Novel fluorinated liquid crystals. Part VI. The synthesis and phase transition of novel cholesteric liquid crystals containing 1,4-tetrafluorophenylene units

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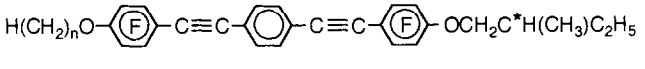
Abstract

1-[(4-n-Alkoxy-2,3,5,6-tetrafluorophenyl)ethynyl]-4-[(4-((*S*)-2-methylbutoxy)-2,3,5,6-tetrafluorophenyl)ethynyl]benzenes have been prepared from the starting material 1-pentafluorophenyl-2-trimethylsilylacetylene. Textural observation by polarizing microscopy showed that these materials were cholesteric liquid crystals when the terminal alkoxy chains were of sufficient length. The effect of symmetrical tetrafluoro substitution of phenyl groups on the mesomorphic behaviour is also discussed.

Introduction

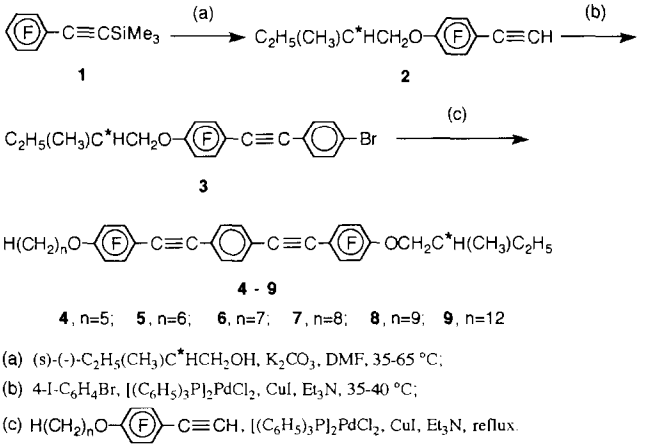
In recent years, intensive research has been undertaken on liquid crystals containing fluorine atoms in backbone structures or terminal chains, in order to discover new liquid crystal materials possessing useful physical properties, and hundreds of liquid crystalline molecules with monofluoro- or difluoro-substituted phenyls have been prepared in this way [1–5]. However, only a limited number of liquid crystalline molecules containing the 1,4-tetrafluorophenylene moiety [6–18] have been reported. In our previous studies, we have reported several types of new liquid crystals with 3,4,5,6-tetrafluoro-1,4-phenylene units [19]. In this paper, we wish to report a novel type of cholesteric liquid crystal containing 1,4-tetrafluorophenylene units (compounds A), which were synthesized using 1-pentafluorophenyl-2-trimethylsilylacetylene as the starting material.



A (n=5 - 9, 12)

Results and discussion

The required compounds were prepared according to Scheme 1.



Scheme 1.

The starting material (compound **1**) was prepared as described in a previous publication [20]. 4-Alkoxy-2,3,5,6-tetrafluorophenylacetylenes (compound **2** and other related intermediates) were prepared by nucleophilic substitution on compound **1** [21]. Selective palladium-catalysed coupling between compound **2** and 1-bromo-4-iodobenzene at 35–40 °C gave compound **3**. Further coupling involving 4-n-alkoxy-2,3,5,6-tetrafluorophenylacetylenes and compound **3** yielded the desired polyfluoro-substituted system (compounds **4–9**).

All of the final compounds were purified by chromatography on silica gel with petroleum ether (b.p. 60–90 °C) as eluent and were recrystallized from acetone methanol. Phase transitions were studied using a Mettler

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FP-52 hot stage and control unit in conjunction with an Olympus BH2 polarizing microscope, while phase identification was made by comparing the observed textures with those in the literature [22, 23].

The transition temperatures of these new fluorinated materials are listed in Table 1.

Most of the new compounds exhibited an enantiotropic cholesteric phase except for that with $n=5$. As far as the influence of the end chain is concerned, firstly the melting points of these homologous compounds decrease with increasing alkoxy chain length. Secondly, the cholesteric–isotropic phase transition temperatures of these mesogens initially increase as the number of carbon atoms in the normal alkoxy chain increases from 6 to 8, and then decrease with further lengthening of the end chain, indicating that the normal odd–even effect is not observed.

