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Synthesis and mesomorphic properties of 4-*n*-alkoxy 4′-[4-((4-*n*-alkoxy-2,3,5,6-tetrafluorophenyl)ethynyl)benzyloxy]benzoates

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Two series of tolane-based liquid crystals have been prepared that incorporate a tetrafluorophenyl moiety and a flexible methyl ether bond into the core structure. The mesomorphic properties have been studied by polarizing microscopic textural observation and DSC measurements. By comparison with their non-fluorinated analogues, the effect of tetrafluorophenylene on mesomorphic behaviour has been discussed in this paper.

1. Introduction

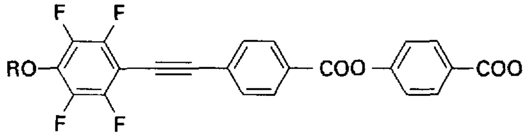
Since liquid crystals with excellent physical properties are indispensable to development of liquid crystal display (LCD) technology, an increasing amount of research has been carried out on the synthesis of liquid crystals so as to search out new potential materials for display devices and other applications.

Recently, considerable attention has been paid to the synthesis of tolane-based liquid crystals, which possess both low viscosity and high birefringence [1–4].

The fluorine atom combines a large electronegativity with a small size, which significantly affects the physical properties of molecules without eliminating the possibility of mesophase formation. In recent years, liquid crystals containing fluorine atoms in the benzene rings or alkyl chains have been extensively studied in order to find new liquid crystals with better physical properties; a lot of liquid crystalline materials with mono-fluoro, difluoro or trifluoro-substituted aromatic rings have been prepared [4–8]. However, only a few liquid crystals with tetrafluorophenylene have been reported [9, 10]. 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 available data for monofluoro- difluoro- or trifluoro-substitutions.

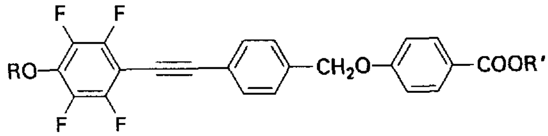
Therefore, we aimed to synthesize some new tolane-based liquid crystals with 2,3,5,6-tetra-fluoro-1,4-phenylene in the core structure so as to obtain new materials for applications [11].

In our previous paper [12], we reported a new family of liquid crystals with the following structure:



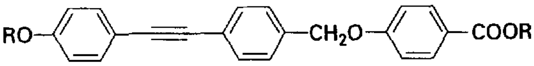
$R = n - C_mH_{2m+1}$; $R' = n - C_nH_{2n+1}$

which exhibit enantiotropic S_A and N phases. Because of the increasing diversification in the application of LCDs (outdoor, car dash-board etc.), properties like low viscosity and chemical stability are becoming more important. In previous publications [13, 14], it was demonstrated that a methyl ether linkage would lead to more chemical and thermal stable LCDs with low viscosity. In this paper, we wish to report the synthesis and mesomorphic properties of liquid crystals containing flexible methyl ether bond and discuss the relationship between mesomorphic properties and structures:



$R = n - C_nH_{2n+1}$, $R' = n - C_mH_{2v+1}$ **A**: $n = 1$–9, $m = 5$;
B: $n = 8$, $m = 1$–5

In order to investigate the effect of tetrafluorination on mesomorphic properties, we also prepared non-fluorinated analogues ($m = 8$);



