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Huiyong Yin[a]; Jianxun Wen[a]
[a] Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, China

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Synthesis and mesomorphic properties of some novel chiral fluorinated liquid crystals containing a flexible oxymethylene linkage in the core

by HUIYONG YIN, JIANXUN WEN*
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
Fenglin Lu 354, Shanghai, 200032, China

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Four series of tolane-based chiral liquid crystals that incorporate a tetrafluorophenyl moiety and a flexible oxymethylene linkage into the core have been synthesized. The mesomorphic properties have been studied by thermal polarizing microscopy. The relationship between the properties and chemical structures of all these target compounds, especially the influence of flexible oxymethylene linkage in core on the formation of mesophases, is also discussed in detail.

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 so as to develop new potential materials for display devices and other applications. The discovery of ferroelectricity in liquid crystals by Meyer *et al.* [1], stimulated the study of ferroelectric liquid crystal materials. More and more research attentions have been paid to ferroelectric fluorinated liquid crystals [2-6], due to the tendency of fluorine substituent(s) to transform a smectic A (S_A) into a smectic C (S_C) mesophase [2, 3], to suppress or eliminate unnecessary smectic mesophases and to improve dielectric anisotropy, viscosity, birefringence and melting points [2-4]. Therefore, a lot of ferroelectric liquid crystalline materials with monofluoro-, difluoro- or trifluoro-substituted aromatic rings have been extensively studied [2-6]. However, only a few liquid crystals with tetrafluorophenylene have been reported [7-11]. Because of the symmetric substitution of fluorine atoms on the benzene ring, the effect of polyfluoro-substitution on the transition temperatures cannot be extrapolated from the extensive data available for monofluoro-, difluoro- or trifluoro-substitutions. Furthermore, considerable attention has been paid to the synthesis of tolane-based liquid crystals, which are reported to possess both low viscosity and high birefringence [12-15]. Therefore, we aimed to synthesize some new tolane-based liquid crystals with 2,3,5,6-tetrafluoro-1,4-phenylene in the core so as to obtain new materials for applications [16-23].

In our previous studies, some target compounds with rigid linkages (such as ester, triple bond etc.) have been emphasized. With the increasing diversification in the application of LCDs (outdoor, car dash-board etc.), the properties like low viscosity and chemical stability are becoming more and more important. In the literature [23, 24], it was found that an oxymethylene linkage would lead to more chemically and thermally stable LCDs with low viscosity. Furthermore, many results for liquid crystals with such a flexible linkage are scattered in the literature [25-27]. In this paper, we wish to report the synthesis and phase transitions of some novel chiral liquid crystals (series **A**, **B**, **C**, **D**) containing a flexible oxymethylene link and discusss the relationship between mesomorphic properties and chemical structures:

2. Experimental

2.1. *Synthesis*

The target molecules were prepared according to schemes 1 and 2.

Compounds **1** and **3a-b** were prepared from a free radical reaction initiated by initiator AIBN in CCl_4. The important intermediates **2a-e**, **4a-b** and **11** were easily synthesized via a convenient condensation reaction between compound **1** or **3a-b** and the corresponding 4-substituted phenols. The (*S*)-2-methylbutyloxy-2,3,5,6-tetrafluorophenylacetylene **5** and 4-*n*-alkoxy-2,3,5,6-tetrafluorophenylacetylenes **5′a-d** were obtained by nucleophilic substitution on the starting material 1-pentafluorophenyl-2-trimethylsilylacetylenes at room

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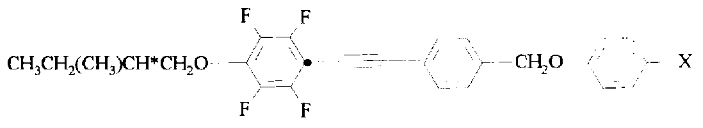
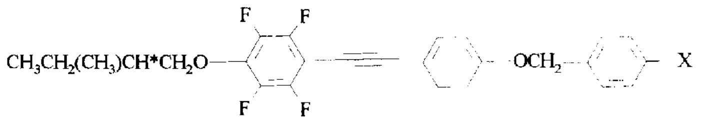
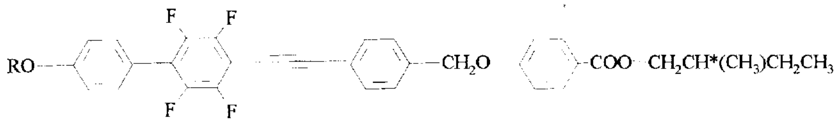
*Author for correspondence.



