Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Synthesis and mesomorphic properties of 4-[(4*n*-alkoxy-2,3-difluorophenyl)ethynyl]phenyl fluoro-substituted benzoates

Hengfeng Li[a]; Yonggang Yang[a]; Jianxun Wen[a]
[a] Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, PR China,

To cite this Article Li, Hengfeng , Yang, Yonggang and Wen, Jianxun(2000) 'Synthesis and mesomorphic properties of 4-[(4*n*-alkoxy-2,3-difluorophenyl)ethynyl]phenyl fluoro-substituted benzoates', Liquid Crystals, 27: 11, 1445 — 1449
To link to this Article: DOI: 10.1080/026782900750018591
URL: http://dx.doi.org/10.1080/026782900750018591

LIQUID CRYSTALS, 2000, VOL. 27, NO. 11, 1445–1449

Synthesis and mesomorphic properties of 4-[(4-*n*-alkoxy-2,3-difluorophenyl)ethynyl]phenyl fluoro-substituted benzoates

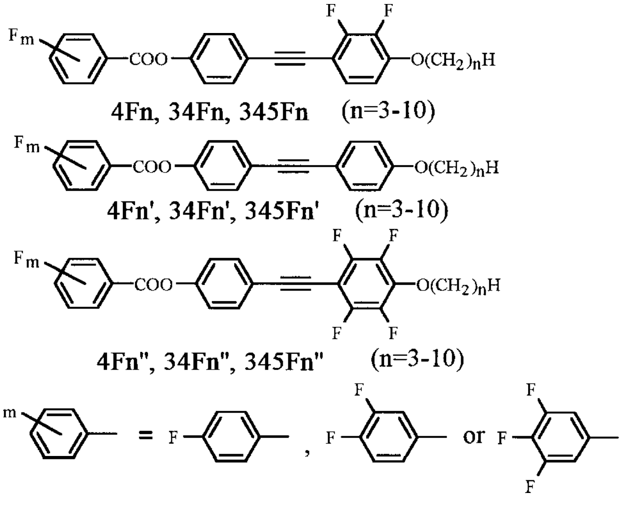
HENGFENG LI, YONGGANG YANG and JIANXUN WEN*
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
Shanghai 200032, PR China

(*Received 11 February 2000; accepted 24 April 2000*)

Three series of novel fluorinated liquid crystals containing a 2,3-difluorotolan unit have been synthesized. Their phase transition temperatures have been measured by texture observation in a polarizing microscope and confirmed by DSC. The influence of the lateral fluoro-substitution is discussed.

1. Introduction

In previous work [1–4], series of liquid crystalline compounds of mono- or poly-fluoro-substituted benzoates containing a tolan or 2,3,5,6-tetrafluorotolan unit have been synthesized, and their mesomorphic properties studied. The lateral fluorine substituent was chosen because of its ability to reduce smectic tendencies and to vary other LC properties, such as viscosity, clearing points, etc. The results showed that the smectic mesophase ranges were much suppressed when using a 2,3,5,6-tetrafluorotolan unit to replace the tolan unit in the mesogenic core. The work of Gray *et al.* [5–7] has shown that the inclusion of a lateral difluorinated phenyl ring into a mesogenic core can produce liquid crystals with negative dielectric anisotropies and biaxialities, and can also lead to the suppression of the more ordered smectic phases and the formation of tilted smectic phases. Recently Reiffenrath has also synthesized many fluoro-substituted tolan-type nematic liquid crystalline materials and used them in supertwisted nematic liquid crystal displays; some good results have been obtained [8, 9]. This paper reports the results on three series liquid crystalline compounds with the 2,3-difluorotolan unit introduced into the core, as shown in scheme 1. The relationships between the molecular structure and the mesomorphic properties are discussed.



Scheme 1.

