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Synthesis and mesomorphic properties of some homologues of fluorinated 4-chlorobenzoate-tolanes

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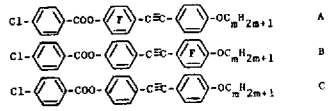
Three homologues series of 4-chloro-substituted benzoate-tolanes were prepared. Thermal optical microscopy and DSC analysis show that these compounds are liquid crystalline. The effect on the mesomorphic properties of different positions of the perfluorophenyl in the molecular core unit is discussed.

1. Introduction

Recently, more and more scientists are interested in fluorinated liquid crystals. Fluorine, as a lateral substituent leads to a subtle modification of physical properties because of its small size and high electronegativity. Liquid crystals containing a perfluorinated phenyl group have been studied for several years [1–6]. Our group recently reported some fluorinated tolanes [7–11]. The perfluorophenyl-containing liquid crystals show low melting points, tendency to form the smectic C phase, give high P_s values, etc.

In the course of our work regarding the synthesis and mesomorphic properties of fluorinated tolane liquid crystals, it became of interest to study the tolanes with perfluorinated phenyl in different positions of the core unit. The work reported here presents two chloro-substituted benzoate-tolanes containing perfluorinated phenyl (series **A** and **B**) and a non-fluorinated homologues (series **C**). Compounds **A** contain the perfluorinated phenyl at the centre of the core unit and compounds **B** have the perfluorinated phenyl at the side of the core unit.



The thermaltropic behaviour of these compounds is reported. In addition, the effect of the position changes of the perfluorophenyl in the molecular core was investigated.

2. Experimental

Transition temperatures were determined by thermal polarizing light microscopy in conjunction with a Mettler FP 52 hot stage and FP 5 control unit. The enthalpies were determined by differential scanning calorimetry using a Shimadzu-DSC50 system. Infrared spectra were obtained using a Shimadzu IR-440 spectrophotometer. ^{1}H NMR with TMS as internal standard or $CHCL_3$ as external standard and ^{19}F NMR with TFA (trifluoroacetic acid) as external standard were recorded on Varian EM390 and Varian EM360L, respectively. For ^{19}F NMR spectra, high field is positive. Mass spectra were determined using HP5989A spectrometer.

The general method for preparing the 4-(4-*n*-alkoxyphenyl)acetylenyl 2,3,5,6-tetrafluorophenyl 4′-chlorobenzoate (series **A**) is shown in Scheme 1.

4-Iodo 2,3,5,6-tetrafluorophenol was prepared from pentafluoroiodobenzene by treated with potassium hydroxide using *tert*-butanol as solvent. The intermediate, 4-iodo 2,3,5,6-tetrafluorophenyl 4′-chlorobenzoate was obtained from a one-pot esterification in mild conditions between 4-chlorobenzoic acid and 4-iodo 2,3,5,6-tetrafluorophenyl in the presence of dicyclohexylcabodiimide (DCC) and 4-pyrrolidinopyridine (PPY) in dried dichloromethane. Another important intermediate, 4-alkoxyphenylacetylenes, were obtained from the original material 4-iodophenol. Firstly, 4-iodophenol was protected with acetyl chloride to give 4-iodophenylacetate. This ester was coupled with trimethylsilylacetylene to give 4-iodophenylacetate. The protecting groups were then removed by treated with sodium hydroxide to yield 4-hydroxyphenylacetylene. This acetylene was substituted with a bromoalkene to give the corresponding 4-*n*-alkoxyphenylacetylene. The 4-iodophenyl 4′-chlorobenzoate was coupled with corresponding 4-*n*-alkoxyphenylacetylene to obtain the appropriate members of series **A**.

The procedure to obtain 4-(4-*n*-alkoxy 2,3,5,6-tetrafluorophenylacetylenyl)phenyl 4′-chlorobenzoates (series **B**) was illustrated in Scheme 2.