$R = n - C_nH_{2n+1}$; $R' = n - C_mH_{2m+1}$

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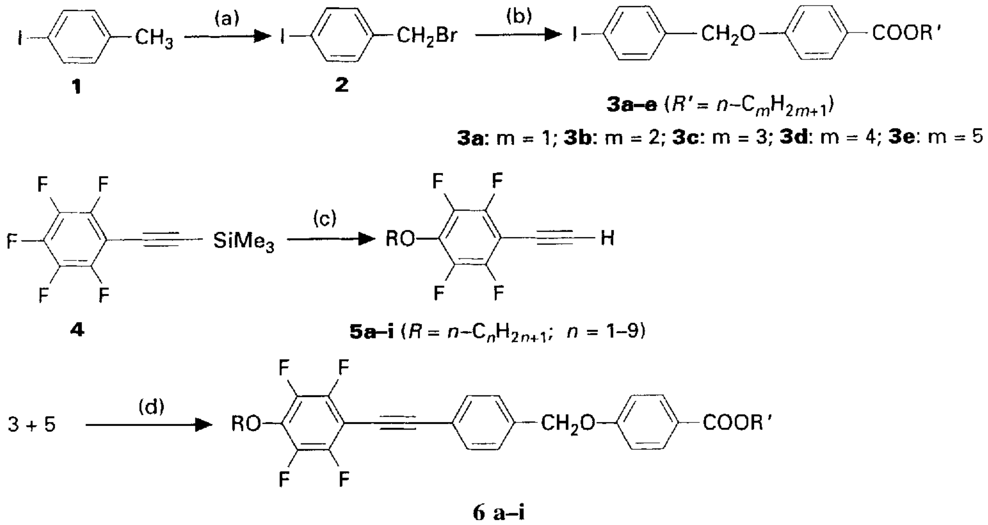
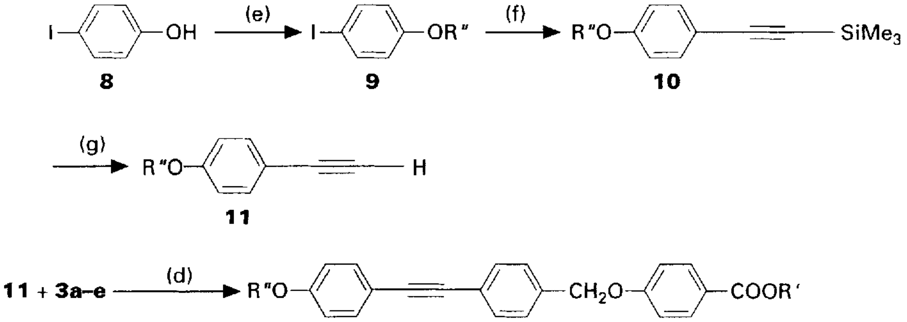


$R = n - C_nH_{2n+1}$, $R' = n - C_mH_{2m+1}$ **A**: $n = 1$–9, $m = 5$; **B**: $n = 8$, $m = 1$–5 (a) NBS. CCl_4, AIBN, Reflux; (b) NaOH, HO–C_6H_4–$COOC_mH_{2m+1}$, DMF; (c) K_2CO_3, DMF, $H(CH_2)_nOH$; (d) CuI, Et_3N, $(PPh_3)_2PdCl_2$, Reflux

Scheme 1. The preparation of compounds in series **A** and **B**.



12a–e ($R'' = n - C_8H_{17}$, $R' = n - C_mH_{2m+1}$, $m = 1$–5) (e) NaOH, R''Br, DMF; (f) HC≡CSiMe$_3$, CuI, Et_3N, $(PPh_3)_2$ $PdCl_2$; (g) NaOH, CH_3OH, r.t

Scheme 2. The preparation of nonfluorinated compounds (in series **C**).

The mesomorphic properties of these target compounds have been studied by polarizing microscopy and differential scanning calorimetry (DSC).

2. Synthesis

The target molecules were prepared according to Scheme 1.

Compound **2** was prepared from a free radical reaction induced by initiator AIBN in CCl4. The important intermediates **3a–e** were easily synthesized via a convenient condensation reaction between compound **2** and the corresponding 4-hydroxy benzoate. The 4-*n*-alkoxy-2,3,5,6-tetrafluorophenylacetylenes (**5a–i**) were obtained by nucleophilic substitution on the starting material **4** at room temperature using K_2CO_3 as the base [15]. The target molecules **6a–i** were easily synthesized by a palladium-catalysed Heck reaction.

The synthesis of the non-fluorinated analogues have been illustrated in the scheme 2, which followed the procedures used in our previous report [16].

3. Experimental

The structures of the intermediates and the final compounds were elucidated by previous spectral methods. IR spectra were determined on a Shimadzu IR-440 spectrometer using a KBr disc pellet. ^{1}H NMR spectra, with TMS as the internal standard and $CDCl_3$ as the solvent, were run on 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 Spectra. The phase transition temperatures of the target compounds have been measured visually by optical microscopy using a polarizing Olympus PM-6 microscope fitted with a Mettler FP 52 heating stage and a FP 5 control unit. The phase identification was determined by comparing the observed textures with those in the literature [17, 18]. All target molecules were also studied by differential scanning calorimetry using a Shimadzu DSC-50 instrument (rate 5°C min^{-1}), and phases were confirmed by DSC analysis.