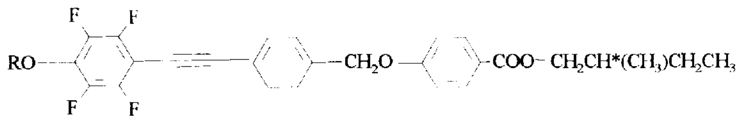
A: X = OCH_3, Br, Cl, $COOC_4H_9$-n, $COOC_5H_{11}$-n



B: X = Br, F



C: R= C_nH_{2n+1}(n= 6, 8, 10, 12)



D: R= C_nH_{2n+1}(n=5,6,7,12)

temperature using K_2CO_3 as the base [28]. The synthesis of intermediates **8a–d** have been reported in a previous paper [29]. The target compounds in series **A**, **B**, **C** and **D** were easily synthesized by a palladium-catalysed Heck reaction.

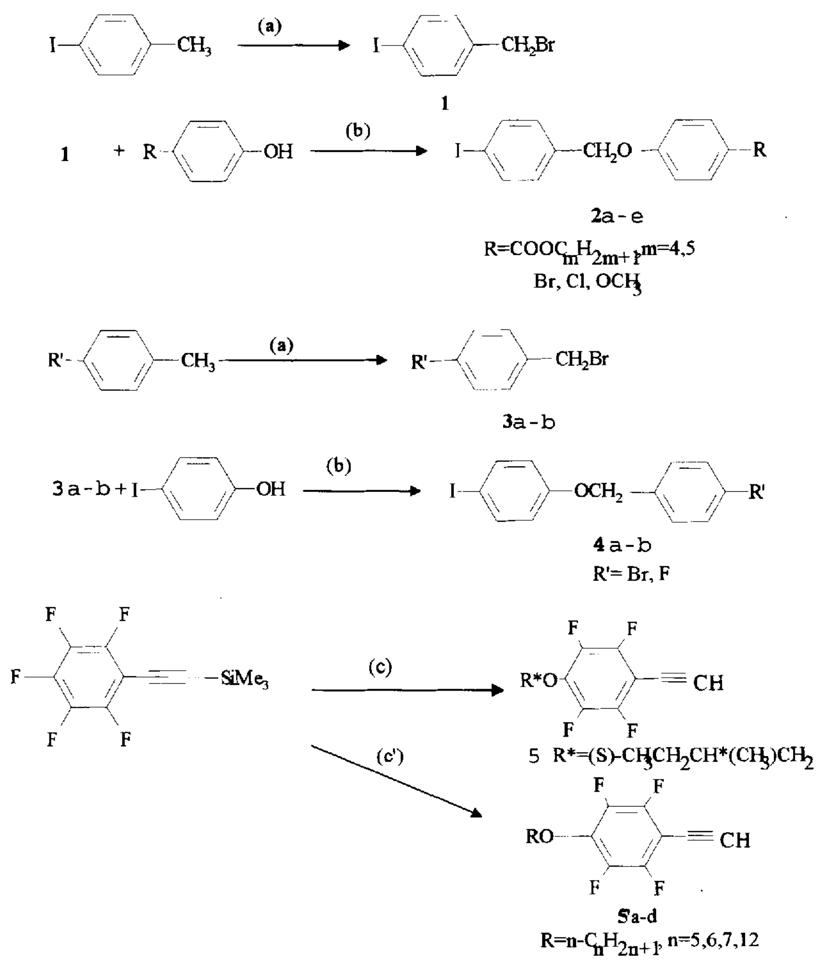
2.2. *Analysis*

The structures of the intermediates and the final compounds were elucidated by spectral methods. IR spectra were determined on a Shimadzu IR-440 spectrometer using a KBr disc pellet. ^1H NMR spectra, with TMS as the internal standard and $CDCl_3$ as the solvent, were run on an FX-90Q (90 MHz) spectrometer. ^{19}F NMR spectra, with trifluoroacetic acid (TFA) as external standard and $CDCl_3$ as the solvent, were recorded on a Varian EM 360L (60 MHz) spectrometer (high field positive). MS spectra were measured with a Finnigan 4021 Spectroscope. The phase transition temperatures of the target compounds were measured visually by optical microscopy using a polarizing Olympus PM-6 microscope fitted with a Mettler FP-52 heating stage and an FP-5 control unit. The phase identification was made by comparing the observed textures with those in the literature [30, 31].

The intermediates **2a–e**, **4a–c**, **5**, **5′a–d** and **8a–d** were prepared by the nucleophilic reaction reported previously [28, 29].

2.3. *n-Pentyl 4-[4-((4-(S)-2-methylbutyloxy)-2,3,5,6-tetrafluorophenyl)ethynyl)benzyloxyl]benzoate (compound A5)*

