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Novel fluorinated liquid crystals

X. The synthesis and mesomorphic states of 1-(4-bromophenyl)2-(4′-*n*-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-yl)acetylene

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A series of 1-(4-bromophenyl)2-(4′-*n*-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-yl)acetylene has been prepared. Polarizing microscopic textural observation shows that they are nematic and smectic A liquid crystals.

1. Introduction

Because of the great potential for the use of liquid crystalline materials, more and more scientists are attracted to search for more mesomorphic compounds with specific properties.

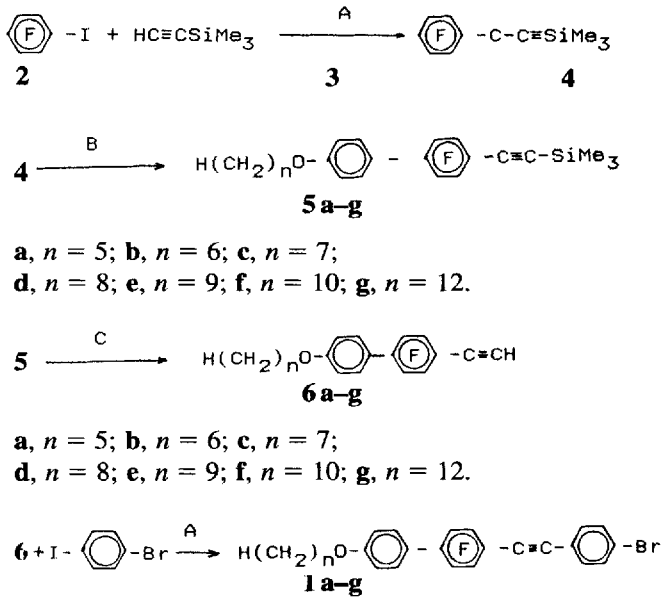
It has been reported that a large number of ferroelectric and other liquid crystals have been obtained by replacing hydrogen atoms with fluorine atoms [1–3]. The symmetry of the molecular structure is reduced when a fluorine atom is introduced into the central aromatic core or side chain of the liquid crystalline molecule. And the incorporation of fluorine into liquid crystalline materials provides lower phase transition temperatures, lower viscosity and better miscibility with other liquid crystalline materials [4–7].

In past years, our research group has successfully synthesized many kinds of liquid crystals with 2,3,5,6-tetrafluore-1,4-phenylene in the core structure to research new materials for display devices and other applications [8–12]. In this communication we provide another novel series of fluorinated liquid crystals with the following structure:

(n = 5–10, 12).

2. Synthesis

The synthesis of the desired new compounds is presented in the following scheme.



a, n = 5; **b**, n = 6; **c**, n = 7;
d, n = 8; **e**, n = 9; **f**, n = 10; **g**, n = 12.

a, n = 5; **b**, n = 6; **c**, n = 7;
d, n = 8; **e**, n = 9; **f**, n = 10; **g**, n = 12.

a, n = 5; **b**, n = 6; **c**, n = 7;
d, n = 8; **e**, n = 9; **f**, n = 10;
g, n = 12.

A. $(Ph_3P)_2PdCl_2$, CuI, Et_3N, 30–50°C. *B*. *p*-$H(CH_2)_n O$–C_6H_4MgBr. THF, reflux. C. CH_3OH/CH_3COCH_3, $NaOH/H_2O$, R.T.

Compound **4** was obtained as described in a previous publication [13]. Compounds **5 a–g** were prepared from 4-alkoxyphenylmagnesium bromide and **4** by nucleophilic substitution [14]. The trimethylsilyl groups of compounds **5 a–g** were removed with sodium hydroxide in methanol

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Phase transition temperatures of compounds **1**.

n	Phase transition temperature/°C
5	C $\underset{81.4}{\overset{112.3}{\rightleftharpoons}}$ N $\underset{185.5}{\overset{186.2}{\rightleftharpoons}}$ I
6	C $\underset{80.9}{\overset{102.0}{\rightleftharpoons}}$ N $\underset{182.3}{\overset{182.4}{\rightleftharpoons}}$ I
7	C $\underset{84.2}{\overset{107.3}{\rightleftharpoons}}$ N $\underset{169.6}{\overset{169.2}{\rightleftharpoons}}$ I
8	C $\underset{80.7}{\overset{103.1}{\rightleftharpoons}}$ N $\underset{168.4}{\overset{168.6}{\rightleftharpoons}}$ I
9	C $\underset{74.6}{\overset{99.7}{\rightleftharpoons}}$ N $\underset{168.7}{\overset{167.8}{\rightleftharpoons}}$ I
10	C $\underset{87.2}{\overset{106.4}{\rightleftharpoons}}$ S_A $\underset{91.9}{\rightleftharpoons}$ N $\underset{156.4}{\overset{156.4}{\rightleftharpoons}}$ I
12	C $\underset{84.9}{\overset{103.0}{\rightleftharpoons}}$ S_A $\underset{93.9}{\rightleftharpoons}$ N $\underset{143.0}{\overset{143.7}{\rightleftharpoons}}$ I

C, crystal; N, nematic; S_A, smectic; I, isotropic.

at ambient temperature to give compounds **6a–g**. Finally the coupling reaction between compounds **6a–g** and 4-bromoiodobenzene under the catalysis of bis(triphenylphosphine)palladium dichloride and copper (I) iodide in anhydrous trithylamine gave the desired products **1a–g** [13].

Transition temperatures and phase assignments were determined by polarized light microscopy.