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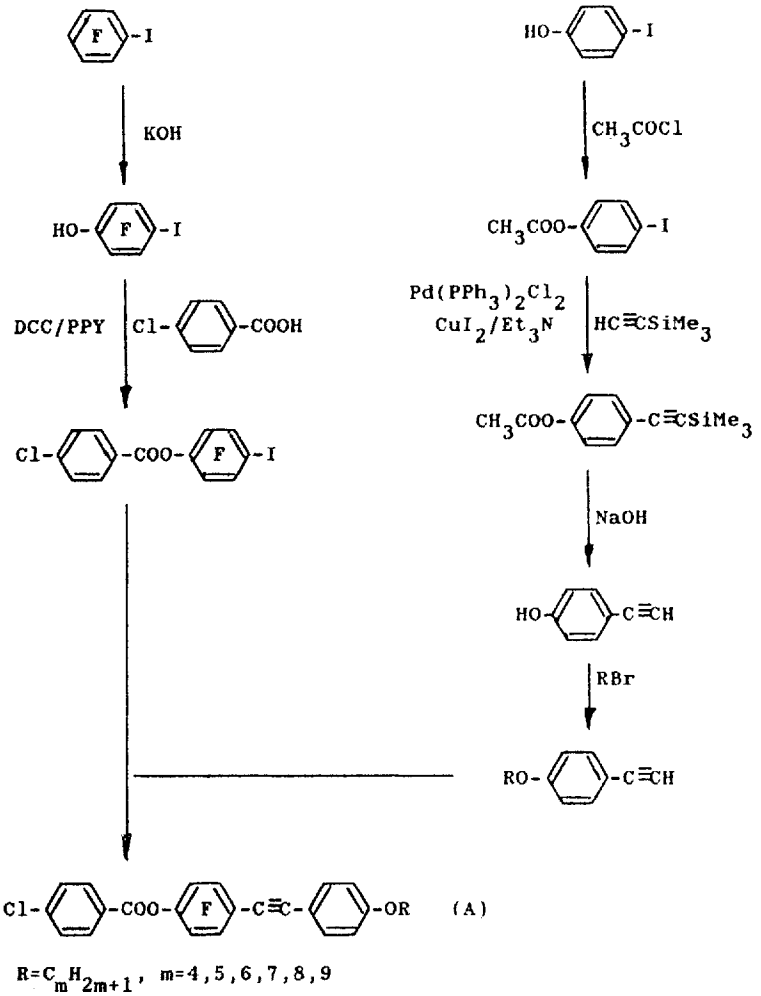


Scheme 1.

Firstly, 4-chlorobenzoic acid was esterified with 4-iodophenol to give 4-iodophenyl 4′-chlorobenzoate. Then this ester was coupled with 4-alkoxy 2,3,5,6-tetrafluorophenylacetylene [12] to give corresponding members of series **B**.