A typical procedure: Under nitrogen, 20 ml of anhydrous triethylamine was added to a mixture of compound **2b** ($R = COOC_5H_{11}$-n) (228 mg, 0·54 mmol), [4-(*S*-2-methylbutoxy-2,3,5,6-tetrafluorophenyl]acetylene (180 mg, 0·69 mmol), bis(triphenyl phosphine)palladium dichloride (30 mg, 0·04 mmol) and copper(I) iodide (15 mg, 0·08 mmol). The resulting mixture was refluxed while stirring until analysis by TLC revealed a complete reaction. The cooled mixture was filtered and the filtrate was washed with anhydrous ether. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C) and ethyl acetate (20 : 1) as eluent to give pale-yellow crystals which were recrystallized from acetone–methanol to yield white crystals of compound **A5**. Yield: 280 mg (93·6%). $[\alpha]_D = +1{\cdot}96$($CHCl_3$, 20°C). ^1H NMR δ_H (90 MHz,



$2 + 5 \xrightarrow{(d)}$ Series **A**1-5 (R= OCH_3, Br, Cl, $COOC_4H_9$, $COOC_5H_{11}$)

$4 + 5 \xrightarrow{(d)}$ Series **B**1-2 (R = Br, F R* = (S)-$CH_3CH_2CH^*(CH_3)CH_2$)

Scheme 1 (a) CCl_4, NBS, AIBN
(b) DMF, NaOH
(c) R*OH, DMF, K_2CO_3, R.T. (c') ROH, DMF, K_2CO_3, R.T.
(d) $Pd(PPh_3)_2Cl_2$/CuI, Et_3N, Reflux.

solvent $CDCl_3$, standard TMS): 1·01–1·99 (m, 17 H), 4·12 (d, 2 H, $J = 6{\cdot}0$ Hz, CO_2CH_2, RCH_2O), 5·16 (s, 2 H, $ArCH_2OAr$), 7·00 (d, 2 H, $J = 9{\cdot}0$ Hz, ArH), 8·01 (d, 2 H, $J = 9{\cdot}0$ Hz, ArH), 7·24 (d, 2 H, $J = 8{\cdot}0$ Hz, ArH), 7·63 (d, 2 H, $J = 9{\cdot}0$ Hz, ArH) ppm; ^{19}F NMR δ_F (60 MHz, solvent $CDCl_3$, standard TFA): 61·10 (m, 2 F,. F arom.), 80·58 (m, 2 F, F arom.), IR (KBr)ν: 2900, 2810, 1710, 1610, 1490, 1270, 1250, 1170, 1100, 980, 850 and 760 cm^{-1} MS m/z (rel., int./per cent): 556 (M^+, 0·15). Elemental analysis $C_{32}H_{32}F_4O_4$ calc. C, 69·06; H, 5·76; F, 13·67. Found: C, 68·95; H, 5·75; F, 13·53 per cent.