2. Experimental

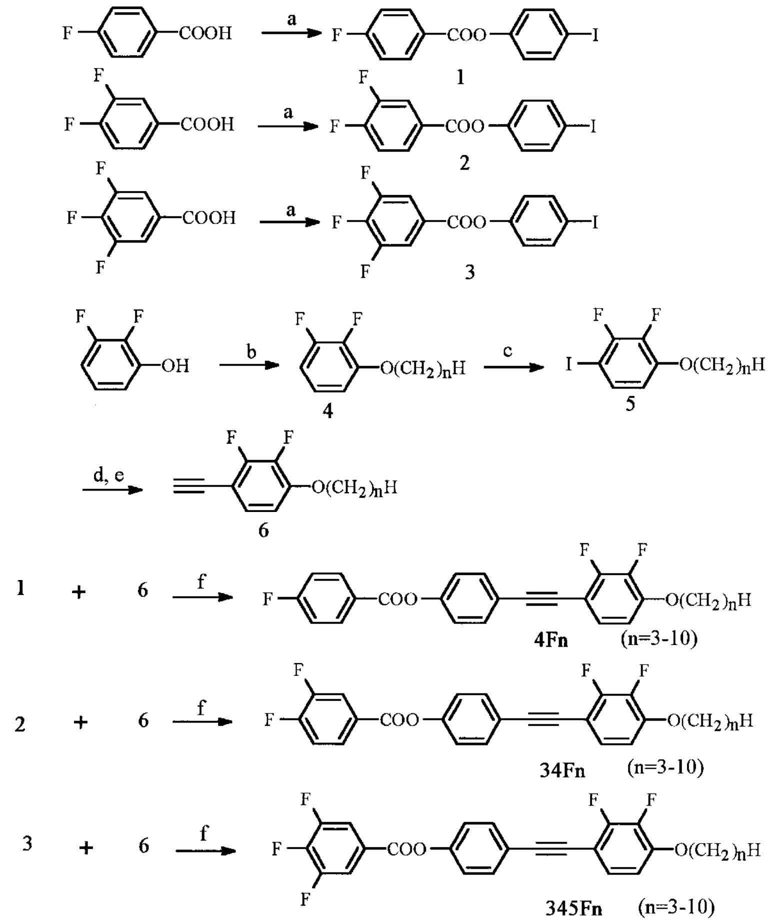
2.1. *Synthesis*

The paths to the fluorinated liquid crystals **4F*n*** ([4-(4-*n*-alkyloxy-2,3-difluorophenyl)ethynyl]phenyl 4-fluorobenzoate), **34F*n*** ([4-(4-*n*-alkyloxy-2,3-difluorophenyl)ethynyl]phenyl 3,4-difluorobenzoate), **345F*n*** ([4-(4-*n*-alkyloxy-2,3-difluorophenyl)ethynyl]phenyl 3,4,5-trifluorobenzoate) are outlined in scheme 2. The 4-alkyloxy-2,3-difluorophenylacetylene (**6**) was prepared according to our published procedure [10]. The fluoro-substituted benzoic acid can be easily obtained according to a reported procedure [4]. The fluorinated intermediates **1**, **2**, and **3**, were prepared via a mild one-pot esterification procedure [4], between the fluoro-substituted benzoic acid and *p*-iodophenol in the presence of dicyclohexylcarbodiimide (DCC) and DMAP as catalyst in the THF. Finally the coupling reaction between compound **1**, **2** or **3** and **6** under the catalysis of bis(triphenylphosphine)palladium dichloride, and copper(I) iodide in dry triethylamine gave the target compounds.

---

*Author for correspondence;
e-mail: wenjianxun@pub.sioc.ac.cn

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
http://www.tandf.co.uk/journals



Scheme 2. Reagents and conditions: (a) *p*-iodophenol, DCC, DMAP, THF; (b) $H(CH_2)_nBr$, K_2CO_3, acetone; (c) n-BuLi, -78°C, then I_2/THF; (d) trimethylsilylacetylene, $Pd(PPh_3)Cl_2$, CuI, NEt_3; (e) NaOH, CH_3OH, acetone; (f) $Pd(PPh_3)Cl_2$, CuI, NEt_3.