3.1. *4-Iodobenzyl bromide* (*compound* **2**)

In a 50 ml round bottom flask, *N*-bromosuccinimide (NBS) (850, 4·77 mmol) and azo-bis-isobutylnitrile (AIBN) (75 mg, 0·46 mmol) were added to a solution of *p*-iodotoluene (1·0 g, 4·59 mmol) in dry CCl_4 (15 ml). The resulting mixture was stirred under reflux and isolated under N_2 until TLC revealed a complete reaction. The resulting suspended substance was filtered and washed with dry CCl_4. The filtrate was concentrated to give a pale-red residue which was purified by column chromatography on silica gel with petroleum ether (b.p. 60–90°C) as eluent to yield white flaky crystals of compound **2**. Yield 0·83 g (61·0 per cent). m.p. 77·4°C. ^{1}H NMR δ_H 60 MHz, solvent CCl_4, standard TMS): 4·38 (s, 2 H, $ArCH_2Br$), 7·03 (d, 2 H, $J = 8·0$ Hz, ArH ortho to CH_2Br), 7·70 (d, 2 H, $J = 8·0$ Hz, ArH ortho to I) ppm.

3.2. *Pentoxy 4-(4-iodobenzyloxy) benzoate* (*compound* **3e**)

To a solution of *n*-pentoxy 4-hydroxybenzoate (2·11 g, 10·1 mmol) in DMF (30 ml) was added NaOH (406 mg, 10·1 mmol) and stirred at 110–130°C for 15 min until all the NaOH was dissolved. A solution of compound **2** (3·00 g, 10·1 mmol) was then added to the cooled mixture. The resulting mixture was stirred at 120°C until TLC analysis revealed a complete reaction. The mixture was cooled to room temperature, 20 ml H_2O added extracted with ether (3 × 30 ml). The extract was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel with petroleum ether (b.p. 60–90°C) as the eluent to give white crystals of compound **3e** (2·97 g, 69·3 per cent). m.p. 37·2°C. ^{1}H NMR δ_H 90 MHz, solvent CCl_4, standard TMS): 0·78 (t, 3 H, $J = 6·0$ Hz, CH_3), 0·8–1·9 (m, 6 H), 4·08 (t, 2 H, OCH_2), 4·88 (s, 2 H, $ArCH_2OAr$), 6·96 (d, 2 H, $J = 8·0$ Hz, ArH), 7·52 (d, 2 H, $J = 8·0$ Hz, ArH) ppm.

Compounds **3a–d** were prepared similarly. Compounds **5a–i** were prepared by the nucleophilic reaction reported previously [15].

3.3. *n-Pentoxy 4-[4-((4-n-octyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)benzyloxyl]benzoate* (*compound* **6h**)

A typical procedure: Under nitrogen 20 ml of anhydrous triethylamine was added to a mixture of compound **3h** (292 mg, 0·68 mmol), (4-*n*-octyloxy-2,3,5,6-tetrafluorophenyl) acetylene (200 mg, 0·66 mmol), bis(triphenylphosphine)palladium dichloride (30 mg, 0·04 mmol) and copper(I) iodide (15 mg, 0·08 mmol). The resulting mixture was stirred under reflux until analysis by TLC revealed a complete reaction. The cooled mixture was filtered and 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 ethylacetate (20 : 1) as eluent to give pale-yellow crystals which were recrystallized from acetone–methanol to yield white crystals of compound **6h**. Yield: 370 mg (93·6 per cent). ^{1}H NMR δ_H (90 MHz, solvent $CDCl_3$, standard TMS): 0·56–2·06 (m, 24 H), 4·13 (t, 4 H, $J = 6·0$ Hz, CO_2CH_2, RCH_2O), 5·01 (s, 2 H, $ArCH_2OAr$), 6·81 (d, 2 H, $J = 8·0$ Hz, ArH), 7·81 (d, 2H, $J = 8·0$ Hz, ArH), 7·28d, 2H, $J = 8·0$ Hz, ArH), 7·47dd, 2H, $J = 8·0$ Hz, ArH) ppm; ^{19}F NMR δ_F (60 MHz, solvent $CDCl_3$, standard TFA): 59·10 (m, 2 F, F arom.), 79·30 (m, 2 F, F arom.), IR (KBr) ν: 2920, 2810, 1710, 1610, 1500, 1270, 1250, 1170, 1100, 980, 820 and 690 cm^{-1}. MS *m/z* (rel. int.): 598 (M^+, 1·7), 511 (M^+-87, 5·4), 391 (M^+-207, 92·7), 179 (100). Elemental analysis: $C_{35}H_{38}F_4O_4$ calculated C, 70·22, H, 6·40, F, 12·69; found: C, 70·10, H, 6·45, F, 12·47 per cent.