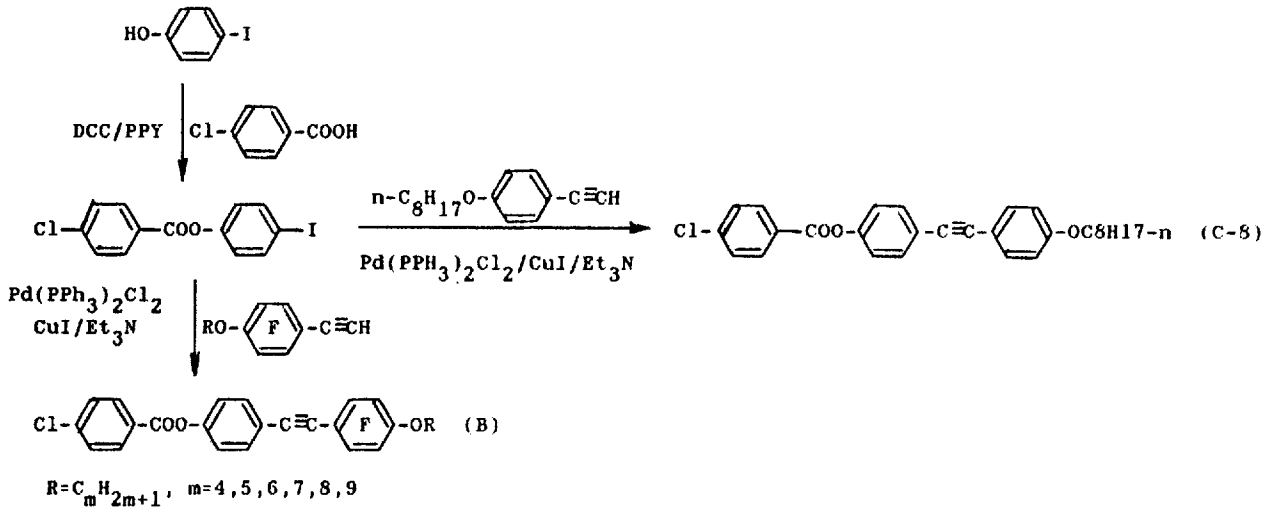
Compound **C-8**, 4-(4-*n*-octyloxyphenylacetylenyl)-phenyl 4′-chlorobenzoate, was prepared from 4-iodophenyl 4′-chlorobenzoate coupling with 4-*n*-octyl-oxyphenylacetylene (Scheme 2).

2.1. *Preparation of 4-iodo 2,3,5,6-tetrafluorophenol*

14·7 g (50 mmol) of pentafluoroiodobenzene, 8·4 g (150 mmol) of potassium hydroxide and 30 ml of *tert*-butanol were refluxed for 6·5 h. ^{19}F NMR analysis of the reaction mixture showed that the reaction was complete. 20 ml of 5 per cent aqueous hydrochloric acid was added to it and the aqueous solution of *tert*-butanol (about 22 ml) was distilled off. The residue was acidified with 30 ml of 5 per cent aqueous hydrochloric acid and cooled. After standing for 30 min, white crystals formed. The mixture was filtered and the crystals washed with cooled ethanol. The filtrate was extracted with ether and dried over anhydrous sodium sulphate. The sodium sulphate was removed by filtration, the solvent removed under reduced pressure and the residue dried *in vacuo* to give a white solid. This solid was combined with the former white crystals to yield the product, 12·8 g (88 per cent). ^{1}H NMR (CCl_4), δ 6·0 (s, OH); ^{19}F NMR (CCl_4) δ 48·35 (d, 2 F, J = 18·8 Hz), 83·60 (d, 2 F, J = 18·8 Hz). m.p. 46·0–46·5°C.

2.2. *Preparation of 4-iodo 2,3,5,6-tetrafluorophenyl 4′-chlorobenzoate*

1·57 g (10 mmol) of 4-chlorobenzoic acid, 2·92 g (10 mmol) of 4-iodo 2,3,5,6-tetrafluorophenol, 2·27 g (11 mmol) of *N,N*-dicycloxylcarbodiimide (DCC) and 74 mg (0·5 mmol) 4-pyrrolidinopyridine (PPY) were added to 50 ml of dried dichloromethane. The mixture was stirred at room temperature for 40 h. ^{19}F NMR analysis revealed complete reaction. The white precipitate was



Scheme 2.

filtered and the filtrate was washed with 5 per cent aqueous acetic acid and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure. The crude yellow product was purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (30:1) as eluent to yield a white solid, 2·75 g (64 per cent), m.p. 115·8–117·0°C. ^{1}H NMR ($CDCl_3$), δ 8·05 (d, 2 H) 7·44 (d, 2 H), (AA'BB', J = 7·5 Hz, arom. H), ^{19}F NMR ($CDCl_3$) δ 42·4 (d, 2 F, J = 18·8 Hz), 73·2 (d, 2 F, J = 18·8 Hz).