2.2. *Analysis*

The structures of all intermediates and final mesogens were determined by spectroscopic methods. IR spectra were recorded on a PE-983G spectrometer using a KBr disc. ^1H NMR spectra (with TMS as the internal standard) and ^{19}F NMR spectra (with trifluoroacetic acid (TFA) as external standard) in $CDCl_3$ as the solvent, were recorded on an FX-90Q (90 MHz) or Bruker 300AM instrument. For ^{19}F NMR spectra, the high field was positive. MS spectra were measured with a Finnign 4021 spectrometer. The phase transition temperatures of all the target compounds were measured by optical microscopy using a polarizing optical microscope (POM, Olympus PM-6) equipped with a hot stage (Mettler FP-80) and a control unit (FP-82); also by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system) with heating and cooling rates of 5°C min^{-1}. The transition temperatures shown in this paper are the peak values of the transitions on DSC traces. Phase identification was made by comparing the observed textures with those reported in the literature [11, 12].

2.3. *[4-(4-n-Alkoxy-2,3-difluorophenyl)ethynyl]phenyl 4-fluorobenzoate (**4Fn**, n = 3–10)*

Under dry nitrogen, into a mixture of compound 4-*n*-alkoxy-2,3-difluorophenylacetylene (0.73 mmol), 4-iodophenyl 4-fluorobenzoate (200 mg, 0.61 mmol), bis(triphenylphosphine)palladium dichloride (10 mg), and copper(I) iodide (15 mg) was added 10 ml of anhydrous triethylamine. The resulting mixture was stirred at 50°C for 24 h. The precipitate formed was filtered and washed with ether, and the filtrate washed with water, then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)–dichloromethane (3 : 1) as the eluent. This gave pale yellow crystals which were recrystallized from petroleum ether (b.p. 60–90°C) to yield white flaky crystals of compound **4F*n***. The yield of the product was normally greater than 75%. The following data for [4-(4-*n*-propyloxy-2′,3′-difluorophenyl)ethynyl]phenyl 4-fluorobenzoate (**4F3**) are representative of the series. Found: C 70.19, H 4.05, F 13.53; $C_{24}H_{17}F_3O_3$ requires C 70.24, H 4.18, F 13.89%. δ_H ($CDCl_3$) 1.07 (t, 3H, CH_3), 1.87 (m, 2H, CH_2), 4.02 (t, 2H, OCH_2), 6.72–8.24 (m, 10H, Harom) ppm. δ_F ($CDCl_3$) 24.2 (m, 1F), 54.4 (m, 1F), 78.8 (m, 1F) ppm. *m*/*z*(%): 410 (M^+, 27.64). ν_{max} (KBr): 29.18, 28.53, 1737, 1600, 1517, 1157, 1068 cm^{-1}.

2.4. *[4-(4-n-Alkoxy-2,3-difluorophenyl)ethynyl]phenyl 3,4-difluorobenzoate (**34Fn**, n = 3–10)*

Members of the homologous series **34F*n*** (*n* = 3–10) were prepared using a procedure similar to that described for the synthesis of compounds **4F*n***. The following data for [4-(4-*n*-propyloxy-2,3 -difluorophenyl)ethynyl]phenyl 3,4-difluorobenzoate (**34F3**) are representive of the series. Found: C 67.56, H 3.71, F 17.46; $C_{24}H_{16}F_4O_3$ requires C 67.29, H 3.77, F 17.74%. δ_H ($CDCl_3$) 1.07 (t, 3H, CH_3), 1.87 (m, 2H, CH_2), 4.04 (t, 2H, OCH_2), 6.72–8.03 (m, 9H, Harom) ppm. δ_F ($CDCl_3$) 53.8 (m, 1F), 58.6 (m, 1F), 60.6 (m, 1F), 82.9 (m, 1F) ppm. *m*/*z*(%): 429 (M^{+1}, 23.93). ν_{max} (KBr): 2969, 2884, 1744, 1614, 1517, 1202, 1168, 862 cm^{-1}.