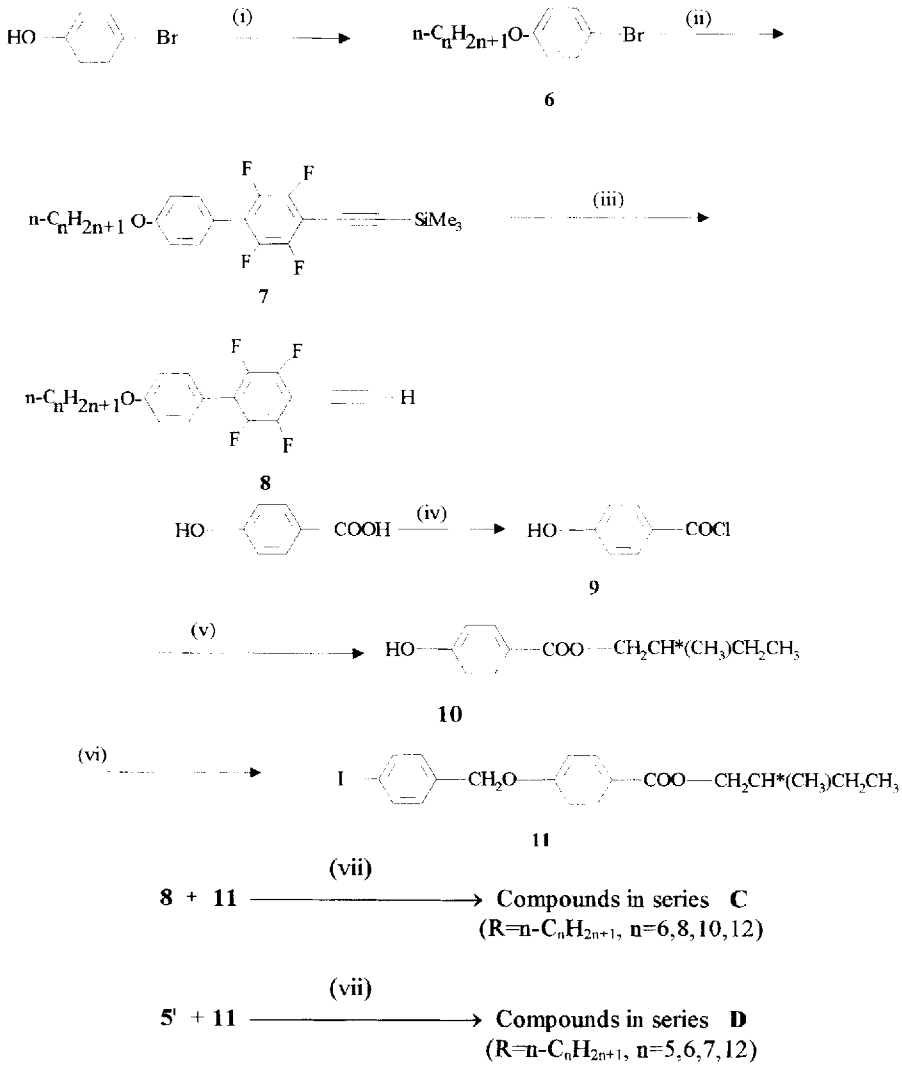
All of these new compounds **A 1–5**, **B 1–2**, **C 1–4** and **D 1–4** were prepared similarly; they all have satisfactory elemental analyses and appropriate IR, MS, ^1H and ^{19}F NMR spectra data.

3. Results and discussion

3.1. *Phase transition temperatures of compounds in series A and B*

The phase transition temperatures of compounds in series **A** and **B**, and **A**′ are listed in tables 1 and 2, respectively.

Most of the compounds in series **A** and **B** show no

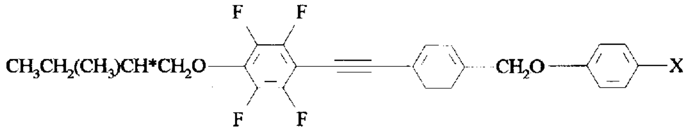


Scheme 2 (i) NaOH, n-$C_nH_{2n+1}Br$
(ii) Mg. THF, $C_6F_5C{\equiv}CSiMe_3$, Reflux.
(iii) CH_3OH/CH_3COCH_3, $NaOH/H_2O$, R.T.
(iv) $SOCl_2$
(v) $HOCH_2CH^*(CH_3)CH_2CH_3$
(vi) p-I-C_6H_4-CH_2Br, DMF, NaOH
(vii) $Pd(PPh_3)_2Cl_2/CuI$, Et_3N.

