{1}H NMR ($CDCl_3$/TMS, 90 MHz) δ_H (ppm): 1.00 (m, 3H), 1.50 (m, 2H), 1.70–1.90 (m, 2H), 4.00 (s, 3H), 4.15 (t, 2H, $J=6.5$ Hz), 6.90 (m, 1H), 7.30 (m, 1H), 7.60 (d, 2H), 8.07 (d, 2H). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δ_F (ppm): 56.0 (m, 2F), 81.0 (m, 2F).

3.2. *Methyl 4-(4-n-octyloxy-2,3-difluorophenyl)ethynyl]benzoate (5b)*

Compound **5b** was prepared using a procedure similar to that described for the synthesis of **5a**. ^{1}H NMR ($CDCl_3$/TMS, 90 MHz) δ_H (ppm): 0.90 (m, 3H), 1.30–1.85 (m, 12H), 4.00 (s, 3H), 4.15 (t, 2H, $J=6.5$ Hz), 6.90

(m, 1H), 7.30 (m, 1H), 7.60 (d, 2H), 8.07 (d, 2H). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δ_F (ppm): 56.0 (m, 2F), 81.0 (m, 2F).

3.3. *4-[(4-n-Butoxy-2,3-difluorophenyl)ethynyl]benzoic acid (**6a**)*

Methanol (20 ml) was added to a mixture of compound **5a** (1032 mg, 3 mmol) and NaOH (480 mg, 12 mmol); the resulting mixture was stirred at room temperature. The reaction was monitored by the TLC; when **5a** had disappeared, HCl was added slowly to give pH 3. 50 ml diethyl ether and 25 ml water were then added. The organic layer was washed with water, then dried over anhydrous sodium sulfate; the solvent was removed *in vacuo* and the white residue recrystallized from ethanol to yield white flaky crystals of compound **6a**; yield 825 mg (83%). ^{1}H NMR (D6-acetone/TMS, 90 MHz) δ_H (ppm): 1.00 (m, 3H), 1.50 (m, 2H), 1.70–1.90 (m, 2H), 4.15 (t, 2H, $J = 6.5$ Hz), 6.90 (m, 1H), 7.30 (m, 1H), 7.60 (d, 2H), 8.07 (d, 2H), 10.35 (s, 1H). ^{19}F NMR (D6-acetone/TFA, 56.4 MHz) δ_F (ppm): 56.0 (m, 2F), 81.0 (m, 2F).

3.4. *4-[(4-n-Octyloxy-2,3-difluorophenyl)ethynyl]-benzoic acid (**6b**)*

Compound **6b** was prepared using a procedure similar to that described for the synthesis of **6a**. ^{1}H NMR (D6-acetone/TMS, 90 MHz) δ_H (ppm): 1.00 (m, 3H), 1.35–1.90 (m, 12H), 4.15 (t, 2H, $J = 6.5$ Hz), 6.90 (m, 1H), 7.30 (m, 1H), 7.60 (d, 2H), 8.07 (d, 2H), 10.35 (s, 1H). ^{19}F NMR (D6-acetone/TFA, 56.4 MHz) δ_F (ppm): 56.0 (m, 2F), 81.0 (m, 2F).

3.5. *Resorcyl di[4-(4-butoxy-2,3-difluorophenyl)-ethynyl]benzoate (**7a**)*

A mixture of compound **6a** (660 mg, 2.0 mmol), (DCC) (412 mg, 2.0 mmol), resorcinol (100 mg, 0.9 mmol) and (DMAP) as catalyst, in dry THF (10 ml) was stirred for 48 h at room temperature. Water was then added, and solids filtered off. The filtrate was extracted by diethyl ether, and the filtrate washed with water and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10/1) as eluent to give white crystals which were recrystallized from acetone/methanol to give **7a** as white flaky crystals; yield 330 mg (50%). ^{1}H NMR ($CDCl_3$TMS, 90 MHz) δ_H (ppm): 0.90 (m, 6H), 1.00–1.30 (m, 4H), 1.60–1.90 (m, 4H), 4.20 (t, 4H, $J = 6.5$ Hz), 6.80 (t, 2H, $J = 9$ Hz), 7.10 (d, 4H, $J = 9$ Hz), 7.55 (t, 2H, $J = 9$ Hz), 8.30 (d, 4H, $J = 9$ Hz). ^{19}F NMR ($CDCl_3$/TFA, 56.4M) δ_F (ppm): 56.5 (m, 2F), 81.5 (m, 2F). MS (*m*/*z*, %): 734 (M^+, 5.19), 313 (100.00), 257 (14.22). Analysis for $C_{44}H_{34}F_4O_6$: calc. C 71.93, H 4.55, F 10.08; found C 71.68, H 4.56, F 10.25%. IR (KBr, ν_{max}, cm ^{1}): 2957, 2871, 1725, 1599, 1519, 1474, 1401, 1277, 1166, 1146, 1089, 896, 853, 803, 761, 687, 522.