All of these new compounds **6a–m** and **12a–e** were prepared similarly; they all have satisfactory elemental analysis and appropriate IR, MS, ^{1}H and ^{19}F NMR spectra data.

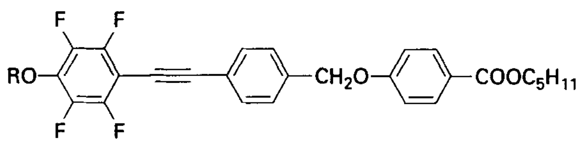
4. Results and discussion

4.1. *Phase transition temperatures*

It is now well established that fluoro-substituents can improve certain characteristics of a material or may completely change its nature. The effect on the transition temperatures of compounds by lateral fluoro-substitution in aromatic rings is well documented and often confers remarkable changes in mesotypes and transition temperatures [4–10]. Generally, melting points are depressed, often quite substantially. Smectic phases (especially high-order smectic phases) are usually much more depressed than the nematic phase, although smectic phases are upheld by the presence of a fluoro-substituent on the outer edge of the core. Fluoro-substitution has, therefore, been successfully used to produce low melting, wide-range nematic materials with a very low smectic tendency. As explained by Gray [19], lateral substituents usually have two opposing effects. That is, while the change in the molecular polarizability may increase the mesophase thermal stability, the decrease in the length/breadth ratio causes a decrease. The latter effect usually dominates.

The phase transition temperatures and enthalpies for

Table 1. Mesomorphic properties of compounds in series **A**.



A: $R = n - C_nH_{2n+1}$, $n = 1–9$.

Compound	*m*	*n*	$T/°C(\Delta H/kJ\ mol^{-1})$			Recryst.
			$Cr–S_A$	$S_A–N$	N–I	
6a	5	1	111·4(41·62)†	—	—	98·9
6b	5	2	104·9(42·75)	(90·7)‡(—)§	(99·8)(0·75)	62·5
6c	5	3	100·7(27·20)	—	—	97·3
6d	5	4	93·0(28·14)	94·6(—)	102·3(0·80)	89·2
6e	5	5	88·1(22·59)	94·2(1·00)	98·4(0·83)	85·2
6f	5	6	89·9(37·74)	95·6(1·29)	98·8(0·99)	83·5
6g	5	7	88·0(36·05)	94·7(1·38)	96·2(0·98)	81·8
6h	5	8	84·3(48·62)	96·6(1·99)	97·3(1·88)	81·5
6i	5	9	84·7(47·62)	96·1(5·86)¶	—	80·2

Cr, Crystal; S_A, Smectic A; N, nematic; I, Isotropic phase. † Phase transition Cr–I; ‡ monotropic; § the phase only observed by polarizing microscopy; ¶ phase transition S_A–I.

materials in Series **A** are listed in table 1 and illustrated in figure 1.

Most of the compounds in series **A** with alkoxy length $n = 4–8$ exhibit enantiotropic smectic A and nematic phases. Compounds **6a** and **6c** show no liquid crystalline phases, whereas **6b** possesses monotropic smectic A and nematic phases. The melting and clearing points both tend to decrease with increasing alkoxy chain length *n*, although the temperature range of the mesophases increases. The tendency of the compound to have nematic properties decreases, whereas its tendency to exhibit smectic properties increases. Compound **6i** exhibits only the enantiotropic smectic A phase for $n = 9$.

To study the influence of the alkoxy chain length in the benzoates, we have synthesized the compounds of series **B**. Their phase transition properties are summarized in table 2 and figure 2.

