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Liquid Crystals

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Synthesis and mesomorphic properties of 4-methoxyphenyl 4′-*n*-alkoxy-2′,3′,5′,6′-tetrafluorobiphenyl-1-carboxylates

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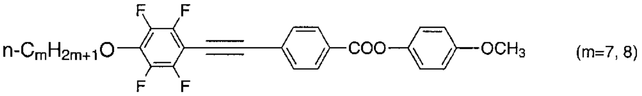
A novel type of 4-methoxyphenyl 4′-*n*-alkoxy-2′,3′,5′,6′-tetrafluorobiphenyl-1-carboxylates have been synthesized. Textural observations by polarizing microscopy and DSC measurements of the phase transitions show that all of these compounds are thermotropic liquid crystals with only a nematic mesophase. The relationship between the properties and chemical structures of these compounds is discussed.

1. Introduction

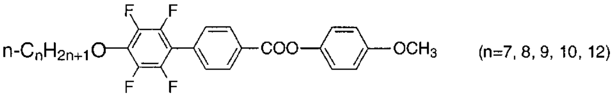
Since liquid crystals with excellent physical properties are indispensable to the development of liquid crystal display (LCD) technology, an increasing amount of research has been carried out on the synthesis of liquid crystals to provide new potential materials for display devices and other applications. In recent years, laterally fluorinated aromatic liquid crystals have attracted much attention [1–10]. The fluorine atom combines strong electro-negativity with small size, so that it significantly affects the physical properties of molecules without eliminating the possibility of mesophase formation. When one or two fluorine atoms are introduced into the aromatic core of liquid crystals, marked effects, such as a drop in melting point, an increase in permittivity (i.e. perpendicular to the director) [11] and a decrease in the length-to-width ratio [12], may be observed. There have been many reports on liquid crystals which contain a perfluorinated phenyl ring [13–24]. These materials have high $\mathbf{P}_s$ values [22–24] and low phase transition temperatures [20]; or else they favour the smectic C phase [19, 21], and thus have potential application in message transportation and image display.

In order to produce new materials with better physical properties, we have designed and synthesized many new fluorinated liquid crystals. In previous work, we synthesized a type of novel fluorinated liquid crystals having the following chemical formula:



A

These compounds are nematic liquid crystals; because of the rigidity of the acetylenic bond, they have high clearing points. The acetylenic bond has an important effect on the mesogenic properties of liquid crystals, but it is not easy to introduce it into molecules. In order to study the influence of the acetylenic bond, in this paper we now report a family of equivalent LC compounds containing no acetylenic linkage. The formula of these new compounds is given below:



B

2. Experimental

2.1. *Synthesis*

The 4-methoxyphenyl 4′-alkoxy-2′,3′,5′,6′-tetrafluorobiphenyl-1-carboxylates (compounds **B**) were prepared according to the scheme. In the first step, *p*-tolullithium (which was prepared from 4-bromotoluene) reacted with hexafluorobenzene to yield 4-pentafluorophenyl toluene

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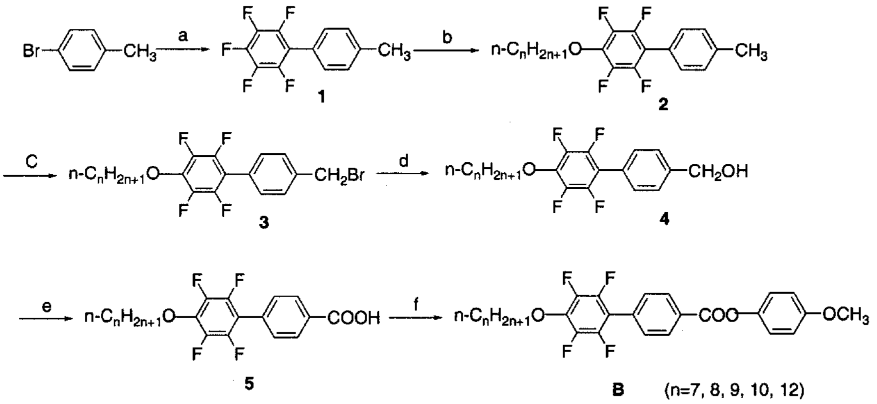

Conditions and reagents. a: 1 Li/Et_2O 2 C_6F_6/Et_2O. b: $n\text{-}C_nH_{2n+1}OH$/THF, NaOH, 35–40°C. c: AIBN, NBS, CCL_4, reflux. d: $CaCO_3/H_2O$, THF, reflux. e: $KMnO_4/Na_2CO_3$, H_2O, 1,4-dioxan, reflux. f: *p*-hydroxyanisole, DCCI/DMAP, THF.

