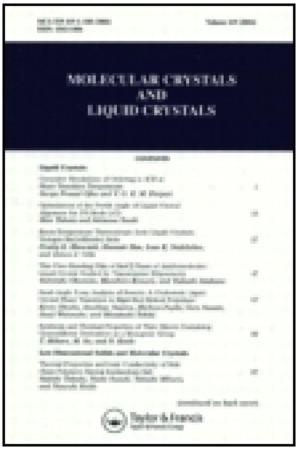

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Novel Fluorinated Liquid Crystals. Part VIII. The Synthesis and Mesomorphic Properties of 4“-n-Alkoxyphenyl 4”-[(4-n-Alkoxy-2, 3, 5, 6-tetrafluorophenyl)ethynyl]benzoates

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Novel Fluorinated Liquid Crystals. Part VIII. The Synthesis and Mesomorphic Properties of 4′-*n*-Alkoxyphenyl 4″-[(4-*n*-Alkoxy-2, 3, 5, 6-tetrafluorophenyl)ethynyl]benzoates

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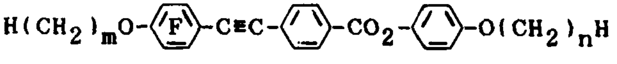
Eighteen members of 4′-*n*-alkoxyphenyl 4″-[(4-*n*-alkoxy-2, 3, 5, 6-tetrafluorophenyl) ethynyl] benzoates have been synthesized. Polarizing microscopic textural observation shows that they exhibit enantiotropic nematic phase and smetic C phase.

Keywords: Liquid crystal, 1, 4-tetrafluorophenylene, synthesis, mesomorphic behaviour.

INTRODUCTION

Fluorinated liquid crystals are of tremendous interest because the replacement of fluorine for hydrogen in liquid crystal systems has a dramatic effect on mesomorphic behaviors and other physical properties. The following examples illustrate the valuable effects which appropriate fluoro-substitution is able to achieve: (a) the tendency of the fluorine substituent to transform Smectic A (S_A) into Smectic C (S_C) mesophases;[1-2] (b) suppress and eliminate more ordered smectic mesophases; (c) influence the dielectric anisotrophy,[1-3] viscosity, birefringence and the melting point. So a large number of mono-fluoro, di-fluoro or tri-fluoro-substituted liquid crystalline compounds[1-7] have been prepared. However, only a few liquid crystal materials containing symmetrically tetrafluorinated phenyl units[8-15] have been reported. We recently described the synthesis and mesomorphic behavior of some series of liquid crystals with 2, 3, 5, 6-tetrafluoro-1, 4-phenylene moiety in the core structures.[16-22]

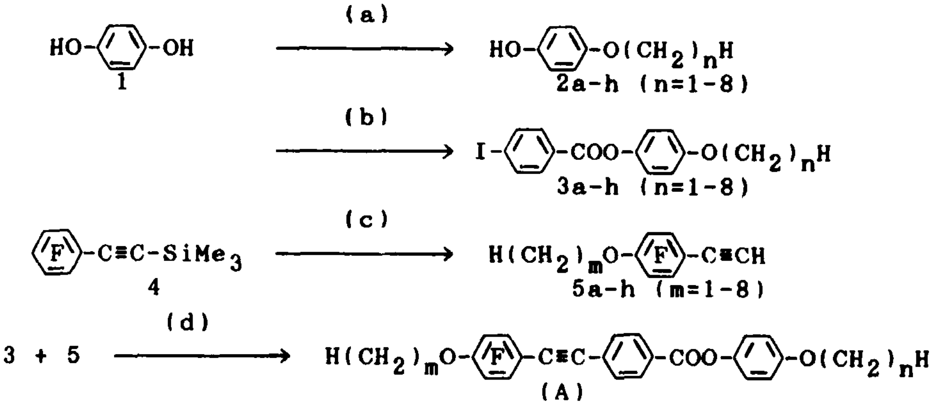
In this paper, we wish to report the synthesis and mesomorphic behavior of 4′-*n*-alkoxyphenyl 4″-[(4-*n*-alkoxy-2, 3, 5, 6-tetrafluorophenyl)ethynyl]benzoates (A).



(A)

SYNTHESIS

Compounds (A) were prepared via the following scheme:



SCHEME Reagents: (a) NaOH, $H(CH_2)_nBr$, CH_3OH. (b) $I\text{-}C_6H_4\text{-}COOH$, $SOCl_2$, toluene, pyridine, reflux; (c) K_2CO_3· DMF,$H(CH_2)_mOH$, R.T.; (d) CuI, Et_3N, $(Ph_3P)_2PdCl_2$, reflux.