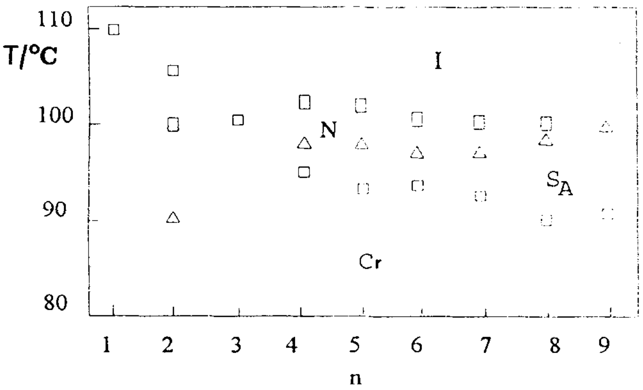
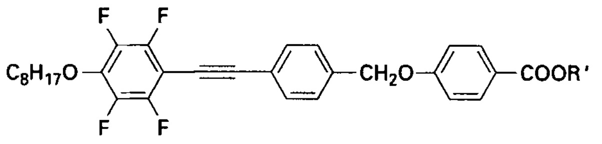


Figure 1. Transition temperatures of series **A** as a function of *n*. Melting point (□); S_A–N (△); N–I (□).

In table 2 and figure 2, all of the compounds of series **B** exhibit an enantiotropic smectic A and nematic phases; by increasing the alkoxy length *m*, the melting and clearing points decrease similarly to those of compounds of series **A**. However, the variation of the alkoxy length *m* has a dramatic effect on the influence of the melting points than that in series **A**. Moreover, with increasing the alkoxy chain length, the temperature ranges of the nematic phases are depressed whereas that of the smectic A phase changes irregularly. However, the whole temperature ranges of the mesophases is narrowed, but the mesophase temperature ranges of compounds of series **A** is widened. The clearing points of compounds of series **A** demonstrate an odd–even effect with the even-numbered compounds being higher than that of odd-numbered compounds; whereas compounds in series **B** show an opposite odd–even effect, i.e. the clearing points of the odd-numbered compounds are higher than those of even-numbered ones. Comparing the thermal properties of the two series, we find that the variation of the alkoxy length of the tetrafluorophenyl ring plays a less important role than the change of the alkoxy chain length of the benzoate ring in influencing the melting points and the temperature ranges of the mesophases. We suppose that those differences contribute to the steric effect of the alkoxy group attaching to the benzoate ring so that the length/breadth ratio decreases, which damages the alignment of the target molecules.

In order to investigate the effect of substitution –COO– with the more flexible methyl ether bond in our desired

Table 2. Phase transition temperatures and enthalpies for series **B**.



B: $R' = n - C_mH_{2m+1}$, $m = 1$–5.

Compound	m	n	T/°C(ΔH/kJ mol^{-1}) Cr–S$_A$	S$_A$–N	N–I	recryst.
6j	1	8	110·1 (39·06)	127·3 (0·15)	140·5 (1·32)	93·5
6k	2	8	94·4 (43·36)	102·8 (0·41)	115·2 (1·56)	88·5
6l	3	8	91·0 (40·25)	101·9 (0·62)	109·3 (1·18)	87·1
6m	4	8	88·7 (29·21)	90·6 (1·32)	93·2 (1·15)	84·5
6n	5	8	84·3 (48·62)	96·6 (1·99)	97·3 (1·38)	81·5

Cr, Crystal; S$_A$, Smectic A; N, Nematic; I, Isotropic phase.

molecules, we list some of our previous results in table 3 [12].

As we reported previously, the melting points of compounds with the flexible methyl ether bond is lower than that of compounds with an ester bond. But from table 3, we obtain contrary results. Except for the dramatic depression in the temperature range of mesophases, the liquid crystals with two such kinds of linking bridges show many common mesomorphic properties. Especially, the change of alkoxy chain length attaching to the benzoate ring plays a more important role in influencing the thermal behaviour of the liquid crystals, as we have discussed in the previous section. Generally, the liquid crystals with a flexible methyl ether bond possess low viscosity and other physical properties better than those of liquid crystals with an ester bond, which are under investigation.