In our previous study, we have reported that the phase-transition temperatures of 1,4-bis[(4-n-pentyloxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzene follow the sequence [19]:

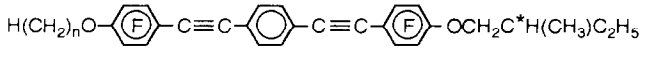
$$C \xrightarrow{125.4\ ^\circ C} N \xrightarrow{167.8\ ^\circ C} I \xrightarrow{167.0\ ^\circ C} N \xrightarrow{124.4\ ^\circ C} C$$

As with the 1,4-bis[(4-n-alkoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzenes, it is clear that branching of the terminal alkoxy chain has a destabilizing effect on the liquid crystalline phase.

Pugh and co-workers [24, 25] reported the synthesis and thermotropic behaviour of some aryl-acetylene dimers containing the same skeleton as those of compounds A. Their phase-transition temperatures are listed in Table 2.

From the comparison between the phase-transition temperatures for compounds A and B, we believe that symmetrical tetrafluoro substitution on phenyl rings decreases both the temperature of melting and isotropization, and has a destabilizing effect on the smectic phase, even though the effect of the terminal alkoxy chain should also be considered. The influence of the introduction of 1,4-tetrafluorophenylene units on thermotropic behaviour is still being studied.

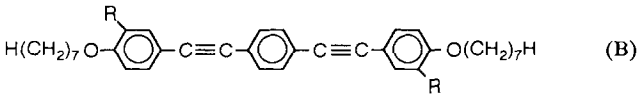
TABLE 1. Phase transition temperatures (°C)[a] of compounds A



n	C→Ch	Ch→I	I→Ch	Ch→C
5	129.0[b]	–	–	128.4
6	114.1	122.3	121.1	112.1
7	107.3	128.6	128.0	105.3
8	106.3	135.8	135.6	106.0
9	99.1	112.8	112.4	97.0
12	89.2	95.7	94.5	84.9

[a]C, crystalline; Ch, cholesteric; I, isotropic.
[b]The compound with $n=5$ exhibited no mesophase either on heating or cooling.

TABLE 2. Phase-transition temperatures (°C) of some aryl-acetylene dimers reported by Pugh and co-workers [24, 25]



(B)

R	Phase transition temperatures[a] (°C)
H	C 68.1 C 127.7 C 176.8 C/S 178.8 N 223.1 I I 218.5 N 173.5 S/C 170.0 C 121.6 C 117.0 C 61.8 C 55.4 C
F	rC 57.1 C 100.2 S 130.0 S_C 155.9 N 196.3 I I 192.3 N 152.2 S_C 126.0 S 55.1 C

[a]C, crystalline; rC, recrystallization; S, smectic; N, nematic; I, isotropic; first line of data obtained from heating scans of DSC analysis, second line from cooling scans.

Experimental

IR spectra were recorded on a Shimadzu IR-440 spectrophotometer, using KBr pellets of solid or films of liquids. ^1H NMR spectra with TMS as internal standard and ^{19}F NMR spectra with trifluoroacetic acid (TFA) as external standard were recorded on a Varian EM-360L spectrometer (60 MHz) or an FX-90 Q spectrometer (90 MHz). For ^{19}F NMR spectra, high field is positive. Mass spectra were recorded on a Finnigan-4021 spectrometer.

Preparation of 4-[(S)-2-methylbutoxy]-2,3,5,6-tetrafluorophenylacetylene (2)

Quantities: compound **1** (6.0 g, 22.7 mmol), potassium carbonate (9.0 g, 65.1 mmol), (*S*)-(−)-2-methyl-1-butanol (4.0 g, 45.5 mmol), DMF (12.0 ml); reaction conditions: 35–40 °C for 46 h and then at 60–65 °C for 6 h. The experimental procedure was as described previously [21]. The crude product was purified by column chromatography on silica gel with petroleum ether (b.p. 60–90 °C) as eluent to give compound **2** as a pale yellow liquid. Yield 5.40 g (90.3%). ^1H NMR (CCl_4/TMS) δ: 0.82–1.90 (m, 9H); 3.34 (s, 1H, C≡CH): 3.94 (d, 2H, $J=6.0$ Hz, OCH_2) ppm. ^{19}F NMR (CCl_4/TFA) δ: 60.47 (d, 2F, $J=18.8$ Hz, F_{arom}); 80.47 (d, 2F, $J=18.8$ Hz, F_{arom}) ppm.