Scheme. Preparation of compounds **B**.

(**1**). The nucleophilic substitution reaction between compound **1** and an alkanol in THF with NaOH as base gave compound **2**, which was then brominated using NBS and AIBN in anhydrous carbon tetrachloride to produce compound **3**. The 4′-*n*-alkoxyl-2′,3′,5′,6′-tetrafluorobiphenyl-1-methanol (**4**) was then prepared through the hydrolysis of compound **3**. The oxidation of compound **4** with potassium permanganate gave compound **5**, and finally ester **B** was obtained from the esterification reaction between compound **5** and *p*-hydroxyanisole with DCCI and DMAP.

The preparation of the intermediates 1, 2, 3, 5 followed literature procedures [25]. Details of the preparations of compounds **4** and **B** are given below.

2.1.1. *4′-n-Heptyloxy-2′,3′,5′,6′-tetrafluorobiphenyl-1-methanol (**4a**)*

In a 25 ml round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser, were put 3.625 g (8.37 mmol) of compound **3a**, 4.18 g (41.86 mmol) of calcium carbonate, 25 ml of water and 25 ml of 1,4-dioxan. The stirred reaction mixture was heated under reflux for 12 h (TLC analysis revealed complete reaction). After cooling to room temperature, the mixture was poured into 200 ml of 10N HCl, and then extracted with ether (3 × 50 ml). The combined ethereal extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed in vacuum and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C) ethyl acetate (1/1) as eluent to give a white solid **4a** with 407 mg of compound **3a** recovered; yield 2.17 g (78.9%). ^1H NMR: δ_H (90 MHz; CCl_4; TMS); 0.8 (t, 3H, $J = 7.2$ Hz, CH_3), 1.0–1.9 (m, 10H), 2.1 (s, 1H, OH), 4.05 (t, 2H, $J = 7.0$ Hz, OCH_2), 4.45 (s, 2H, CH_2OH), 7.20 (m, 4H, Harom). ^{19}F NMR: δ_F (60 MHz, CCl_4; TFA): 67.5 (m, 2F, Farom), 79.5 (m, 2F, Farom).

Compounds **4b**–**4e** were prepared by the same method and had satisfactory ^1H and ^{19}F NMR spectra.

2.1.2. *4-Methoxyphenyl 4′-n-heptyloxy-2′,3′,5′,6′-tetrafluorobiphenyl-1-carboxylate (B_1)*

In a dry 25 ml round-bottomed flask were put 126 mg (0.328 mmol) of compound **5a**, 43 mg (0.346 mmol) of *p*-hydroxyanisole, 70 mg (0.34 mmol) of *N*,*N*-dicyclohexylcarbodiimide (DCCI), 3 mg (0.025 mmol) of 4-dimethylaminopyridine (DMAP) and 10 ml of dried THF. The reaction mixture was protected from air and stirred at room temperature for 80 h. Analysis by TLC revealed a complete reaction. Then the white precipitate formed was filtered off and the filtrate washed with water. Then the solvent was then removed, and the residue purified by column chromatography on silica gel using a mixture of light petroleum (b.p. 60–90°C)/ethyl acetate (10/1) as eluent to give a yellow solid; this was recrystallized from acetone/methanol to yield white crystals of compound **B₁**; yield 139 mg (86.5%). ^1H NMR: δ_H (90 MHz; CCl_4; TMS): 0.95 (t, 3H, $J = 7.2$ Hz, CH_3), 1.15–1.9 (m, 10H), 3.80 (s, OCH_3), 4.15 (t, 2H, $J = 7.0$ Hz, OCH_2), 6.80 (d, 2H)/7.05 (d, 2H) (AA′BB′, $J = 8.5$ Hz, $-C_6H_4-$), 7.50 (d, 2H)/8.25 (d, 2H) (AA′BB′, $J = 8.5$ Hz, $-C_6F_4-C_6H_4-$). ^{19}F NMR: δ_F (60 MHz; CCl_4; TFA): 67.0 (m, 2F, Farom), 79.0 (m, 2F, Farom). IR (KBr) ν/cm^{-1}: 2980, 2854.6, 1734.0, 1653.0, 1610, 1596, 1500, 1483, 1398.4, 1271.1, 1247.9, 1192.0, 1176.6, 1093.6, 1022.3, 993.3, 852.9, 756.1. MS (*m/z*, %): 490 (M^+, 4.88). Elemental analysis: found C 65.85, H 5.31, F 12.56; calc. for $C_{27}H_{26}F_4O_4$ C 66.12, H 5.31 F 12.56%.

