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

Synthesis and mesomorphic properties of the homologous series of 4'-bromophenyl 4''-[(4-*n*-alkoxy-2,3,5,6 tetrafluorophenyl)ethynyl]benzoates

Yuelian Xu[a]; Qi Chen[a]; Jianxun Wen[a]
[a] Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai, China

To cite this Article Xu, Yuelian , Chen, Qi and Wen, Jianxun(1993) 'Synthesis and mesomorphic properties of the homologous series of 4'-bromophenyl 4''-[(4-*n*-alkoxy-2,3,5,6 tetrafluorophenyl)ethynyl]benzoates', Liquid Crystals, 15: 6, 915 — 918
To link to this Article: DOI: 10.1080/02678299308036511
URL: http://dx.doi.org/10.1080/02678299308036511

LIQUID CRYSTALS, 1993, VOL. 15, NO. 6, 915–918

Synthesis and mesomorphic properties of the homologous series of 4′-bromophenyl 4″-[(4-*n*-alkoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoates

by YUELIAN XU, QI CHEN and JIANXUN WEN*

Shanghai Institute of Organic Chemistry, Academia Sinica,
345 Lingling Lu, Shanghai 200032, China

(*Received 19 March 1993; accepted 3 June 1993*)

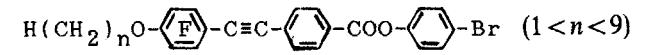
A homologous series of 4′-bromophenyl 4″-[(4-*n*-alkoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoates has been synthesized. The transition temperatures were studied by polarizing optical microscopy. The compounds exhibit nematic and smectic A phases.

1. Introduction

The structure and the nature of rod-like skeletons are known to play a significant part in the determination of the properties of liquid crystals. Therefore, we are interested in the study of liquid crystals with polyfluoroaromatic rings as core structures. The replacement of hydrogen atoms by fluorine produces a change in the intermolecular interactions and consequently in mesomorphic properties caused by geometric and electronic factors.

Until now, few liquid crystal molecules with polyfluoro-aromatic ring structures have been prepared. Except for anils [1, 2, 3], which increase the thermal stability of short alkoxy groups, the other molecules exhibit decreased thermal stability. These compounds are bis-(*p*-alkyl/alkoxy/phenyl)tetrafluoroterephthalates [4, 5], 4-cyano-2,3,5,6-tetrafluorophenylbenzoates [4] and 4-*n*-alkoxyperfluorobenzoates [6].

Previously we have reported two series of novel fluorinated liquid crystals containing 1,4-tetrafluorophenylene [7, 8]. We have now synthesized and studied 4′-bromophenyl 4″-[(4-*n*-alkoxy-2,3,5,6-tetrafluorphenyl)ethynyl]benzoates of the general structure (1).



$(1 < n < 9)$ (1)

2. Experimental

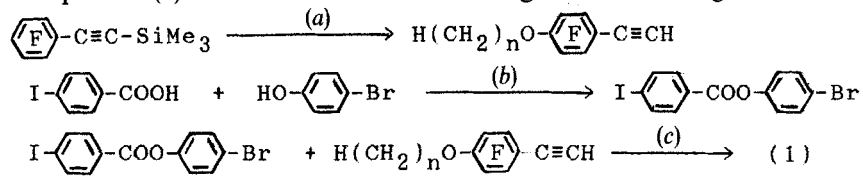
IR spectra were recorded on a Shimadzu IR-440 spectrophotometer. ^{1}H NMR spectra, with TMS as the internal standard, and ^{19}F NMR spectra, with trifluoroacetic acid (TFA) as external standard, were recorded on a Varian EM 360L spectrometer (60 MHz) or FX-90Q spectrometer (90 MHz). For ^{19}F NMR spectra, the high field is positive. Mass spectra were measured on a Finnigan-4021 spectrometer.

Transition temperatures were measured by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a Mettler FP 52 heating stage and FP 5 control unit. Phase identification was made by comparing the observed textures with those in the literature [11, 12].

* Author for correspondence.