2.5. *[4-(4-n-Alkoxy-2,3-difluorophenyl)ethynyl]phenyl 3,4,5-trifluorobenzoate (**345Fn**, n = 3–10)*

Members of homologous series **345F*n*** (*n* = 3–10) were prepared using a procedure similar to that described for the synthesis of compounds **4F*n***. The following data for [4-(4-*n*-butyloxy-2,3-difluorophenyl)ethynyl]phenyl 3,4,5-difluorobenzoate (**345F4**) are representive of the series. Found: C 65.18, H 3.69, F 20.53; $C_{25}H_{17}F_5O_3$ requires C 65.22, H 3.72, F 20.63%. δ_H ($CDCl_3$) 0.99 (t, 3H, CH_3), 1.53–1.83 (m, 4H, CH_2), 4.07 (t, 2H, OCH_2), 6.72–7.83 (m, 8H, Harom) ppm. δ_F ($CDCl_3$) 57.3 (m, 2F), 58.8 (m, 1F), 77.1 (m, 1F), 83.3 (m, 1F) ppm. *m*/*z*(%): 460 (M^+, 27.36). ν_{max} (KBr): 2920, 2859, 1742, 1602, 1518, 1225, 1166 cm^{-1}.

3. Results and discussion

The phase transition temperatures of all the synthesized compounds were determined by DSC with heating and cooling rates of 5°C min^{-1}. Mesomorphic textures were observed on the polarizing optical microscope for determining the types of mesophases. The transition temperatures shown in the table are the maxima of transition peaks on each DSC traces.

As mentioned, our target was to synthesize mesogens with a 2,3-difluorotolan unit in the core, and compare their mesomorphic properties with those of homologues

Table. Phase transition temperature of target compounds. Cr = crystal, SmA = smectic A phase, N = nematic phase, I = isotropic, Rec = recrystal.

Compounds	*n*	Transition temperature/°C
4F3	3	Cr 105.5 N 215.4 I 213.6 N 72.0 Rec
4F4	4	Cr 105.0 N 211.4 I 209.8 N 50.5 Rec
4F5	5	Cr 87.2 N 198.0 I 196.4 N 58.0 Rec
4F6	6	Cr 84.1 N 192.3 I 191.1 N 48.3 Rec
4F7	7	Cr 105.5 N 181.8 I 180.5 N 58.1 Rec
4F8	8	Cr 86.1 N 177.1 I 176.0 N 49.6 Rec
4F9	9	Cr 84.5 N 169.9 I 168.8 N 59.1 Rec
4F10	10	Cr 78.3 N 166.1 I 165.0 N 60.7 Rec
34F3	3	Cr 102.3 N 187.9 I 186.7 N 62.3 Rec
34F4	4	Cr 71.1 N 186.9 I 186.0 N 37.1 Rec
34F5	5	Cr 63.4 N 175.8 I 174.4 N 32.6 Rec
34F6	6	Cr 73. N 172.1 I 171.0 N 36.4 Rec
34F7	7	Cr 67.7 N 164.0 I 163.2 N 42.7 Rec
34F8	8	Cr 66.1 N 160.5 I 159.1 N 37.1 Rec
34F9	9	Cr 74.5 N 154.7 I 153.3 N 52.2 Rec
34F10	10	Cr 69.2 N 151.6 I 150.4 N 45.3 Rec
345F3	3	Cr 109.5 N 159.7 I 158.7 N 74.0 Rec
345F4	4	Cr 85.4 SmA 105.7 N 159.8 I 158.3 N 103.8 SmA 52.6 Rec
345F5	5	Cr 73.0 SmA 120.5 N 153.6 I 151.9 N 118.7 SmA 59.6 Rec
345F6	6	Cr 79.1 SmA 125.7 N 150.5 I 149.4 N 124.7 SmA 50.4 Rec
345F7	7	Cr 59.4 SmA 132.8 N 145.7 I 144.8 N 131.7 SmA 43.0 Rec
345F8	8	Cr 87.7 SmA 123.6 N 132.9 I 131.9 N 123.3 SmA 32.4 Rec
345F9	9	Cr 66.3 SmA 137.2 N 139.9 I 138.5 N 135.5 SmA 42.5 Rec
345F10	10	Cr 58.4 SmA 138.1 I 136.7 SmA 39.7 Rec