As we mentioned previously, 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 available data for monofluoro-, difluoro- or trifluoro-substitution. It is necessary to investigate the effect of tetrafluorophenyl-substitution on the mesomorphic properties to enlarge our understanding of fluorinated liquid crystals. Therefore, we synthesized the non-fluorinated analogues of series **A** and **B** ($n = 8$) and the results are summarized in table 4 and figure 3.

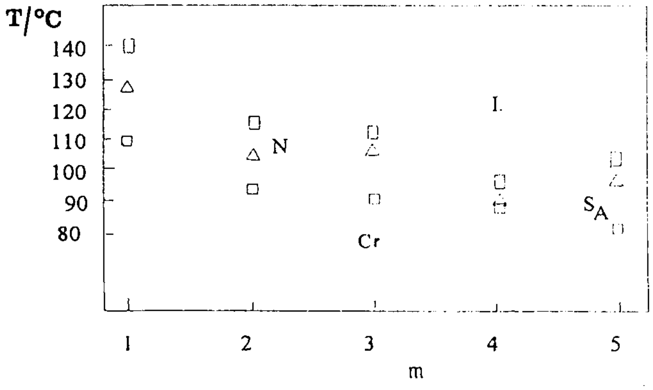
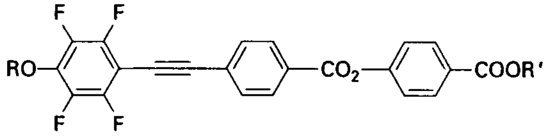


Figure 2. Transition temperatures of series **B** as a function of *m*. Melting point (□); S$_A$–N (△); N–NI (□).

Table 3. Transition temperatures and enthalpies of liquid crystals containing an ester bond in backbone.

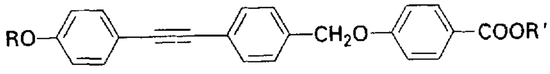


$R = n - C_mH_{2m+1}$; $R' = n - C_nH_{2n+1}$

m	n	T/°C(ΔH/kJ mol^{-1}) Cr–S$_A$	S$_A$–N	N–I	Recryst.
1	5	97·8 (30·55)†	—	169·4 (0·39)	98·9
2	5	97·5 (40·50)	123·6 (0·06)	179·1 (0·51)	73·0
3	5	87·7 (32·02)	134·5 (0·44)	174·3 (0·53)	68·4
4	5	86·3 (22·15)	148·6 (0·89)	176·4 (0·61)	64·0
5	5	82·5 (24·76)	149·3 (0·75)	168·3 (0·31)	64·8
6	5	76·3 (20·24)	149·2 (0·85)	164·3 (0·48)	62·3
7	5	75·5 (28·26)	145·6 (1·04)	156·0 (0·39)	57·3
8	1	104·6 (26·93)	169·8 (0·24)	212·5 (0·75)	90·8
8	2	80·6 (25·03)	154·2 (0·64)	182·9 (0·67)	70·6
8	3	68·0 (27·70)	147·8 (0·61)	169·8 (0·64)	61·2
8	4	80·7 (30·01)	144·9 (1·20)	154·2 (0·60)	60·2
8	5	65·4 (25·9)	144·5 (1·16)	153·0 (0·75)	58·0

Cr, Crystal; S$_A$, Smectic A; N, Nematic; I, Isotropic Phase; † S$_A$–I.

Table 4. Mesomorphic properties of non-fluorinated analogues.



$R = n - C_nH_{2n+1}$; $R' = n - C_mH_{2m+1}$

		T/°C (ΔH/kJ mol^{-1})				
n	m	m.p.	CrE–S_B	S_B–S_C	S_C–S_A	S_A–I
8	1	111·9 (17·6)	(94·1)†(2·37)	153·5 (3·31)	—	177·8 (6·33)
8	2	91·7 (3·66)	(71·3) (1·34)	130·4 (3·09)	—	161·5 (6·24)
8	3	97·4 (14·97)	—	120·0 (3·80)	122·6 (—)†	156·4 (6·53)
8	4	76·5 (7·38)	(51·5) (0·28)	115·8 (2·49)	129·4 (—)	144·8 (4·45)
8	5	86·3 (13·64)	—	116·4 (3·26)	133·5 (—)	145·9 (6·46)

m.p., Melting point; CrE, crystal E; S_A, S_B, S_C, Smectic A, B, C, respectively; I, isotropic phase.
† Monotropic; ‡ enthalpies are too small to be measured by DSC.