0267–8292/93 $10·00

Compounds (1) have been obtained according to the following scheme:



Reagents: (*a*) K_2CO_3, DMF, $H(CH_2)_nOH$, r. t.; (*b*) DCCI, PPY, CH_2Cl_2, r. t.; (*c*) CuI, Et_3N, $(Ph_3P)_2PdCl_2$, 35–40°C.

4-Alkoxy-2,3,5,6-tetrafluorophenylacetylene was prepared according to the method given in [9].

4′-Bromophenyl 4-iodobenzoate was obtained by a mild one pot esterification [10] between 4-iodobenzoic acid and 4-bromophenol in the presence of both dicyclohexylcarbodiimide (DCCI) and 4-pyrrolidinopyridine (PPY) catalysts in anhydrous dichloromethane.

All of the 4′-bromophenyl 4″-[(4-*n*-alkoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoates have been prepared following the same general procedure. Their structures are identified by IR, MS, ^{1}H NMR, ^{19}F NMR spectra and elemental analyses. As an example of the synthesis, preparation of the nonyloxy derivative is described.

2.1. *Synthesis of 4′-bromophenyl 4″-[4-*n*-nonyloxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoates*

In a 50 ml round-bottom three-necked flask equipped with a magnetic stirring bar, a nitrogen inlet and a bubbler, were placed 4′-bromophenyl 4-iodobenzoate 0·403 g (1·0 mmol), 4-nonyloxy-2,3,5,6-tetrafluorophenylacetylene 0·316 g (1·0 mmol), bis (triphenylphosphine)palladium(II) dichloride 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 at 35–40°C for 24 h; a brown precipitate formed. Analysis by TLC revealed a complete reaction. The precipitate was filtered off and extracted with ether. The filtrate was washed with water, and dried over anhydrous sodium sulphate. The solvent was removed under 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 pale yellow crystals. The product was recrystallized from acetone–methanol to yield white flaky crystals. Yield 0·5 g (84·6 per cent), C 101·7°C S_A 161·3°C N 176·4°C I.

^{1}H NMR($CDCl_3$): δ 0·76–1·94(m, 17 H), 4·28 (t, 2 H, $J = 5{\cdot}4$ Hz), 7·14 (d, 2H)/7·54 (d, 2 H) (AA′BB′, $J = 8{\cdot}1$ Hz), 7·67 (d, 2 H)/8·16 (d, 2 H) (AA′BB′, $J = 8{\cdot}1$ Hz); ^{19}F NMR($CDCl_3$): δ 60·5 (m, 2 F), 80·1 (m, 2 F); IR(KBr); γ 2 850, 2 790, 1 724, 1 596, 1 480 1 430, 1 378, 1 256, 1 180, 1 160, 1 052, 1 000, 970, 840, 750, 680 cm^{-1}; MS(*m*/*z*): 590(M^+, 1·31), 419 (100·00), 293 (37·04); Elemental analysis, found: C 60·67 per cent H 4·40 per cent F 12·61 per cent Br 13·70 per cent; calculated: (for $C_{30}H_{27}F_4O_3Br$) C 60·91 per cent H 4·57 per cent F 12·88 per cent Br 13·56 per cent.

3. Results and discussion

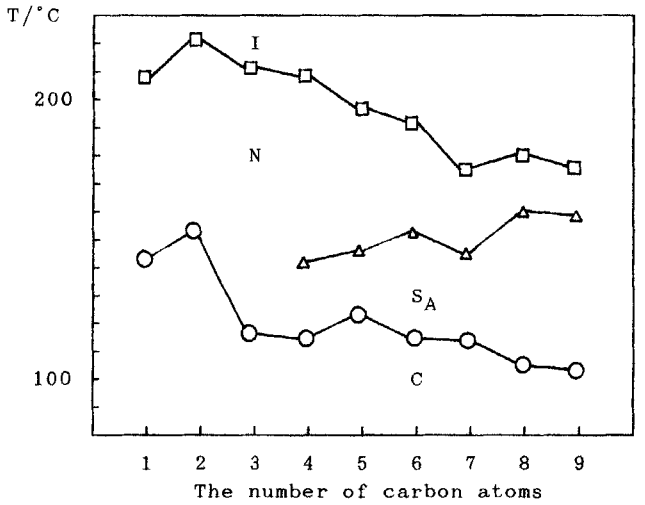
The phase behaviour of the series is given in the table.