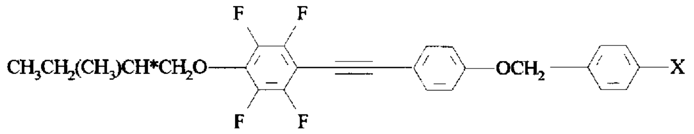
mesogenic phases, except that **A3** and **B1** exhibit a monotropic cholesteric phase. We suggest that the rigidity of the target molecule has been dramatically weakened with the introduction of the flexible oxymethylene linkages into the backbones which damages the alignment of the molecules. The $-OCH_2-$ linkage (in series **B**) is preferable for promoting liquid crystallinity compared to the $-CH_2O$ linkage (in series **A**) with the same end groups (for example, Br), and has been summarized in another paper [32]. The results depend on the conjugation of the oxygen atom in $-OCH_2-$ to the whole core structure, which enhances the rigidity of the molecule to a certain extent [26, 32].

In our previous studies [31], the compounds with $-COO-$ as the linkage exhibit enantiotropic S_C^* and Ch phases with the $-COOC_nH_{2n+1}$ ($n = 4$ or 5) end group. It is obvious that the ester rather than the oxymethylene link is preferable for the formation of mesophases

Table 1. Phase transition temperatures of compounds of series **A** and **B**.



A: X=OCH_3, Br, Cl, $COOC_4H_9$-n, $COOC_5H_{11}$-n

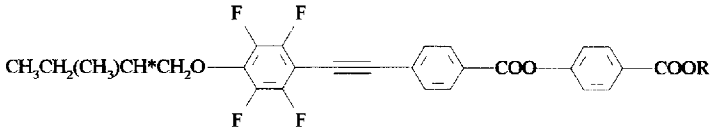


B: X=Br, F

		Transition temperatures/°C			
Compound	*X*	Cr	Ch	I	Recryst.
A1	Cl	•	107·5	•	104·6
A2	Br	•	107·6	•	102·5
A3	OCH_3	•	102·1 (• 101·3)	•	79·2
A4	$COOC_5H_{11}$	•	105·9	•	100·0
A5	$COOC_4H_9$	•	107·4	•	101·0
B1	Br	•	116·9 (• 111·0)	•	109·2
B2	F	•	102·9	•	100·6

Parentheses denote a monotropic transition.
Cr: crystal; Ch: cholesteric; I: isotropic.

Table 2. Phase transition temperatures of compounds of series **A′**.



A′: R = C_nH_{2n+1}

	Transition temperatures/°C						
n	Cr		S_C^*		Ch		I
4	•	105·8	•	122·0	•	128·6	•
5	•	103·6	•	127·5	•	141·4	•

Cr: crystal; S_C^*: chiral smectic C; Ch: cholesteric; I: isotropic.

because of the conjugation of the ester moiety with the bilateral aromatic rings.

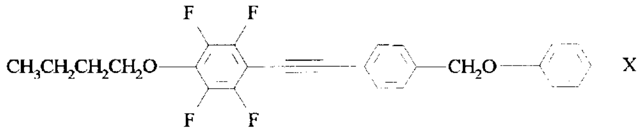
Furthermore, in order to discuss the effect of the chiral end group on the phase transition properties, it was compared with some of our previous results listed in table 3 [33].

Most of the compounds in series **A″** and **B″** exhibit enantiotropic mesophases except for compound **A″**5. These results show that the introduction of a methyl branched chiral end group (such as, $CH_3CH_2(CH_3)CH^*CH_2O$) destablizes the molecular alignment due to the steric effect [34–36].