2.3. *Preparation of trimethylsilylacetylenylphenyl acetate*

4'-iodophenylacetate was obtained by typical esterification with acetylchloride and 4-iodophenol. *Trimethylsilylacetylenylphenyl acetate*. 7·86 g (30 mmol) or 4-iodophenylacetate, 70 mg (0·1 mmol) of bis(triphenylphosphine)palladium dichloride, 38 mg (0·2 mmol) of copper(I) iodide and 50 ml of dried triethylamine were stirred under nitrogen, and 2·94 mg (30 mmol) of trimethylsilylacetylene added by syringe. The mixture was stirred at 30–35°C for 48 h. TLC analysis indicated complete reaction. The precipitate was filtered off and washed with ether. The filtrate was washed and dried and the solvent removed under reduced pressure to yield 7·90 g of a grey solid. This crude produced was used in the next reaction without further purification. ^{1}H NMR ($CDCl_3$) δ 7·67 (d, 2 H), 7·03 (d, 2 H), (AA'BB', J = 9 Hz, arom. H), 2·30 (s, 3 H, CH_3), 0·28 (s, 9 H, $(CH_3)_3$).

2.4. *Preparation of 4-hydroxyphenyl acetylene*

5·80 g (25 mmol) of crude trimethylsilylacetylenylphenyl acetate in 50 ml of methanol and 10 ml acetone was treated with 2·0 g (50 mmol) of sodium hydroxide at room temperature for 12 h. TLC analysis indicated complete reaction. Most of the solvent was removed under reduced pressure and 50 ml of 10 per cent aqueous hydrochloric acid added to the mixture. The black precipitate was filtered off and washed with ether. The filtrate was extracted with ether, washed, dried and concentrated by evaporating *in vacuo* to give a brown oil. The crude product was purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (9:1) to yield pale yellow liquid, 1·92 g (65 per cent, by comparison with 4-iodophenyl acetate). ^{1}H NMR (CCl_4), δ 7·09 (d, 2 H)/6·52 (d, 2 H), (AA'BB', J = 9 Hz, arom. H), 2·67 (s, 1 H, C≡CH).

2.5. *Preparation of 4-n-alkoxyphenylacetylene*

The typical method of preparing 4-*n*-alkoxyphenylacetylene: *4-n-Nonyloxyphenyl acetylene*: 590 mg (5 mmol) of 4-hydroxyphenyl acetylene and 1·55 g (7·5 mmol) of 1-bromononane were treated with 220 mg (5·5 mmol) of sodium hydroxide and 20 ml of DMF and refluxed for 4 h. TLC analysis revealed that the reaction was over. The mixture was washed with 5 per cent aqueous hydrochloric acid and dried over anhydrous sodium sulphate. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (10:1) to yield pale yellow liquid, 890 mg (74 per cent). ^{1}H NMR (CCl_4), δ 7·14 (d, 2 H)/6·54 (d, 2 H), (AA'BB', J = 9 Hz, arom. H), 3·70 (t, 2 H, J = 6 Hz, OCH_2), 2·67 (s, 1 H, C≡CH), 0·8–2·0 (m, 13 H, $(CH_2)_5CH_3$).

2.6. *Preparation of 4-(4-n-alkoxyphenyl)acetylenyl 2,3,5,6-tetrafluorophenyl 4'-chlorobenzoates (series A)*

The typical method of preparing 4-(4-*n*-alkoxyphenyl)acetylenyl 2,3,5,6-tetrafluorophenyl 4'-chloro-