containing the tolan or 2,3,5,6-tetrafluorotolan unit. Therefore, three series of compounds **4F*n***, **34F*n*** and **345F*n*** were synthesized for investigation. Their phase transition temperatures are summarized in the table. Compounds **4F*n*** and **34F*n*** show a simple mesophase sequence. The nematic (N) mesophases are relatively wide. Their temperature ranges decrease as the alkyl chain grows from 3 to 10 methylene units, as shown in figures 1 and 2. The series **345F*n*** shows both enantiotropic SmA and enantiotropic N phases, and the SmA mesophase ranges increase while the N mesophase ranges decrease as the alkyl chain grows from 3 to 10 methylene units, as shown in figure 3. From these three series it is seen that replacement of a terminal *meta*-hydrogen in a molecule by a fluorine atom affects the breadth of the molecule. Similar phenomena were discussed in our previous papers [2–4].

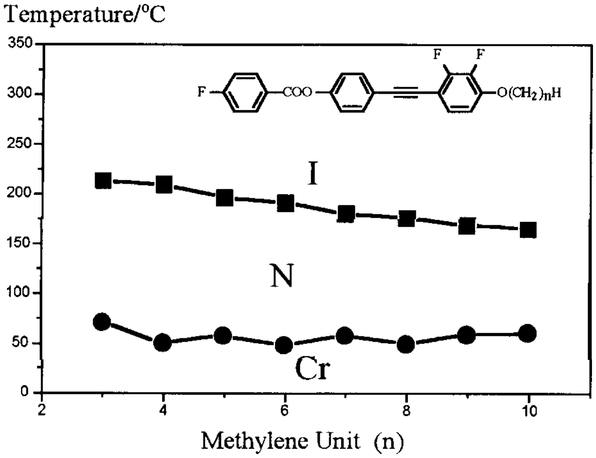


Figure 1. The transition behaviour of compounds **4F*n***: dependence of transition temperatures on the number (*n*) of the alkoxy chain.

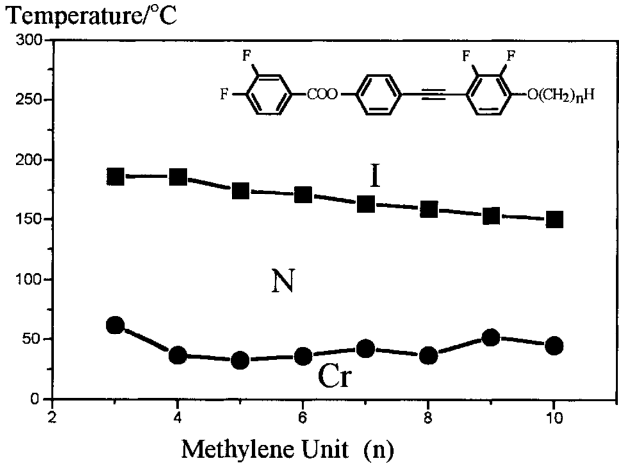


Figure 2. The transition behaviour of compounds **34F*n***: dependence of transition temperatures on the number (*n*) of the alkoxy chain.

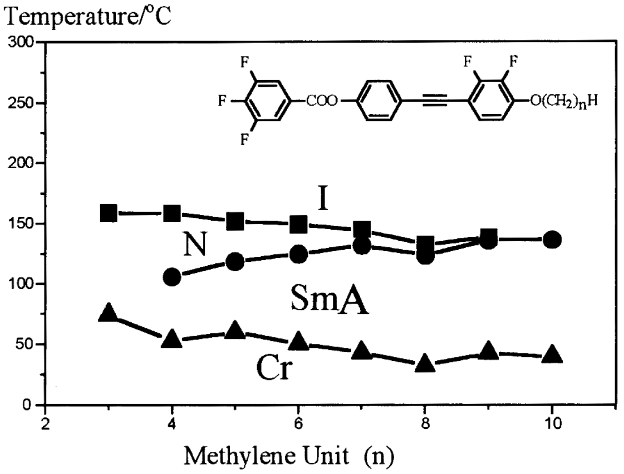


Figure 3. The transition behaviour of compounds **345F*n***: dependence of transition temperatures on the number (*n*) of the alkoxyl chain.