3.6. *Resorcyl di[4-(4-octyloxy-2,3-difluorophenyl)-ethynyl]benzoate (**7b**)*

Compound **7b** was prepared using a procedure similar to that described for the synthesis of **7a**. ^{1}H NMR ($CDCl_3$/TMS, 90 MHz): 0.90 (t, $J = 6$ Hz, 6H, CH_3), 1.35–1.90 (m, 24H, aliphatic H), 4.10 (t, $J = 6$ Hz, 4H, OCH_2), 6.75 (t, $J = 9$ Hz, 2H, ArH), 7.15–7.35 (m, 3H, ArH), 7.55 (t, $J = 9$ Hz, 2H, ArH), 7.70 (d, $J = 9$ Hz, 4H, ArH), 8.23 (d, $J = 9$ Hz, 4H, ArH). ^{19}F NMR (56.4 MHz, $CDCl_3$/TFA): 56.5 (m, 2F), 81.5 (m, 2F). MS (*m*/*z*, %): 847 ($M + 1^+$, 8.76), 369 ($C_8H_{17}OC_6H_2F_2C{\equiv}CC_6H_4CO^+$, 100.00). Analysis for $C_{52}H_{50}F_4O_6$: calc. C 73.74, H 5.95, F 8.97; found C 73.32, H 6.13, F 8.82%. IR (KBr, ν_{max}, cm ^{1}): 2921, 2852, 2214, 1731, 1601, 1515, 1471, 1406, 1304, 1263, 1131, 1083, 1022, 893, 853, 690, 520.

4. Phase characterization and conclusions

Compound **7a** was observed by polarizing optical microscopy (POM) using a heating stage. On cooling to 133 C a smectic A-type texture forms a stable down to 125 C where it crystallizes after about 30 min. The textures show no electro-optical response under low frequency electric fields (up to 20 V μm ^{1}). It is clear that the phase is not polar: neither B2 with SmCP structure, nor B7. Although the polarization current curves show some peaks (see figure 1), such peaks can be seen even at 140 C (in the isotropic phase). It is clear that the peaks are due to ions.

Compound **7b** shows a metastable antiferroelectric phase on fast cooling at around 123 C; however this phase crystallizes after about 30 s. Nevertheless a polarization current can be recorded that indicates antiferroelectric behaviour with a polarization value of about 130 nC cm ^{2}. During the transition electro-optical switching can be observed; it is very difficult to record but indicates that the antiferroelectric structure that appears on cooling is chiral. Based on the observed texture during the phase transition, the mesophase is not a B7 phase, but has a SmC_aP_A structure. The polarization curve together with that appearing after crystallization is shown in figure 2. In heating, clearing takes place gradually above 127 C.

Compound **7b** is therefore very interesting and promising; it could be useful in mixtures. In order to obtain better mesomorphic properties, further compounds with a longer alkoxy chain (C_{10} or C_{12}) are desirable. On comparing **7b** with similar unfluorinated compounds showing no mesophases [5], it is clear that introduction of the 2,3-difluoro substituents increases the stability of mesomorphic properties in this banana-shaped system.

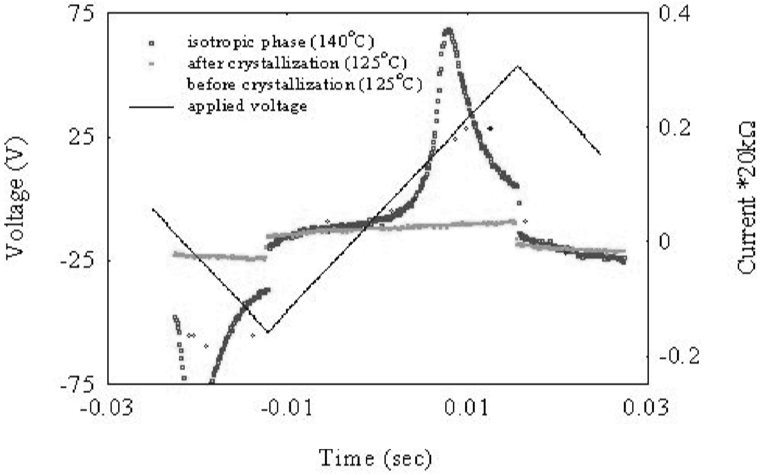

Figure 1. Polarization current curves of compound **7a** at 125 C before and after crystallization and at 140 C: film thickness 4 µm.

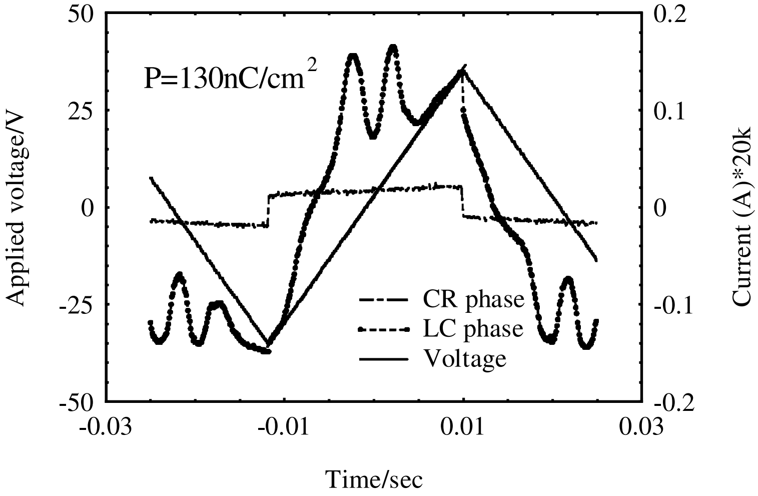

Figure 2. Polarization curves of compound **7b**: temperature 123 C, film thickness 4 µm.