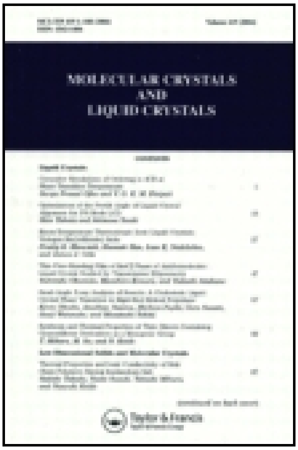


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Novel Fluorinated Liquid Crystals. Part IV. The Synthesis and Phase Transition of 4′-(n-Alkoxycarbonyl)phenyl 4″-[(4-(s)-2′ Methylbutoxy-2,3,5,6-tetrafluorophenyl)ethynyl benzoates

Yuelian Xu [a], Qi Chen [a] & Jianxun Wen [a]
[a] Shanghai Institute of Organic Chemistry, Academia Sinica, 345# Lingling Lu, Shanghai, 200032, China

To cite this article: Yuelian Xu , Qi Chen & Jianxun Wen (1994): Novel Fluorinated Liquid Crystals. Part IV. The Synthesis and Phase Transition of 4′-(n-Alkoxycarbonyl)phenyl 4″-[(4-(s)-2′ Methylbutoxy-2,3,5,6-tetrafluorophenyl)ethynyl benzoates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 241:1, 243-248

To link to this article: http://dx.doi.org/10.1080/10587259408029761

Mol. Cryst. Liq. Cryst., 1994, Vol. 241, pp. 243–248
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Novel Fluorinated Liquid Crystals. Part IV. The Synthesis and Phase Transition of 4′-(*n*-Alkoxycarbonyl)phenyl 4″-[(4-(*s*)-2′-Methylbutoxy-2,3,5,6-tetrafluorophenyl)ethynyl] benzoates

YUELIAN XU, QI CHEN and JIANXUN WEN†
Shanghai Institute of Organic Chemistry, Academia Sinica, 345# Lingling Lu, Shanghai 200032, China

(Received April 8, 1993; in final form June 7, 1993)

A series of 4′-(*n*-alkoxycarbonyl)phenyl 4″-[(4-(*s*)-2′-methylbutoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoates have been prepared. Polarizing microscopic textural observation shows that they are liquid crystals with chiral smectic C phase.

Keywords: 1,4-Tetrafluorophenylene, synthesis, chiral smectic C phase

INTRODUCTION

Meyer *et al.*[1] showed in 1975 that the chiral smectic C phase exhibited ferroelectric properties. Since Clark and Lagerwall[2] reported the electrooptical properties (fast switching and bistability) of a ferroelectric chiral smectic C liquid crystal, there has been considerable interest in the synthesis of new chiral smectic C materials and studies of display devices based on ferroelectrics. The ferroelectric liquid crystals may be ideally suited for large area matrix display devices capable of operating at very fast frame rates.

In recent years, the great scientific and practical interest in liquid crystals has generated an increasing requirement for compounds with specific properties. The fluorine atom combines the properties of large electronegativity with small size so that it significantly affects the physical properties of molecules without eliminating the possibility of mesophase formation. So more and more mono-fluoro, di-fluoro and tri-fluoro-substituted liquid crystalline compounds[3–9] have been synthesized. Nevertheless, little work on liquid crystalline compounds containing polyfluorophenyl[10,11] has been reported. We aim to synthesize new liquid crystals with 2,3,5,6-tetrafluoro-1,4-phenylene in the core structures to research new materials for display devices and other applications.[12] In a previous paper,[13] we have reported 4′-[(*s*)-2-methylbutoxyl]phenyl 4″-[(4-*n*-alkoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoates (7) as new materials exhibiting ferroelectric behavior. In this paper, we wish to report the synthesis of additional chiral compounds and their transition temperatures.