In table 4 and figure 3, compounds **12 a**, **12 b** and **12 d** show monotropic CrE and enantiotropic S_B and S_A phases, whereas **12 c** and **12 e** exhibit enantiotropic S_B and S_A phases, and enantiotropic S_C phases exist when $n > 2$. The melting and clearing points both tend to decrease as the alkoxy length increases, but the temperature range of the mesophase is slightly narrowed. And the depression of the melting point of compounds with tetrafluorophenyl group are not obvious. Moreover, the introduction of the tetrafluorophenyl moiety conduces to the formation of a nematic phase with less types of smectic phases, which is similar to monofluoro, difluoro- or trifluoro-substitution on the benzene ring [4–10].

4.2. *Differential scanning calorimetric studies*

These studies were performed on a Shimadzu DSC-50 instrument with the scanning rate 5°C min^{-1} and the results are listed in tables 1, 2 and 3. The melting enthalpies for series **A** and **B** vary from 22·59 kJ mol^{-1} to 48·62 kJ mol^{-1}. In both series, the melting enthalpies vary irregularly with the change of the alkoxy chain length of m or n. For series **B**, the enthalpies of the S_A–N transition increase with increasing alkoxy chain length, but those of series **A** change irregularly. As for series **B**, the enthalpies of the S_A–N and N–I transitions increase as the alkoxy chain length grows longer, but the former is larger than that of the latter with the same alkoxy length.

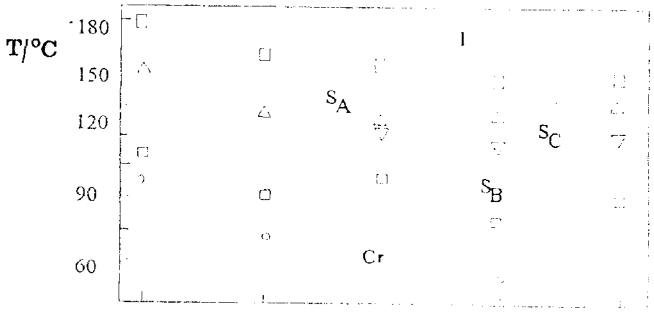


Figure 3. Transition temperatures of series **C** as a function of m. Melting point (□); S_B–CrE (°); S_B–S_C(▽); S_C–S_A (△); S_A–I. (□).

Another phenomenon that should be pointed out is that the melting enthalpies of non-fluorinated analogues are smaller than those of the fluorinated liquid crystals because of the increasing molecular interaction with the introduction of fluorine atoms.

5. Conclusions

In this paper two series of novel tolane-based liquid crystals containing a tetrafluorophenyl moiety and a flexible methyl ether bond in the backbones have been synthesized as well as their non-fluorinated analogues. Polarizing textural observation and DSC analysis show that these target compounds with the introduction of a tetrafluorophenyl moiety and flexible methyl ether linkage to the backbone brought about several unique properties:

(i) For series **A**, the tendency of a compound to have nematic properties decreases, whereas its tendency to exhibit smectic properties increases with the increasing alkoxy chain length. The variation of the alkoxy chain length of the tetrafluorophenyl ring plays a less important role than that of the benzoate ring in influencing the melting and clearing points as well as the temperature range of the mesophases. The clearing points of series **A** exhibit an odd–even effect, whereas those of series **B** show an opposite alternation effect.

(ii) By comparison with their analogues with an ester linkage, the melting points of the liquid crystals containing an ether bond increase, which is different from our previous report [12].

(iii) Comparison with non-fluorinated analogues, the depression of the melting point is not so obvious with the introduction of the tetrafluorophenyl moiety, but the temperature ranges of the mesophases is slightly narrowed with this modification. Liquid crystals containing tetrafluorophenylene are conductive to the formation of the nematic phase as well as the simplification of mesomorphic smectic types, which is similar to that of the less fluorinated liquid crystals [4–10].

(iv) Moreover, other physical properties of these liquid crystals containing a tetrafluorophenylene moiety and a flexible methyl ether bond are currently under investigation.

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