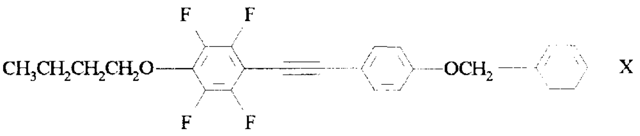
3.2. *Phase transition properties of compounds of series C and D*

The phase transition temperatures of compounds in series **C** and **D** are listed in table 4. As shown in table 4, compounds of series **D** show no mesogenic phases, whereas the compounds of series **C** exhibit an enantiotropic Ch phase when $n=6$ or 8, and enantiotropic

Table 3. Phase transition temperatures of the achiral analogues of series **A** and **B** [33].



A″: X=OCH_3, Br, Cl, $COOC_4H_9$-n, $COOC_5H_{11}$-n

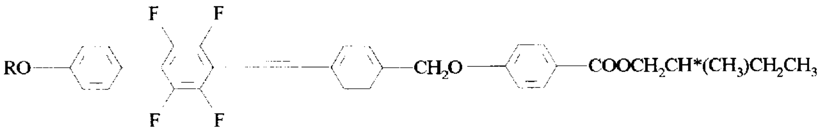


B″: X=Br, F

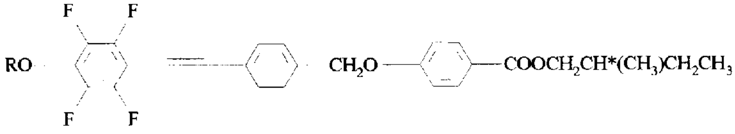
		Transition temperatures/°C				
Compound	*X*	Cr	S_A	N	I	Recryst.
A″1	Cl	• 86·5		• 121·7	•	83·5
A″2	Br	• 92·0		• 123·2	•	80·1
A″3	OCH_3	• 70·3		• 125·8	•	62·1
A″4	$COOC_5H_{11}$	• 93·0	• 94·6	• 98·4	•	85·2
A″5	$COOC_4H_9$	• 102·2			•	99·1
B″1	Br	• 91·7	• 101·9	• 133·2	•	85·8
B″2	F	• 89·6		• 109·4	•	76·5

Cr: crystal; S_A: smectic A; N: nematic; I: isotropic.

Table 4. The phase transition temperatures of compounds of series **C** and **D**.



C: R = n-C_nH_{2n+1}, n = 6,8,10,12



D: R = n-C_nH_{2n+1}, n = 5, 6,7, 12

		Transition temperatures/°C				
Compound	*n*	Cr	S_C^*	Ch	I	Recryst.
C1	6	• 132·5		• 192·9	•	
C2	8	• 132·4		• 191·9	•	
C3	10	• 119·1	• 155·3	• 179·7	•	
C4	12	• 86·2	• 165·5	• 185·2	•	
D1	5	• 110·0			•	104·9
D2	6	• 106·6			•	101·1
D3	7	• 100·1			•	95·9
D4	12	• 92·5			•	85·4

S_C^* and Ch phases with $n = 10$ or 12. The great difference of the mesomorphic properties depend on the differences in structure, i.e. compounds of series **C** have one more benzene ring than those of molecules of series **D**, which enhances the rigidity of the molecules of series **C**.

As we have mentioned previously, the rigidity of the whole molecule has a great influence on mesogenic properties of the liquid crystals. Substitution of –COO– by a more flexible oxymethylene linkage damages the ability of mesophase formation because of the decrease in the rigidity of the whole molecule [37].