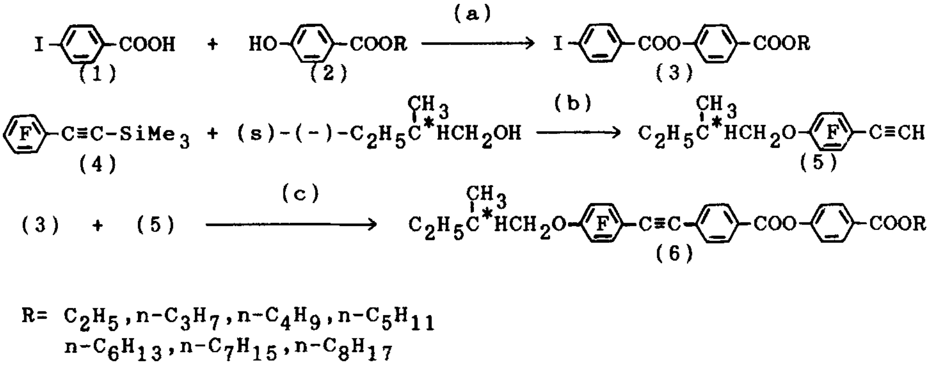
SYNTHESIS

The 4′-(*n*-alkoxycarbonyl)phenyl 4″-[(4-(*s*)-2′-methylbutoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoates (6) were synthesized by the route shown in the scheme. Compound (3) was obtained from the mild one pot esterification[14] between 4-hydroxybenzoic acid ester and 4-iodobenzoic acid in presence of both dicyclohexylcarbondiimide (DCCI) and 4-pyrrolidinopyridine (PPY) catalyst in anhydrous ether. Compound (4) was prepared as described in a previous publication.[15] 4-[(*s*)-2′-Methylbutoxy-2,3,5,6-tetrafluorophenyl]acetylene (5) was obtained from compound (4) by nucleophilic substitution of (*s*)-2-methyl-1-butanol at room temperature using K_2CO_3 as the base.[16] Finally the coupling reaction[17] between compound (3) and (5) under the catalysis of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in anhydrous triethylamine gave the desired products (6).

RESULTS AND DISCUSSION

Measurements of the transition temperatures and assignment of the mesophases were carried out by a micro melting point apparatus equipped with polarizers and were determined by DSC. Phase identification was made by comparing the observed textures with those in the literature.[18,19] All compounds exhibited mesophases. Phase transition temperatures for compounds (6) and the corresponding compounds (7) are given in the Table I.

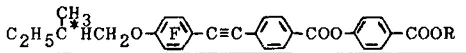
Compounds (6) have chemical structures in which two terminal substituents of compounds (7) are exchanged. The major difference between the chemical structures of compounds (6) and (7) is that the alkoxy group is conjugated with the



SCHEME I (a) DCCI, PPY, Et_2O, R.T.; (b) K_2CO_3, DMF; (c) CuI, Et_3N, $[(C_6H_5)_3P]_2PdCl_2$, reflux.

TABLE I

Phase transition temperatures (°C) of compounds 6 and 7



$C_2H_5\overset{CH_3}{\overset{|}{C^*}}HCH_2O-C_6F_4-C{\equiv}C-C_6H_4-COO-C_6H_4-COOR$ (6)