Compounds (1) with a short alkoxy chain ($n = 1, 2$) exhibit a nematic phase only, over a wide temperature range. When the length of the alkoxy chain increases, a smectic

Transition temperatures of compounds of general formula (1).

n	Transition temperatures/°C									
1	C	141·8 ⇌ 94·7			N	207·0 ⇌ 206·2				I
2	C	152·0 ⇌ 110·6			N	220·8 ⇌ 220·4				I
3	C	115·3 ⇌ 82·6	S_A	116·8	N	212·7 ⇌ 212·7				I
4	C	114·3 ⇌ 94·2	S_A	140·0 ⇌ 139·9	N	209·0 ⇌ 208·8				I
5	C	123·2 ⇌ 108·5	S_A	147·6 ⇌ 148·0	N	198·3 ⇌ 197·7				I
6	C	115·3 ⇌ 98·3	S_A	153·3 ⇌ 153·0	N	192·7 ⇌ 192·7				I
7	C	114·8 ⇌ 96·7	S_A	146·1 ⇌ 146·7	N	175·4 ⇌ 174·6				I
8	C	109·8 ⇌ 96·8	S_A	161·5 ⇌ 160·2	N	183·1 ⇌ 182·3				I
9	C	101·7 ⇌ 92·1	S_A	161·3 ⇌ 160·6	N	176·4 ⇌ 175·6				I

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



Transition temperatures as a function of *n*, the number of carbon atoms in the alkoxy chain of compounds (1). Melting points are denoted by ○, △ indicates smectic A–nematic phase transitions, and □ nematic to isotropic phase transitions.

A phase appears (monotropic for $n=3$, enantiotropic for $n>4$). The nematic range decreases whilst the smectic A range increases, with increasing alkoxy chain length (see the figure). Odd–even effects of the clearing points are not obvious. Similar wide S_A temperature ranges (see table) are also exhibited by the 4-*n*-alkoxyperfluorobenzoate series of liquid crystals [6].

4. Conclusion

A homologous series of 4′-bromophenyl 4″-[(4-*n*-alkoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoates was prepared via Pd-catalysed coupling reaction. Thermal optical microscopy showed that these compounds were liquid crystalline, and each homologue exhibited a nematic and/or a wide smectic A phases.

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

References

[1] GOLDMACH, J., and BARTON, L. A., 1967, *J. org. Chem.*, **32,** 476.
[2] MURZA, M. M., TATAUROV, G. P., POPOV, L. I., and SVETKIN YU, V., 1977, *Z. org. Khim.*, **13,** 1046.
[3] GRAY, G. W., 1979, *Molec. Crystals liq. Crystals*, **7,** 127.
[4] BEQUIN, A., and DUBOIS, J. C., 1978, 8th Congress International Cristaux Liquides, Bordeaux, Poster AP 1.
[5] SIRUTKAITIS, R., and ADOMENAS, P., 1980, *Advances in Liquid Crystal Research and Applications*, edited by Lajos Bata (Pergamon Press), p. 1023.
[6] LE BARNY, P., RAVAUX, G., and DUBOIS, J. C., 1985, *Molec. Crystals liq. Crystals*, **127,** 413.
[7] WEN, J. X., TIAN, M. Q., and CHEN, Q., 1993, *J. fluorine Chem.* (in the press).
[8] WEN, J. X., XU, Y. L., and CHEN, Q., 1993, *J. fluorine Chem.* (in the press).
[9] ZHANG, Y. D., and WEN, J. X., 1990, *J. fluorine Chem.*, **49,** 293.
[10] HASSNER, A., and ALEXANIAN, V., 1978, *Tetrahedron Lett.*, **46,** 4475.
[11] DEMUS, D., and RICHTER, L., 1978, *Textures of Liquid Crystals* (Verlag Chemie, Weinheim).
[12] GRAY, G. W., and GOODBY, J. W., 1984, *Smectic Liquid Crystals, Textures and Structures* (Leonard Hill).