Preliminary Note

Novel fluorinated liquid crystals. Part I. Synthesis of compounds possessing (*p*-substituted-tetrafluorophenyl)ethyne substituents as materials for liquid crystals

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Abstract

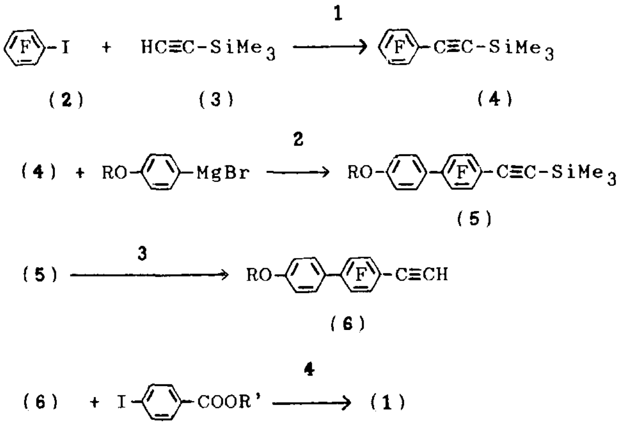
[4-(2,3,5,6-Tetrafluoro-4'-octyloxybiphenylyl)] [4-alkoxycarbonylphenyl]acetylenes have been prepared via a Pd-catalyzed coupling reaction. These compounds form mesomorphic phases over a wide temperature range and provide a new series of liquid crystal materials containing 1,4-tetrafluorophenylene in their basic structure.

Recently, considerable interest has centered around the synthesis of liquid crystals containing fluorine atoms [1–3]. The fluorine atom combines a large electronegativity with a small size, so that it significantly affects the physical properties of molecules without eliminating the possibility of mesophase formation. Introduction of the fluoro substituent has effected a significant improvement in some of the properties of liquid crystals used in electro-optic display devices [4–6]. Although a large number of linear molecules with mono-fluoro- or di-fluoro-substituted phenyls suitable for liquid crystals have been prepared [7–9], little work has been done on tetra-fluoro substituents in mesogens [10, 11]. We wish to report the preparation of compounds of type **1**, i.e. [4-(2,3,5,6-tetrafluoro-4'-octyloxybiphenylyl)] [4-alkoxycarbonylphenyl]acetylenes, and have found that they form liquid crystals. All exhibit a nematic phase over a wide temperature range (30–90 °C). The mesomorphic ranges of **1** may be measured visually by means of an optical microscope using a polarizing Olympus PM-6 microscope fitted with a Mettler FP 52 heating stage and FP 5 control unit. The results obtained are summarized in Table 1. Other properties of these acetylenes are now under study.

TABLE 1. Transition temperatures[a] of compounds **1**

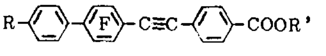
1	R'	T(C→N)[b] (°C)	T(N→I)[b] (°C)
a	CH$_3$	102.8	193.0
b	C$_2$H$_5$	109.3	164.3
c	n-C$_3$H$_7$	97.9	154.1
d	n-C$_4$H$_9$	98.1	134.4
e	n-C$_5$H$_{11}$	99.0	135.1
f	n-C$_6$H$_{13}$	94.8	131.8
g	n-C$_8$H$_{17}$	90.5	120.8

[a] The phase ranges were determined from data obtained during the cooling process.
[b] C = crystal phase; N = nematic phase; I = isotropic phase.



Scheme 1. Reagents: 1, (Ph$_3$P)$_2$PdCl$_2$, CuI, Et$_3$N, 30–35 °C; 2, THF; 3, CH$_3$OH, CH$_3$COCH$_3$, NaOH; 4, (Ph$_3$P)$_2$PdCl$_2$, CuI, Et$_3$N.

Compounds **1** were synthesized via the reactions shown in Scheme 1.



(1)

(R = OC$_8$H$_{17}$, R' = C$_n$H$_{2n+1}$: **1a**, $n = 1$; **1b**, $n = 2$; **1c**, $n = 3$; **1d**, $n = 4$; **1e**, $n = 5$; **1f**, $n = 6$; **1g**, $n = 8$)

The intermediate compound, [(pentafluorophenyl)ethynyl]trimethylsilane (**4**), was obtained from the palladium-catalyzed coupling reaction between pentafluoroiodobenzene (**2**) and trimethylsilylacetylene (**3**) [12]. Compound **5** was prepared from *p*-alkyloxyphenylmagnesium bromide and **4** by nucleophilic substitution [13]. Removal of the trimethylsilyl group from compound **5** with sodium hydroxide in methanol at ambient temperature gave compound **6**. Compounds **1** were prepared from **6** and *p*-iodobenzoate esters in high yield via a Pd-catalyzed coupling reaction. The structures of com-

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pounds **1a–g** are consistent with analytical data including mass, IR and NMR spectra, and elementary analysis.