	R	Phase transition temperatures (°C)^a
6-1	C_2H_5	$C \underset{92.8}{\overset{107.1}{\rightleftarrows}} S_{C*} \underset{130.5}{\overset{132.9}{\rightleftarrows}} Ch \underset{171.4}{\overset{171.8}{\rightleftarrows}} I$
6-2	$n\text{-}C_3H_7$	$C \underset{88.7}{\overset{104.1}{\rightleftarrows}} S_{C*} \underset{130.9}{\overset{133.5}{\rightleftarrows}} Ch \underset{161.6}{\overset{161.6}{\rightleftarrows}} I$
6-3	$n\text{-}C_4H_9$	$C \underset{94.4}{\overset{105.8}{\rightleftarrows}} S_{C*} \underset{122.3}{\overset{122.0}{\rightleftarrows}} Ch \underset{138.6}{\overset{138.6}{\rightleftarrows}} I$
6-4	$n\text{-}C_5H_{11}$	$C \underset{84.9}{\overset{103.6}{\rightleftarrows}} S_{C*} \underset{126.1}{\overset{127.5}{\rightleftarrows}} Ch \underset{141.4}{\overset{141.4}{\rightleftarrows}} I$
6-5	$n\text{-}C_6H_{13}$	$C \underset{76.4}{\overset{93.9}{\rightleftarrows}} S_{C*} \underset{123.3}{\overset{122.2}{\rightleftarrows}} Ch \underset{132.4}{\overset{132.4}{\rightleftarrows}} I$
6-6	$n\text{-}C_7H_{15}$	$C \underset{71.8}{\overset{85.4}{\rightleftarrows}} S_{C*} \underset{124.6}{\overset{125.2}{\rightleftarrows}} Ch \underset{132.7}{\overset{133.5}{\rightleftarrows}} I$
6-7	$n\text{-}C_8H_{17}$	$C \underset{67.1}{\overset{84.3}{\rightleftarrows}} S_{C*} \underset{108.1}{\overset{110.5}{\rightleftarrows}} Ch \underset{118.4}{\overset{118.6}{\rightleftarrows}} I$

carbonyl group in compounds (7), but not in compounds (6). Compounds (6) show enantiotropic S_{C*} phase and Ch phase. Compounds (7) show monotropic S_{C*} phase when the length of the alkoxy chain is short. When the length of the alkoxy chain increases, compounds (7) show enantiotropic S_{C*} phase, but the S_{C*} range is short. Compounds (7) exhibit S_A phases, which do not occur in compounds (6). The transition temperatures to the isotropic state for compounds (6) are lower than those for the corresponding compounds (7).

EXPERIMENTAL

IR spectra were determined with a Shimadzu IR-440 spectrometer. ^{1}H-NMR spectra were run on a FX-90Q (90 MHz) spectrometer. ^{19}F-NMR were recorded on a Varian EM 360L (60 MHz) spectrometer (high field is positive). MS spectra were measured with a Finnigan-4021 spectrometer. The transition temperatures were obtained using a Mettler FP-52 hot-stage and FP-5 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).

4-[(s)-2′-Methylbutoxy-2,3,5,6-tetrafluorophenyl]acetylene (5)

1-Pentafluorophenyl-2-trimethylsilylacetylene 4 (5.13 g, 20 mmol), potassium carbonate (3.4 g, 24 mmol), (*s*)-(−)-2-methyl-1-butanol (2.72 g, 30 mmol), DMF (20 mL) and a reaction time of 30 hr at room temperature. The experimental procedure was the same as described in a previous publication.[16] Analysis using ^{19}F NMR revealed a complete reaction. The crude product was purified by column chro-

TABLE I (*Continued*)

(7)