The preparation of the required mesogens was based on a palladium catalyzed coupling reaction involving polyfluorophenylacetylene and an appropriate aryl iodide (see scheme). In the first step, *p*-alkoxyphenols (2*a*-*h*) except for *p*-methoxyphenol, were prepared from a Williamson type alkylation[23] of hydroquinone. The compounds 3*a*-*h* were synthesized from an esterification reaction between 4-iodobenzoic acid and compound 2 with thionyl chloride as acylating promote in anhydrous toluene and pyridine. In our previous study,[24] we have reported the synthesis of 1-pentafluorophenyl-2-trimethylsilylacetylene by a palladium-catalyzed coupling reaction between 1-pentafluoriodobenzene and trimethylsilylacetylene. Then the 4-*n*-alkoxy-2,3,5,6-tetrafluorophenylacetylene was easily obtained by the nucleophilic substitution[25] of *n*-alkyl alcohol on compound 4 at room temperature using K_2CO_3 as base. Finally the coupling reaction between compounds 3 and 5 under the catalysis of bis(triphenylphosphine) palladium dichloride and copper (I) iodide in dried triethylamine gave the desired polyfluoro-substituted homologous compounds.

All of the final compounds were purified by chromatography on silica gel with petroleum ether (bp 60–90°C)/ethyl acetate (20:1) as eluent and were recrystallized from acetone-methanol. Their structures were identified by elemental analyses, MS, IR spectra and ^1H, ^{19}F NMR spectra. The transition temperatures were studied using a Mettler FP52 hot stage and FP5 control unit in conjunction with an Olympus BH2 polarizing microscope and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7 system and data station), while phase identification was determined by comparing the observed textures with those in the literature.[26,27]

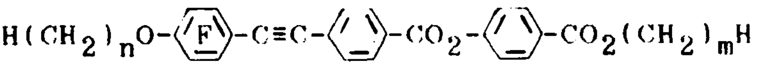
RESULTS AND DISCUSSION

The transition temperatures of these new flourinated materials are summarized in Table 1.

The lower members preferably exhibit nematic behavior, and the higher homologues posses additional smectic phase of the type C. The smectic C phase (S_C) exhibited the Schlieren textures.[28] When the terminal group on the hydrogen phenyl ring is fixed as methoxyl, all of the new fluorinated compounds exhibit enantiotropic nematic phase and the melting points and clearing points of the homologous compounds drop with increasing alkoxy chain length. However, when the terminal groups on the fluorophenyl ring is fixed as normal octyloxy, the compounds for $n = 4, 6, 7$ and 8 exhibhit enantiotropic nematic and smectic C phases and the other members show only a nematic phase, and the transition temperatures are irregular. The fluorinated materials have a wide temperature range of mesophase and its tendency to exhibit smectic C properties increases as the terminal chain grows longer.

There is the possibility of comparing the behavior of some isometric compounds. The clearing temperatures are different if the two alkyl chain length m and n are similar (e.g. 5/8 and 8/5, 6/8 and 8/6). With the same chain length the group m causes a larger tendency to exhibit higher clearing temperatures than n. If we compare the influence of m and n on the temperatures $T_{Sc/N}$, the enhancement of $T_{Sc/N}$ by m is still more pronounced (e.. 6/8 and 8/6, 7/8 and 8/7).

In our previous studies,[22] we reported a new family of fluorinated liquid crystals with following structure:



(B)

($n = 1$–7, $m = 5$; $n = 8$, $m = 1$–6)

These compounds mostly exhibit enantiotropic smectic A and nematic phases except for $n = 1, m = 5$. From comparison between the transition temperatures for compounds *A* and *B*, we note that a compound of series *A* tends to have a higher melting point and clearing point than one of series *B* with the same terminal *n*-alkoxy chain. Besides, smectic C phase is observed in compounds A, whereas smectic A phase is observed in compounds B. 4′-*n*-Alkoxyphenyl 4″-[(4-*n*-alkoxy-2, 3, 5, 6-tetrafluorophenyl) ethynyl] benzoates (A) favor smectic C properties. Typically, as m and n increase in value (to $m = 8$, $n = 4$) smectic properties are injected into the homologous series. The diester configuration favors smectic A phase more strongly.

EXPERIMENTAL

IR spectra were recorded on a Shimadzu IR-440 spectrometer. ^{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 spectrometer (60 MHz) or FX-90Q spectrometer (90 MHz). For ^{19}F NMR spectra, high field is positive. Mass spectra were measured on a Finnigan-4021 spectrometer.