Preparation of 1-(4-bromophenyl)-2-[4-((S)-2-methylbutoxy)-2,3,5,6-tetrafluorophenyl]acetylene (3)

Under dry nitrogen and to a mixture of compound **2** (3.07 g, 11.8 mmol), 1-bromo-4-iodobenzene (3.34 g, 11.8 mmol), bis(triphenylphosphine)palladium dichlor-

ide (300 mg, 0.428 mmol) and copper(I) iodide (163 mg, 0.857 mmol), was added anhydrous triethylamine (60 ml). The resulting mixture was stirred at 35–40 °C for 48 h whilst isolated from the air. Analysis by TLC revealed complete reaction. The precipitate formed was then filtered off, washed with ether and water, and dried over anhydrous sodium sulphate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90 °C) as eluent to yield compound **3** as white crystals. Yield 4.29 g (87.6%), m.p. 45.5 °C. ^{1}H NMR (CCl_4/TMS) δ: 0.82–2.09 (m, 9H); 4.04 (d, 2H, $J=6.0$ Hz, OCH_2); 7.40 (s, 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 60.00 (d, 2F, $J=18.8$ Hz, F_{arom}); 79.50 (d, 2F, $J=18.8$ Hz, F_{arom}) ppm. MS *m/z* (rel. int.): 416 (M^+, 43.61); 414 (M^+, 35.73); 346 (83.90): 344 (100.00).

Preparation of 1-[(4-n-pentyloxy-2,3,5,6-tetrafluorophenyl)ethynyl]-4-[(4-((S)-2-methylbutoxy)-2,3,5,6-tetrafluorophenyl)ethynyl]benzene (4)

Typical procedure: under dry nitrogen and to a mixture of compound **3** (374 mg, 0.90 mmol), 4-n-pentyloxy-2,3,5,6-tetrafluorophenylacetylene (235 mg, 0.90 mmol), bis(triphenylphosphine)palladium dichloride (30 mg, 0.043 mmol) and copper(I) iodide (17 mg, 0.089 mmol), was added anhydrous triethylamine (12 ml). The resulting mixture was refluxed with stirring for 8 h. Analysis by TLC revealed complete reaction. The precipitate formed was then filtered off, washed with ether and water, and dried over anhydrous sodium sulphate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90 °C) as eluent to yield compound **4** as a white solid together with 168 mg of compound **3**. The product was recrystallized from acetone/methanol to yield white crystals. Yield 192 mg (56.0%), m.p. 129.0 °C. ^{1}H NMR (CCl_4/TMS) δ: 0.62–2.00 (m, 18H); 4.00 (d, 2H, $J=5.0$ Hz, OCH_2); 4.11 (t, 2H, $J=5.0$ Hz, OCH_2); 7.45 (s, 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 60.03 (m, 4F, F_{arom}); 79.75 (m, 4F, F_{arom}) ppm. IR (KBr) (cm^{-1}): 2960; 2870; 2200; 1520; 1505; 1490; 1440; 1390; 1130; 985; 840; 690. MS *m/z* (rel. int.): 594 (M^+, 23.49); 524 (18.26); 454 (100.00).

The new fluorinated compounds **5–9** were prepared by a similar procedure.

1[(4-n-Hexyloxy-2,3,5,6-tetrafluorophenyl)ethynyl]-4-[(4-((*S*)-2methylbutoxy)-2,3,5,6-tetrafluorophenyl)-ethynyl]benzene (**5**): yield 55.9%, m.p. 114.1 °C. ^{1}H NMR (CCl_4/TMS) δ: 0.65–2.01 (m, 20H); 4.01 (d, 2H, $J=5.0$ Hz, OCH_2); 4.12 (t, 2H, $J=5.0$ Hz, OCH_2); 7.46 (s, 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 60.05 (m, 4F, F_{arom}); 79.77 (m, 4F, F_{arom}) ppm. IR (KBr) (cm^{-1}): 2960; 2870; 2200; 1520; 1505; 1485; 1438; 1390; 1125; 982; 840; 688. MS *m/z* (rel. int.): 608 (M^+, 66.74); 538 (25.79); 454 (100.00).