	R	Phase transition temperatures (°C)^a
7-1	C_2H_5	$C \xrightarrow{95.4} S_A \underset{109.6}{\overset{110.3}{\rightleftharpoons}} Ch \underset{174.2}{\overset{174.7}{\rightleftharpoons}} I$ $S_A \xrightarrow{95.1} S_{C*} \xrightarrow{58.8} C$
7-2	$n\text{-}C_3H_7$	$C \xrightarrow{93.6} S_A \underset{117.2}{\overset{118.0}{\rightleftharpoons}} Ch \underset{164.1}{\overset{164.4}{\rightleftharpoons}} I$ $S_A \xrightarrow{93.4} S_{C*} \xrightarrow{62.2} C$
7-3	$n\text{-}C_4H_9$	$C \underset{73.7}{\overset{90.4}{\rightleftharpoons}} S_{C*} \underset{90.6}{\overset{90.8}{\rightleftharpoons}} S_A \underset{135.7}{\overset{136.0}{\rightleftharpoons}} Ch \underset{168.8}{\overset{169.2}{\rightleftharpoons}} I$
7-4	$n\text{-}C_5H_{11}$	$C \underset{70.6}{\overset{89.5}{\rightleftharpoons}} S_{C*} \underset{89.7}{\overset{90.0}{\rightleftharpoons}} S_A \underset{124.2}{\overset{124.7}{\rightleftharpoons}} Ch \underset{152.9}{\overset{153.1}{\rightleftharpoons}} I$
7-5	$n\text{-}C_6H_{13}$	$C \underset{70.3}{\overset{88.8}{\rightleftharpoons}} S_{C*} \underset{89.5}{\overset{89.8}{\rightleftharpoons}} S_A \underset{132.4}{\overset{132.8}{\rightleftharpoons}} Ch \underset{154.5}{\overset{154.7}{\rightleftharpoons}} I$
7-6	$n\text{-}C_7H_{15}$	$C \underset{61.6}{\overset{77.8}{\rightleftharpoons}} S_{C*} \underset{78.0}{\overset{78.6}{\rightleftharpoons}} S_A \underset{129.0}{\overset{129.6}{\rightleftharpoons}} Ch \underset{147.2}{\overset{147.5}{\rightleftharpoons}} I$
7-7	$n\text{-}C_8H_{17}$	$C \underset{58.8}{\overset{75.4}{\rightleftharpoons}} S_{C*} \underset{77.2}{\overset{77.7}{\rightleftharpoons}} S_A \underset{129.1}{\overset{129.4}{\rightleftharpoons}} Ch \underset{144.4}{\overset{144.8}{\rightleftharpoons}} I$

matography on silica gel with petroleum ether (bp 60–90°C) as the eluent to yield a pale yellow liquid. Yield 3.38 g (76.5%); ^{1}H NMR (CCl_4/TMS): δ 0.86–2.16 (m, 9H, alkyl), 3.63 (s, 1H, C≡CH), 4.31 (d, 2H, J = 6.0 Hz, OCH_2); ^{19}F NMR (CCl_4/TFA): δ 60.5 (m, 2F, Farom), 80.3 (m, 2F, Farom).

4′-(*n*-Ethoxycarbonyl)phenyl 4″-[(4-(s)-2′-methylbutoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate (6-1)

To a stirred mixture of 4-[(*s*)-2′-methylbutoxy-2,3,5,6-tetrafluorophenyl]acetylene 5 (260 mg, 1 mmol), 4-(ethoxycarbonyl)phenyl 4′-iodobenzoate 3 (0.396 g, 1 mmol), bis(triphenylphosphine)-palladium dichloride (40 mg, 0.057 mmol) and copper(I) iodide (22 mg, 0.116 mmol) under dry nitrogen, was added 20 mL of anhydrous triethylamine. The resulting mixture was refluxed for 2 hr. TLC analysis revealed a complete reaction. Then the resulting precipitate was removed by filtration, washed with ether and the filtrate washed with water, dried over anhydrous sodium sulfate and the solvent rotovaped. The residue was purified by column chromatography on silica gel using petroleum ether (bp 60–90°C)/ethyl acetate (20:1) as the eluent to yield a pale yellow crystal. Recrystallization from acetone-methanol gave white flaky crystals of the acetylene ester 6-1: Yield 380 mg (69.0%); m.p. 107.1°C; ^{1}H NMR ($CDCl_3$/TMS): δ 0.80–1.60 (m, 12H, alkyl), 4.10 (d, 2H, J = 5.4 Hz, OCH_2), 4.38 (q, 2H, J = 5.4 Hz, $COOCH_2$), 7.28 (d, 2H, ArH ortho to