Experimental

IR spectra were determined via a Shimadzu IR-440 spectrometer using KBr discs. ^{1}H NMR spectra with TMS as the internal standard and $CDCl_3$ as the solvent were run on a FX-90Q (90 MHz) spectrometer. ^{19}F NMR spectra, with trifluoroacetic acid (TFA) as external standard and $CDCl_3$ as the solvent, were recorded on a Varian EM 360L (60 MHz) spectrometer (high field positive). MS spectra were measured with a Finnigan 4021 spectrometer.

Fluoro-aromatic acetylenes **5** and **6** were prepared by the method reported previously [13].

Preparation of [4-(2,3,5,6-tetrafluoro-4'-octyloxybiphenylyl)] [4-n-octyloxycarbonylphenyl]acetylene (1g)(nc)

To a stirred mixture of **6** (0.189 g, 0.5 mmol) and *p*-iodobenzoic acid octyl ester (0.142 g, 0.5 mmol) in Et_3N (15 ml) was added $(Ph_3P)_2PdCl_2$ (5 mg) and CuI (2 mg). Stirring was continued with refluxing for 8 h under N_2. Then Et_2O (30 ml) was added to the system. The salt was filtered off using a sintered-glass funnel and rinsed well with Et_2O. The Et_2O solution was washed with H_2O and dried (Na_2SO_4). After removal of the ether, a pale yellow solid product was collected. Recrystallization from acetone/methanol gave white crystals of **1g**, yield 0.26 g (85%).

Compound **1g**: m.p. 107.4 °C. IR (cm^{-1}): 2900; 1718; 1610; 1480; 1115; 1278. ^{1}H NMR δ: 0.64–0.92 (m, 30H); 3.92 (t, 2H, J=6.3 Hz); 4.24 (t, 2H, J=6.3 Hz); 6.98 (d, 2H, arom.); 7.40 (d, 2H, H arom.); 7.63 (d, 2H, H arom.); 8.04 (d, 2H, H arom.) ppm. ^{19}F NMR δ: 60.1 (m, 2F, F arom.); 67.3 (m, 2F, F arom.) ppm. MS *m/z*: 610 (M$^+$). Analysis: Found: C, 72.50; H, 7.04; F, 12.41%. Calc. for $C_{37}H_{42}F_4O_3$: C, 72.76; H, 6.93; F, 12.44%.

Fluoro-aromatic acetylene compounds **1a–f** were prepared by procedures similar to that described above.

Compound **1a**: m.p. 124.8 °C. IR (cm^{-1}): 2900; 1725; 1610; 1480; 1280; 1110. ^{1}H NMR δ: 0.78–1.94 (m, 15H); 3.94 (s, 3H); 4.26 (t, 2H, J=6.3 Hz); 6.98 (d, 2H, J=8.1 Hz, H arom.); 7.40 (d, 2H, J=8.1 Hz, H arom.); 7.64 (d, 2H, J=8.1 Hz, H arom.); 8.04 (d, 2H, J=8.1 Hz, H arom.) ppm. ^{19}F NMR δ: 60.1 (m, 2F, F arom.); 67.3 (m, 2F, F arom.) ppm. MS *m/z*: 512 (M$^+$). Analysis: Found: C, 69.92; H, 5.28; F, 14.82%. Calc. for $C_{30}H_{28}F_4O_3$: C, 70.30; H, 5.51; F, 14.83%.

Compound **1b**: m.p. 123.2 °C. IR (cm^{-1}) 2900; 1718; 1610; 1480; 1278; 1110. ^{1}H NMR δ: 0.78–1.94 (m, 18H); 3.92 (t, 2H, J=6.3 Hz); 4.32 (q, 2H, J=6.3 Hz); 6.99 (d, 2H, J=8.1 Hz, H arom.); 7.40 (d, 2H, J=8.1 Hz, H arom.); 762 (d, 2H, J=8.1 Hz, H arom.); 8.04 (d, 2H, J=8.1 Hz, H arom.) ppm. ^{19}F NMR δ: 60.1 (m, 2F, F arom.); 67.3 (m, 2F, F arom.) ppm. MS *m/z*: 526 (M$^+$). Analysis: Found: C, 70.44; H, 5.85; F, 14.66%. Calc. for $C_{31}H_{30}F_4O_3$: C, 70.71; H, 5.74; F, 14.43%.

Compound **1c**: m.p. 117.6 °C. IR (cm^{-1}) 2900; 1718; 1610; 1480; 1278; 1110. ^{1}H NMR δ: 0.78–1.94 (m, 20H); 3.93 (t, 2H, J=6.3 Hz); 4.23 (t, 2H, J=6.3 Hz); 6.99 (d, 2H, J=8.1 Hz, H arom.); 7.40 (d, 2H, J=8.1 Hz, H arom.); 7.62 (d, 2H, J=8.1 Hz, H arom.); 8.04 (d, 2H, J=8.1 Hz, H arom.) ppm. ^{19}F NMR δ: 60.1 (m, 2F, F arom.); 67.3 (m, 2F, F arom.) ppm. MS *m/z*: 540 (M$^+$). Analysis: Found: C, 71.35; H, 5.74; F, 13.85%. Calc. for $C_{32}H_{32}F_4O_3$: C, 71.09; H, 5.97; F, 14.06%.