TABLE I

Transition temperatures (°C) of the compounds (*A*)

m	*n*	C—S_C	S_C—N	N—I	Recryst
1	1	147.2		238.7	109.6
2	1	111.6		240.1	67.8
3	1	110.4		226.9	64.1
4	1	114.4		220.8	70.8
5	1	116.4		206.9	70.4
6	1	116.1		200.2	66.4
7	1	114.0		189.8	69.8
8	1	100.4		184.4	58.2
5	8	98.5		164.0	83.3
6	8	92.5	(92.4)	170.1	67.1
7	8	84.6	98.9	163.1	65.9
8	2	107.1		191.6	83.6
8	3	93.7		176.0	78.5
8	4	94.4	96.3	167.5	75.0
8	5	91.4		164.6	76.4
8	6	92.7	96.7	181.0	70.2
8	7	89.4	105.0	165.1	70.7
8	8	81.0	108.8	162.2	66.6

C, crystal; N, nematic phase; I, isotropic phase.

1. 4-Methoxyphenyl 4′-Iodobenzoate

In a 50 ml round-bottom three-necked flask equipped with a magnetic stirring bar, thionyl chloride (8 ml, 13.2 g, 0.112 mol) was added slowly, dropwise to a stirred cooled mixture of 4-iodobenzoic acid (4.0 g, 16.13 mmol) and 10 ml toluene, over a period of 5 min. Then the reaction mixture was allowed to warm to room temperature, stirred at 110°C for 7 hr. The solution was removed by vacuum distillation. Then the residue was dissolved in 15 ml toluene and 5 ml pyridine, and *p*-methoxyphenol (2.0 g, 16.1 mmol) was added in the mixture. The reaction mixture was boiled with stirring for 7 hr. TLC analysis denoted completion of reaction. Then the precipitate was filtered off and washed with ether and the filterate washed with water, and dried over anhydrous sodium sulphate. The solvent was removed in vacum and the residue was recrystallized from acetone-methonol to give a white crystal of (3a).

Yield 4.22 g(74.6%). ^{1}H NMR(CCl_4/TMS): 3.90 (*s*, 3H, CH_3), 7.00 (*d*, 2H)/7.25(*d*, 2H) (AA'BB', $J = 8.4$ Hz, COO-C_6H_4-O), 7.97(*s*, 4H, I-C_6H_4COO).

Compounds 3*b*–h were prepared similarly. All of them had appropriate ^{1}H NMR spectral data.

2. 4′-Methoxyphenyl 4″-[(4-*n*-Octyloxy-2,3,5,6-tetrafluorophenyl) ethynyl] benzoate

Typical procedure: In a 50 ml round-bottom three-necked flask equipped with a magnetic stirring bar, a nitrogen inlet and a bubbler, were placed (3a) (318 mg, 1.05 mmol), 4-octyloxy-2, 3, 5, 6-tetrafluorophenylacetylene (355 mg, 1 mmol), bis(triphenyl phosphine) palladiumudichloride (35 mg, 0.05 mmol) and copper (I) iodide (17 mg, 0.089 mmol). The reaction system was filled with dry nitrogen, and 10 mL of anhydrous triethylamine was added to the reaction mixture under nitrogen. The resulting mixture was stirred under reflux for 2 hr, and brown precipitate formed. Analysis by TLC revealed a complete reaction. Then the precipitate was filtered off and washed with ether. The filtrate washed with water, dried over anhydrous sodium sulfate. The solvent was removed in vacuum and the residue was purified by column chromatography on silica gel using petroleum ether (bp 60–90°C)/ethyl acetate (20:1) as eluent to give a pale yellow crystal which was recrystallized from acetone-methanol to yield white flaky crystals. Yield 0.370 g (70.0%).

mp 100.4°C. Anal. Calcd: C, 68.17; H, 5.34; F, 14.38. Found: C, 68.17; H, 5.30; F, 14.42. γ_{max} (KBr): 2940(s,C–H), 1730(vs, $C = O$), 1605(S, C_6H_4), 1486(vs, C_6F_4), 1260, 1190, 1125 (s,C–O–C) cm^{-1}. $\delta_H(CDC1_3)$: 0.92(sH, *t*, $J = 5.OHz$); 1.10–2.05(12H, *m*); 3.85(3H, *s*, CH_3); 4.33(2H, *t*, $J = 6.0$ Hz, OCH_2), 6.95(2H, *d*)/7.20(2H, *d*) (AA'BB', $J = 8.1$ Hz, C_6H_4); 7.71(2H, *d*)/8.24(2H, *d*) (AA'BB', $J = 8.1$ Hz, C_6H_4) ppm. $\delta_F(CDC1_3)$: 60.16(2F, *m*); 79.70(2F, *m*). ppm. m/z(%): 528(M^+, 4.69), 405(100), 293(32.06).

The other compounds (*A*) have been prepared following the same general procedure. All of them had satisfactory elementary analyses and appropriate ^1H and ^{19}F NMR, IR and MS spectral data.

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