OCOAr)/8.10 (d, 2H, ArH ortho to COOR) (AA'BB', J = 8.0 Hz), 7.68 (d, 2H, ArH ortho to $C\equiv C$)/8.18 (d, 2H, ArH ortho to COOAr) (AA'BB', J = 8.0 Hz); ^{19}FNMR(CDCl$_3$/TFA): δ 60.58 (m, 2F, Farom), 80.33 (m, 2F, Farom); IR (KBr): 3000 (CH), 1760 (COOR), 1732 (COOAr), 1620 (Ar), 1508 (Farom) cm^{-1}; MS (m/z): 528 (M$^+$), 363, 293, 265, 237, 217; Elem. anal., Calcd. for $C_{29}H_{24}F_4O_5$: C 65.62%, H 4.55%, F 14.40%; Found: C 65.45%, H 4.48%, F 14.26%.

This same procedure was used to prepare the other esters 6.

4'-(n-Propoxycarbonyl)phenyl 4"-[(4-(s)-2'-methylbutoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate (6-2). m.p. 104.1°C; ^{1}H NMR (CDCl$_3$/TMS): δ 0.80–1.96 (m, 14H, alkyl), 4.11 (d, 2H, J = 5.4 Hz, OCH$_2$), 4.30 (t, 2H, J = 7.2 Hz, COOCH$_2$), 7.30 (d, 2H, ArH ortho to OCOAr)/8.10 (d, 2H, ArH ortho to COOR) (AA'BB', J = 8.0 Hz), 7.68 (d, 2H, ArH ortho to $C\equiv C$)/8.16 (d, 2H, ArH ortho to COOAr) (AA'BB', J = 8.0 Hz); ^{19}F NMR (CDCl$_3$/TFA): δ 60.58 (m, 2F, Farom), 80.33 (m, 2F, Farom); IR (KBr): 3000 (CH), 1758 (COOR), 1734 (COOAr), 1620 (Ar), 1508 (Farom) cm^{-1}; MS (m/z): 542 (M$^+$), 364, 293, 265, 237, 216; Elem. anal., Calcd. for $C_{30}H_{26}F_4O_5$: C 66.42%, H 4.80%, F 14.02%; Found: C 66.40%, H 4.50%, F 13.98%.

The other esters 6 had the same type of NMR spectrum.

4'-(n-Butoxycarbonyl)phenyl 4"-[(4-(s)-2'-methylbutoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate (6-3). m.p. 105.8°C; (KBr): 3020 (CH), 1760 (COOR), 1736 (COOAr), 1624 (Ar), 1508 (Farom) cm^{-1}; MS (m/z): 556 (M$^+$), 363, 293, 265, 237, 217; Elem. anal., Calcd. for $C_{31}H_{28}F_4O_5$: C 66.91%, H 5.04%, F 13.67%; Found: C 66.89%, H 4.75%, F 13.44%.

4'-(n-Pentyloxycarbonyl)phenyl 4"-[(4-(s)-2'-methylbutoxy-2,3,5,6 tetrafluorophenyl)ethynyl]benzoate (6-4). m.p. 103.6°C; IR (KBr): 2990 (CH), 1740 (COOR), 1718 (COOAr), 1608 (Ar), 1510 (Farom) cm^{-1}; MS (m/z): 570 (M$^+$), 363, 293, 265, 237, 217; Elem. anal., Calcd. for $C_{32}H_{30}F_4O_5$: C 67.33%, H 5.26%, F 13.33%, Found: C 67.45%, H 5.50%, F 13.30%.

4'-(n-Hexyloxycarbonyl)phenyl 4"-[(4-(s)-2'-methylbutoxy-2,3,5,6 tetrafluorophenyl)ethynyl]benzoate (6-5). m.p. 93.9°C; IR (KBr): 2990 (CH), 1740 (COOR), 1718 (COOAr), 1608 (Ar), 1490 (Farom) cm^{-1}; MS (m/z): 584 (M$^+$), 364, 293, 265, 237, 217; Elem. anal., Calcd. for $C_{33}H_{32}F_4O_5$: C 67.81%, H 5.48%, F 13.01%; Found: C 67.62%, H 5.31%, F 13.04%.