Compound **1d**: m.p. 118.4 °C. IR (cm^{-1}): 2910; 1718; 1610; 1480; 1278; 1110. ^{1}H NMR δ: 0.78–1.94 (m, 22H); 3.92 (t, 2H, J=6.3 Hz); 4.32 (q, 2H, J=6.3 Hz); 6.98 (d, 2H, J=8.1 Hz, H arom.); 7.40 (d, 2H, J=8.1 Hz, H arom.); 7.64 (d, 2H, J=8.1 Hz, H arom.); 8.04 (d, 2H, J=8.1 Hz, H arom.) ppm. ^{19}F NMR δ: 60.1 (m, 2F, F arom.); 67.3 (m, 2F, F arom.) ppm. MS *m/z*: 554 (M$^+$). Analysis: Found: C, 71.81; H, 6.12; F, 13.33%. Calc. for $C_{33}H_{34}F_4O_3$: C, 71.48; H, 6.14; F, 13.72%.

Compound **1e**: m.p. 109.3 °C. IR (cm^{-1}): 2910; 1718; 1610; 1480; 1278; 1110. ^{1}H NMR δ: 0.78–1.94 (m, 24H); 3.92 (t, 2H, J=6.3 Hz); 4.32 (t, 2H, J=6.3 Hz); 6.98 (d, 2H, J=8.1 Hz, H arom.); 7.39 (d, 2H, J=8.1 Hz, H arom.); 7.64 (d, 2H, J=8.1 Hz, H arom.); 8.04 (d, 2H, J=8.1 Hz, H arom.) ppm. ^{19}F NMR δ: 60.1 (m, 2F, F arom.); 67.3 (m, 2F, F arom.) ppm. MS *m/z*: 568 (M$^+$). Analysis: Found: C, 71.57; H, 6.23; F, 13.33%. Calc. for $C_{34}H_{36}F_4O_3$: C, 71.83; H, 6.34; F, 13.38%.

Compound **1f**: m.p. 104.2 °C. IR (cm^{-1}): 2910; 1718; 1610; 1480; 1278; 1110. ^{1}H NMR δ: 0.78–1.94 (m, 26H); 3.92 (t, 2H, J=6.3 Hz); 4.24 (t, 2H, J=6.3 Hz); 6.98 (d, 2H, J=8.1 Hz, H arom.); 7.40 (d, 2H, J=8.1 Hz, H arom.); 7.62 (d, 2H, J=8.1 Hz, H arom.); 8.04 (d, 2H, J=8.1 Hz, H arom.) ppm. ^{19}F NMR δ: 60.1 (m, 2F, F arom.); 67.3 (m, 2F, F arom.) ppm. MS *m/z*: 582 (M$^+$). Analysis: Found: C, 72.14; H, 6.52; F, 13.14%. Calc. for $C_{35}H_{38}F_4O_3$: C, 72.16; H, 6.53; F, 13.06%.

References

1 S. Sugawara, *Jpn. Kokai Tokkyo Koho JP 01 272 552* (1989); [*Chem. Abs.*, 112:208092V].

2 S. Sugawara, *Jpn. Kokai Tokkyo Koho JP 01 294 653* (1989); [*Chem. Abs.*, 112:208094X].

3 S. Saito, H. Inoue, K. Terashima, T. Inukai and K. Furukawa, *US Pat. 4 737 313* (1988); [*Chem. Abs.*, 110:125634f].

4 G.W. Gray, C. Hogg and D. Lacey, *Mol. Cryst. Liq. Cryst.*, *67* (1981) 1.

5 P.H. Balkwill, D.I. Bishop, A.D. Pearson and I.C. Sage, *Mol. Cryst. Liq. Cryst.*, *123* (1985) 1.

6 R. Eidenschink, *Mol. Cryst. Liq. Cryst., 123* (1985) 57.

7 M. Hird, G.W. Gray and K.J. Toyne, *Liq. Cryst., 11* (1992) 531.

8 G.W. Gray, D. Lacey, J.E. Stanton and K.J. Toyne, *Liq. Cryst., 1* (1986) 407.

9 L.K.M. Chan, G.W. Gray and D. Lacey, *Mol. Cryst. Liq. Cryst., 123* (1985) 185.

10 A. Beguin and J.C. Dubois, *J. Phys. (Paris), 40C* (1979) 9.

11 J.C. Dubois, A. Zann Beguin and P. Le Barny, *4th Liq. Cryst. Conf. Socialist Countries,* Tbilisi, Oct. 1981.

12 Y. Zhang and J. Wen, *J. Fluorine Chem., 47* (1990) 533.

13 Y. Zhang, J. Wen and W. Du, *J. Fluorine Chem., 49* (1990) 293.