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References

[1] MEYER, R. B., LIEBERT, L., STRZELOCHI, L., and KELLER, P., 1975, *J. Phys. (Paris)*, **36**, L69.
[2] REIFFENRATH, V., KRAUSE, J., PLACH, H. F., and LOEBER, G., 1989, *Liq. Cryst.*, **5**, 159.
[3] GRAY, G. W., HIRD, M., LACEY, D., and TOYNE, K. J., 1989, *J. chem. Soc., Perkin Trans. II*, 2041.
[4] NABOR, M. F., NGUYEN, H. T., DERRADE, C., and MARCEROU, J. P., *Liq. Cryst.*, **10**, 785.
[5] PUGH, C., ANDERSON, S. K., and TOYNE, K. J., 1991, *Liq: Cryst.*, **10**, 299.
[6] HIRD, M., GRAY, G. W., and TOYNE, K. J., 1992, *Liq. Cryst.*, **4**, 531.
[7] GOLDMACHER, J., and BARTON, L. A., 1967, *J. org. Chem.*, **32**, 476.
[8] MURZA, M. M., TATAUROV, G. P., POPOV, L. I., and SVETKIN YU, S., 1977, *Z. Org. Khim.*, **13**, 1046.
[9] GRAY, G. W., 1969, *Mol. Cryst. liq. Cryst.*, **7**, 127.
[10] BEGUIN, A., and DUBIOS, J. C., 1979, *J. Phys. (Paris)*, **40**, 9.
[11] LEBARNY, P., REVAUX, G., and DUBIOS, J. C., 1985, *Mol. Cryst. liq. Cryst.*, **127**, 413.
[12] CHANG-H., HSINE, and GING HO HSINE, 1994, *Liq. Cryst.*, **16**, 469.
[13] PUGH, C., ANDERSON, S. K., and PERCEC, V., 1991, *Liq. Cryst.*, **10**, 229.
[14] VINEY, C., BROWN, D. J., DANNIELS, C. M., and TWIEG, R. J., 1993, *Liq. Cryst.*, **13**, 95.
[15] PUGH, C., and PERCEC, V., 1991; *Chem. Mater.*, **3**, 107.
[16] YULIAN, X., CHEN, Q., and WEN, J., 1993, *Liq. Cryst.*, **15**, 915.
[17] WEN, J., XU, Y., and CHEN, Q., 1994, *J. Fluorine Chem.*, **66**, 15.
[18] WEN, J., TIAN, M., and CHEN, Q., 1994, *Liq. Cryst.*, **16**, 445.
[19] XU, Y, FAN, P., CHEN, Q., and WEN, J., 1994, *J. Chem. Research*, 240.
[20] XU, Y., CHEN, Q., and WEN, J., 1994, *Mol. Cryst. liq. Cryst.*, **241**, 243.
[21] WEN, J., XU, Y., TIAN, M., and CHEN, Q., 1994, *Ferroelectrics*, **148**, 129.
[22] WEN, J., YU, H., and CHEN, Q., 1994, *J. mater. Chem.*, **4**, 1715.
[23] WEN, J., YIN, H., TIAN, M., and CHEN, Q., 1995, *Chinese J. Chem.*, **13**, 73.
[24] OSMAN, A., 1982, *Mol. Cryst. liq. Cryst.*, **16**, 445.
[25] CARR, N., and GRAY, G. W., 1985, *Mol. Cryst. liq. Cryst.*, **124**, 27.
[26] NGUYEN, H. T., GASPROUX, H., and DESTRADE, C., *Mol. Cryst. liq. Cryst.*, **123**, 271.
[27] GOTO, Y., KITANO, K., and OGAWA, T., 1989, *Liq. Cryst.*, **5**, 225.
[28] ZHANG, Y., and WEN, J., 1990, *J. Fluorine Chem.*, **49**, 533.
[29] WEN, J., TIAN, M., and CHEN, Q., 1995, *Mol. Cryst. liq. Cryst.* (in the press).
[30] DEMUS, D., and RICHTER, L., 1978, *The Texture of Liquid Crystals* (Leipzig: VEB Deutcher Verlag fur Grundstoff industrie).
[31] GRAY, G. W., and GOODBY, J. W., 1984, *Smectic Liquid Crystals – Textures and Structures* (Glasgow: Leonard Hill).
[32] WEN, J., and YIN, H., 1995 (to be published).
[33] YIN, H., 1995, Masters Thesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.
[34] PUGH, C., and PERCEC, V., 1990, *Mol. Cryst. liq. Cryst.*, **178**, 193.
[35] PUGH, C., and PERCEC, V., 1991, *Mol. Cryst. liq. Cryst.*, **195**, 185.
[36] PUGH, C., and PERCEC, V., 1990, *J. Polym. Sci. Polym. Chem. Ed.*, **28**, 1101.
[37] WEN, J., YIN, H., TIAN, M., and CHEN, Q., 1995, *Liq. Cryst.* (in the press).