In previous work, we synthesized many fluorinated liquid crystals containing a tolan or a 2,3,5,6-tetrafluorotolan unit [2–4]. Thereafter we selected nine compounds and compared their mesomorphic properties; the result is shown in figure 4. From this figure, we see that, in the 4-fluorobenzoate systems, all the three compounds (**4F*n*′**, **4F*n***, **4F*n*″**, *n* = 7) exhibit a simple nematic phase sequence, but the nematic temperature range of **4F7** is wider than the other two. Comparison of the compounds (**34F*n*′**, **34F*n***, **34F*n*″**, *n* = 7) show that nematic character is increased and the smectic mesophase entirely suppressed by replacing with 2,3-difluorotolan unit. In the 3,4,5-trifluorobenzoate system, the influence of the 2,3-difluorotolan unit is not obvious; we think in this system the bulky 3,4,5-trifluorophenyl ring plays a major role in the mesomorphic properties.

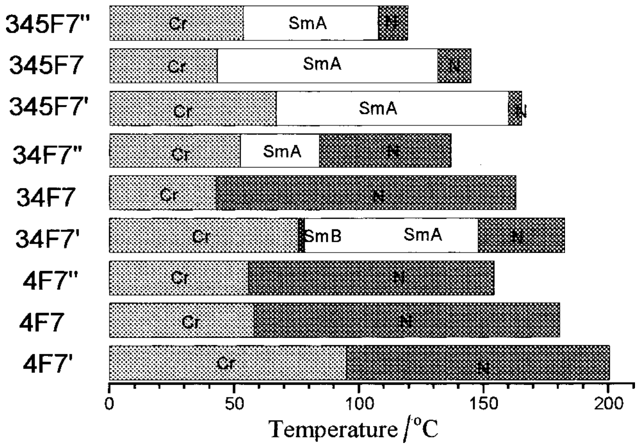


Figure 4. Comparison of mesomorphic properties of selected compounds.

To summarize, this investigation, together with a previous study on the mesogen with a 2,3,5,6-tetrafluorophenyl ring, reveals that mesogens with a 2,3-difluorotolan unit can suppress the smectic mesophase and make the nematic range wider. Their ability to suppress the smectic mesophase grows as follows: tolan < 2,3-difluorotolan < 2,3,5,6-tetrafluorotolan. This shows that lateral fluoro-substitution has a considerable effect on their mesomorphic properties and results in the reduction of the nematic thermostabilities, and in most cases the smectic thermostabilities, due to the lateral fluoro-substituent broadening the molecule and reducing intermolecular forces.

The authors acknowledge gratefully the National Natural Science Foundation of China for financial support.

References

[1] Wen, J. X., Tian, M. Q., Yu, H. B., Guo, Z. H., and Chen, Q., 1994, *J. mater. Chem.*, **4,** 327.

[2] Wen, J. X., Tang, G., and Yang, Y. G., *Mol. Cryst. liq. Cryst.* (to be published).

[3] Yang, Y. G., and Wen, J. X., 1999, *Chin. J. Chem.*, **17,** 69.

[4] Yang, Y. G., and Wen, J. X., *Mol. Cryst. liq. Cryst.* (to be published).

[5] Gray, G. W., 1987, *Thermotropic Liquid Crystals* (Chichester: Wiley).

[6] Gray, G. W., Hird, M., and Toyne, K. J., 1991, *Mol. Cryst. liq. Cryst.*, **204,** 43.

[7] Dong, C. C., Styring, P., Goodby, J. M., and Chan, K. M., 1999, *J. mater. Chem.*, **9,** 1669.

[8] Hirschmann, H., Reuter, M., and Reiffenrath, V., 1999, Patent DE 19 828 149.

[9] Hirschmann, H., Suchuepfer, S., Reiffenrath, V., and Schoen, S., 1999, Patent DE 19 844 321.

[10] Chen, X. M., Li, H. F., and Wen, J. X., *Liq. Cryst.* (in the press).

[11] Demus, D., and Richter, L., 1978, *The Texture of Liquid Crystals* (Leipzig: VEB Deutcher Verlag fur Grandstoff Industrie).

[12] Gray, G. W., and Goodby, J. W., 1984, *Smectic Liquid Crystals—Textures and Structures* (Glasgow: Leonard Hill).