Compounds **B2**–**B5** were prepared in a similar way. All had satisfactory elemental analyses and appropriate ^1H and ^{19}F NMR, IR and MS spectra.

2.2. *Characterization*

The final products were rigorously purified by flash chromatography over silica gel (200–400 mesh) using light petroleum (b.p. 60–90°C)/ethyl acetate (10/1) as the eluent to give pale yellow solids which showed a single spot in thin-layer chromatography. The products were recrystallized from methanol to yield white crystals.

The chemical structures of the intermediates and the final products were elucidated by IR spectroscopy (Shimadzu IR-440 spectrometer), ^1H NMR spectroscopy (Varian EM 390 and Varian EM 360 spectrometers) with TMS as internal standard, ^{19}F NMR spectroscopy (Varian EM 360 spectrometer) with trifluoroacetic acid as external standard, and mass spectrometry (HP 5989 A spectrometer). The spectroscopic data were consistent with the predicted structures.

The transition temperatures and phase assignments for the final products were determined using an Olympus BH2 polarizing microscope in conjunction with a Mettler FP 52 hot stage and FP 5 control unit, while the observed textures were compared with those reported in the literature [26] to identify the mesomorphic phases. The transition enthalpies were investigated by DSC using a Shimadzu DSC 50 calorimeter with a heating rate of 5°C min^{-1}.

3. Results and discussion

3.1. *Optical microscopy*

The liquid crystal transition temperatures obtained by polarizing microscopy for compounds **B** and **A** are listed in tables 1 and 2, respectively. All of these compounds exhibit only an enantiotropic nematic (N) phase, which is very important for STN and TN displays. They are of potential use as new STN and TN liquid crystalline materials.

As far as the influence of the alkoxy chain length is concerned (see table 1), with increasing *n*, the melting points and the clearing points for the homologous series of compounds **B** have a slight decreasing trend. Also, the clearing points vary with an odd–even rule; but this is not very apparent perhaps because the number of compounds **B** is not large enough.

The linking bridge has a great effect on the mesomorphic properties of liquid crystals. Comparing table 1 with table 2, we can see that compounds **B**, which do not contain an acetylenic bond, have lower clearing points and a smaller transition temperature range. However, compounds **A** have a more stable mesophase, due to the larger conjugation, longer molecular length and higher polarizability of their molecules.

Table 1. Transition temperatures (°C) by polarizing microscopy for compounds **B**. Cr = crystal, N = nematic phase, I = isotropic phase.

Compound	*n*	Cr–N	N–I	I–N	N–Cr
B1	7	115.1	133.0	132.0	98.8
B2	8	109.9	135.2	134.4	91.0
B3	9	105.9	128.4	127.4	92.3
B4	10	99.9	127.3	125.8	89.0
B5	12	99.3	118.4	117.3	83.8

Table 2. Transition temperatures (°C) by polarizing microscopy for compounds **A**. Cr = crystal, N = nematic phase, I = isotropic phase.

Compound	*m*	Cr–N	N–I	I–N	N–Cr
A1	7	114.0	189.8	189.3	69.8
A2	8	100.4	184.4	184.1	58.2

3.2. *DSC studies*

The phase transitions were also investigated by DSC. The mesomorphic transition enthalpies for compounds **B** are shown in table 3. The average value of the melting enthalpies of compounds **B** is 70.27 J g^{-1}. The nematic-to-isotropic transition enthalpies are relatively small: 0.22–1.08 J g^{-1}.

Table 3. Transition temperatures (°C) and enthalipes (J g^{-1}) by DSC for compounds **B**. Cr = crystal, N = nematic phase, I = isotropic phase.

Compound	*n*	Cr–N	N–I	I–N	N–Cr
B1	7	117.8 (−67.84)	135.1 (−0.22)	134.4 (0.24)	104.6 (69.36)
B2	8	118.8 (−80.48)	137.0 (−0.91)	135.0 (1.61)	95.4 (78.51)
B3	9	108.2 (−55.31)	130.0 (−0.96)	128.7 (1.08)	97.0 (55.10)
B4	10	101.3 (−60.56)	128.7 (−1.08)	127.5 (1.33)	91.1 (58.94)
B5	12	102.5 (−87.18)	119.8 (−0.68)	118.1 (0.95)	93.7 (85.61)

4. Conclusion

A new type of liquid crystal, containing a central perfluorinated phenylene ring in the aromatic core system, were synthesized and their mesomorphic properties studied. It was found that the removal of the acetylenic bond from liquid crystalline molecules reduces the thermal stability of their nematic phase. The homologous series of compounds **B** possess relatively lower clearing points and the narrower nematic temperature ranges.

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