1-[(4-n-Heptyloxy-2,3,5,6-tetrafluorophenyl)ethynyl]-4-[(4-((*S*)-2-methylbutoxy)-2,3,5,6-tetrafluorophenyl)-ethynyl]benzene (**6**): yield 58.4%, m.p. 107.3 °C. ^{1}H NMR (CCl_4/TMS) δ: 0.67–2.01 (m, 22H); 4.01 (d, 2H, $J=5.0$ Hz, OCH_2); 4.12 (t, 2H, $J=5.0$ Hz, OCH_2); 7.48 (s, 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 60.04 (m, 4F, F_{arom}); 79.76 (m, 4F, F_{arom}) ppm. IR (KBr) (cm^{-1}): 2960; 2870; 2200; 1520; 1505; 1490; 1440; 1390; 1128; 982; 840; 690. MS *m/z* (rel. int.): 622 (M^+, 77.90); 552 (29.03); 454 (100.00).

1-[(4-n-Octyloxy-2,3,5,6-tetrafluorophenyl)ethynyl]-4-[(4-((*S*)-2-methylbutoxy)-2,3,5,6-tetrafluorophenyl)-ethynyl]benzene (**7**): yield 48.7%, m.p. 106.3 °C. ^{1}H NMR (CCl_4/TMS) δ: 0.66–2.00 (m, 24H); 4.00 (d, 2H, $J=5.0$ Hz, OCH_2); 4.14 (t, 2H, $J=5.0$ Hz, OCH_2); 7.50 (s, 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 60.03 (m, 4F, F_{arom}); 79.75 (m, 4F, F_{arom}) ppm. IR (KBr) (cm^{-1}): 2960; 2870; 2200; 1520; 1505; 1495; 1441; 1395; 1130; 990; 840; 694. MS *m/z* (rel. int.): 636 (M^+, 24.33); 566 (11.21); 454 (100.00).

1-[(4-n-Nonyloxy-2,3,5,6-tetrafluorophenyl)ethynyl]-4-[(4-((*S*)-2-methylbutoxy)-2,3,5,6-tetrafluorophenyl)-ethynyl]benzene (**8**): yield 48.6%, m.p. 99.1 °C. ^{1}H NMR (CCl_4/TMS) δ: 0.68–2.00 (m, 26H); 4.00 (d, 2H, $J=5.0$ Hz, OCH_2); 4.12 (t, 2H, $J=5.0$ Hz, OCH_2); 7.48 (s, 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 60.04 (m, 4F, F_{arom}); 79.77 (m, 4F, F_{arom}) ppm. IR (KBr) (cm^{-1}): 2960; 2870; 2200; 1520; 1505; 1495; 1440; 1394; 1130; 990; 840; 694. MS *m/z* (rel. int.): 650 (M^+, 25.11); 580 (15.17); 454 (100.00).

1-[(4-n-Dodecyloxy-2,3,5,6-tetrafluorophenyl)-ethynyl]-4-[(4-((*S*)-2-methylbutoxy)-2,3,5,6-tetrafluorophenyl)ethynyl]benzene (**9**): yield 56.0%, m.p. 89.2 °C. ^{1}H NMR (CCl_4/TMS) δ: 0.70–2.00 (m, 32H); 4.00 (d, 2H, $J=5.0$ Hz, OCH_2); 4.10 (t, 2H, $J=5.0$ Hz, OCH_2); 7.49 (s, 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 60.06 (m, 4F, F_{arom}); 79.80 (m, 4F, F_{arom}) ppm. IR (KBr) (cm^{-1}): 2960; 2870; 2200; 1520; 1505; 1495; 1440; 1394; 1130; 990; 840; 694. MS *m/z* (rel. int.): 692 (M^+, 49.32); 622 (24.20); 454 (100.00).

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