4'-(n-Heptyloxycarbonyl)phenyl 4"-[(4-(s)-2'-methylbutoxy-2,3,5,6 tetrafluorophenyl)ethynyl]benzoate (6-6). m.p. 85.4°C; IR (KBr): 3020 (CH), 1760 (COOR), 1730 (COOAr), 1624 (Ar), 1510 (Farom) cm^{-1}; MS (m/z): 598 (M$^+$), 363, 293, 265, 237, 217; Elem. anal., Calcd. for $C_{34}H_{34}F_4O_5$: C 68.22%, H 5.69%, F 12.71%; Found: C 68.18%, H 5.91%, F 12.61%.

4'-(n-Octyloxycarbonyl)phenyl 4"-[(4-(s)-2'-methylbutoxy-2,3,5,6 tetrafluorophenyl)ethynyl]benzoate (6-7). m.p. 84.3°C; IR(KBr): 2900 (CH), 1740 (COOR), 1720 (COOAr), 1600 (Ar), 1490 (Farom) cm^{-1}; MS (m/z): 612 (M$^+$), 363, 293, 265, 237, 217; Elem. anal., Calcd. for $C_{35}H_{36}F_4O_5$: C 68.63%, H 5.88%, F 12.41%; Found: C 68.67%, H 6.08%, F 12.09%.

Acknowledgment

The authors gratefully acknowledge for the financial support of the Advanced Materials R&D Program of China.

References

1. R. B. Meyer, L. Liebert, L. Strzelecki and P. Keller, *J. Phys. Lett.*, **36**, L68 (1975).
2. N. A. Clark and S. T. Lagewall, *Appl. Phys. Lett.*, **36**, 899 (1980).
3. G. W. Gray, M. Hird, D. Lacey and K. J. Toyne, *J. Chem. Soc. Perkin Trans.*, **2**, 2041 (1989).
4. G. W. Gray, M. Hird, D. Lacey and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **191**, 1 (1990).
5. V. Reiffenrath, J. Krause, H. J. Plach and G. Weber, *Liquid Crystals*, **5**, 159 (1989).
6. J. E. Fearow, G. W. Gray, A. D. Ifill and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **124**, 169 (1985).
7. L. K. M. Chan, G. W. Gray and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **123**, 185 (1985).
8. L. K. M. Chan, G. W. Gray, D. Lacey and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **150B**, 335 (1987).
9. L. K. M. Chan, G. W. Gray, D. Lacey and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **158B**, 209 (1988).
10. S. Sugawara, Jpn. Kokai Tokkyo Koho, JP 02, 11, 570 (90, 11, 570).
11. T. Hirai, A. Yoshizawa, I. Nishiyama and M. Fukumasa, Jpn. Kokai Tokkyo Koho, JP 02, 331, 431 (90, 311, 431).
12. J. X. Wen, *et al.*, Chinese Patent Application No. 92 1 08444.7.
13. J. X. Wen, M. Q. Tian and Q. Chen, submitted to *Liquid Crystals*, (1993).
14. A. Hassner and V. Alexanian, *Tetrahedron Lett.*, **46**, 4475 (1978).
15. Y. D. Zhang and J. X. Wen, *J. Fluorine Chem.*, **47**, 533 (1990).
16. Y. D. Zhang and J. X. Wen, *J. Fluorine Chem.*, **49**, 293 (1990).
17. Y. D. Zhang and J. X. Wen, *J. Fluorine Chem.*, **52**, 333 (1991).
18. D. Demus and L. Richter, "Textures of Liquid Crystals," Verlag Chemie, Weinheim, 1978.
19. G. W. Gray and J. W. Goodby, "Smectic Liquid Crystals, Textures and Structures," Leonard Hill, 1984.