3. Results and discussion

The transition temperatures of these novel fluorinated compounds are listed in the table. Most of the new compounds exhibit a nematic phase. When the length of the alkoxyl chain increases, a smectic A phase appears (monotropic for $n = 10, 12$). Both the melting points and the clearing points of these homologous compounds drop with increasing the alkoxyl chain length. It is interesting to note that these compounds have a nematic phase over a wide temperature range. This fact can be explained from π-bond conjugation in the core structure of the molecule. Therefore, this class of fluorinated liquid crystals has good thermal stability. Other properties of them are now under study.

4. Experimental

IR spectra were recorded on a Shimadzu IR-400 spectrometer, using KBr pellets of solids or films of liquids. ^{1}H 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 instrument (60 MHz). For ^{19}F NMR spectra, high field is positive. Mass spectra were recorded on a Finnigan-4021 spectrometer.

4.1. *1-Trimethylsilyl-2-[4-(4-*n*-octyloxyphenyl)-2,3,5,6-tetrafluorophenyl]acetylene* **5d**

Magnesium turnings 310 mg (12·8 mmol), anhydrous THF 10 ml, 4-*n*-octyloxyphenylmagnesium bromide 2·80 g (9·83 mmol), compound **4** 2·00 g (7·57 mmol). The experimental procedure was as reported previously [14]. The crude product was purified by column chromatography (silica gel/petroleum ether) to yield a pale yellow solid **5d**. Yield 2·00 g (58·7 per cent). ^{1}H NMR (CCl_4/TMS): δ 0·15 (s, 9 H, $Si(CH_3)_3$), 0·79 (t, 3 H, CH_3), 0·98–1·89 (m, 12 H, CH_2), 3·80 (t, 2 H, OCH_2), 7·01 (d, 4 H, Ar) ppm; ^{19}F NMR (CCl_4/TFA): δ 59·43 (m, 2 F), 66·80 (m, 2 F) ppm.

Compounds **5a–c, e–g** were prepared similarly and all of them had appropriate ^{1}H and ^{19}F NMR spectral data.

4.2. *4′-*n*-octyloxy-2,3,5,6-tetrafluorobiphenyl-4-acetylene* **6d**

Compound **5d** 1·65 g (3·66 mmol), methanol 5 ml, acetone 20 ml and 0·2 M sodium hydroxide 3 ml. The experimental procedure was as reported previously [14]. The crude product was recrystallized from acetone–methanol to yield white flaky crystals of **6d**. Yield 1·26 g (91·0 per cent); m.p. 90·3°C; ^{1}H NMR (CCl_4/TMS): δ 0·78 (t, 3 H, CH_3), 0·94–1·98 (m, 12 H, CH_2), 3·42 (s, 1 H, C ≡ CH), 3·84 (t, 2 H, OCH_2), 7·00 (d, 4 H, Ar) ppm; ^{19}F NMR (CCl_4/TFA): δ 59·40 (m, 2 F), 66·50 (m, 2 F) ppm.

Compounds **6a–c, e–g** were prepared similarly and all of them had appropriate ^{1}H and ^{19}F NMR spectral data.

4.3. *1-(4-Bromophenyl)2-(4′-*n*-octyloxy-2,3,5,6-tetrafluorobiphenyl-4-yl)acetylene* **1d**

Under dry nitrogen, to a mixture of compound **6d** 756 mg (2·00 mmol), 4-bromoiodobenzene, 566 mg (2·00 mmol), bis(triphenylphosphine)palladium dichloride 80·9 mg (0·112 mmol) and copper (I) iodide 32·1 mg (0·169 mmol), was added 20 ml of anhydrous triethylamine. The resulting mixture was stirred at 30–35°C for 24 h. Analysis by TLC revealed a complete reaction. The precipitate was filtered off and washed with ether and the filtrate washed with water, dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (50 : 1) as eluent to give a yellow crystal which was recrystallized from acetone–methanol to yield pale yellow crystals of **1d**. Yield 0·57 g (54 per cent); m.p. 103·1°C; IR: 2920, 2850, 1618, 1590, 1522, 1480, 1418, 1400, 1298, 1260, 1180, 1170, 1110, 1070, 1010, 980, 830, 780, 760, 720, 660, 630, 520 cm^{-1}. ^{1}H NMR: δ 0·92–1·87 (m, 15 H, CH_2, 4·06 (t, 2 H, OCH_2), 6·97 (d, 2 H, Ar), 7·12 (d, 2 H, Ar), 7·31 (d, 2 H, Ar), 7·42 (d, 2 H, Ar) ppm. ^{19}F NMR: δ 62·58 (m, 2 F), 67·48 (m, 2 F) ppm; MS (m/z): 532 ($M^+ - 1$). Elementary analysis calculated for $C_{28}H_{25}F_4OBr$ (533·19): C, 63·06;

H, 4·69; F, 14·25; Br, 14·98. Found: C, 62·93; H, 4·54; F, 14·20; Br, 14·57 per cent.

New fluorinated compounds were **1a–c, e–g** were prepared by a similar procedure. All of them had satisfactory elementary analysis and appropriate ^{1}H and ^{19}F NMR, IR and MS spectra data.

5. Conclusions

A new homologous series of 1-(4-bromophenyl)2-(4′-*n*-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-yl)acetylene were prepared via Pd-catalysed coupling reaction. Study by polarizing microscopy showed that they were liquid crystals with nematic and smectic A phases. All exhibited a nematic phase over a wide temperature range (50–104°C).

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