benzoates (series **A**): *4-(4-*n*-nonyloxyphenyl)acetylenyl 2,3,5,6—tetrafluorophenyl 4'-chlorobenzoate* (*compound* ***A-9***: 250 mg (0·58 mmol) of 4-iodo 2,3,5,6-tetrafluorophenyl 4'-chlorobenzoate, 20 mg (0·03 mmol) of bis(triphenylphosphine)palladium dichloride, 11·5 mg (0·06 mmol) of copper(I) iodide and 15 ml of dried triethylamine were stirred under nitrogen with 142 mg (0·58 mmol) of 4-*n*-nonyloxyphenyl acetylene was added to them. The resulting mixture was refluxed for 4 h and TLC analysis indicated complete reaction. The precipitate was filtered off and washed with ether. The filtrate was washed, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (100:1) as eluent to give pale yellow solid which was recrystallized from acetone–methanol to yield a white crystal product, 235 mg (74 per cent). ^{1}H NMR ($CDCl_3$), δ 8·16 (d, 2 H), 7·54 (d, 4 H), 6·91 (d, 2 H), (J = 7·5 Hz, arom. H), 4·00 (t, 2 H, J = 6 Hz, OCH_2), 0·8–2·0 (m, 17 H, $(CH_2)_2CH_3$), ^{19}H NMR ($CDCl_3$), δ 59·8 (d, 2 F, J = 18·8 Hz), 76·0 (d, 2 F, J = 18·8 Hz). IR (KBr, cm^{-1}) 2900, 2850, 2200, 1760, 1590, 1515, 1495, 1440, 1400, 1325, 1250, 1170, 1120, 1090, 1035, 1010, 985, 845. Elemental analysis (per cent): Calculated C 65·87, H 4·94, Cl 6·50, F 13·91; Found. C 65·79, H 5·03, Cl 6·54, F 13·56; MS (*m/z*) 546 (M^+).

The other compounds in series **A** were prepared similarly. All of then had satisfactory elemental analyses and appropriate ^{1}H and ^{19}F NMR, IR and MS spectral data.

2.7. *Preparation of 4-iodophenyl 4'-chlorobenzoate*

The synthesis procedure is similar as the preparation of 4-iodo 2,3,5,6-tetrafluorophenyl 4'-chlorobenzoate: 76 per cent yield. m.p. 124·5–125·0°C. ^{1}H NMR ($CDCl_3$), δ 8·14 (d, 2 H), 7·76 (d, 2 H), 7·50 (d, 2 H), 7·00 (d, 2 H), (J = 9 Hz, arom. H).

2.8. *Preparation of 4-(4-*n*-alkoxy 2,3,5,6-tetrafluorophenylacetylenyl)phenyl 4'-chlorobenzoates* (*series* **B**)

Series **B** was obtained by using the procedure described in § 2.7. 4-Alkoxy 2,3,5,6-tetrafluorophenylacetylenes were prepared according to [12]. *4-(4-*n*-Hexyloxy 2,3,5,6-tetrafluorophenyl acetylenyl)phenyl 4'-chlorobenzoate*: 91 per cent yield. ^{1}H NMR ($CDCl_3$), δ 8·14 (d, 2 H), 7·66 (d, 2 H), 7·48 (d, 2 H), 7·26 (d, 2 H), (J = 9 Hz, arom. H), 4·27 (t, 2 H, J = 6 Hz, OCH_2), 0·8–2·0 (m, 11 H, $(CH_2)_4CH_3$); ^{19}F NMR ($CDCl_3$), δ 60·1 (d, 2 F, J = 18·8 Hz), 79·5 (d, 2 F, J = 18·8 Hz); IR (KBr, cm^{-1}) 2900, 2850, 2200, 1725, 1590, 1510, 1490, 1440, 1400, 1395, 1270, 1240, 1210, 1160, 1100, 1070, 980, 880, 845; Elemental analysis (per cent): Calculated C 64·22, H 4·16, F 15·06, Cl 7·04; Found C 64·53, H 4·23, F 14·67, Cl 6·94; MS(*m/z*) 504 ($M^+ - 1$).

The other compounds in series **B** were prepared similarly. All of them had satisfactory elemental analyses and appropriate ^{1}H and ^{19}H NMR, IR and MS spectral data.

2.9. *Preparation of 4-(4-*n*-octyloxyphenyl-acetylenyl)phenyl 4'-chlorobenzoate* (**C-8**)

Compound **C-8** was obtained by using the procedure described in § 2.7. 84 per cent yield. ^{1}H NMR ($CDCl_3$), δ 8·17–6·80 (m, 12 H, arom. H), 3·96 (t, 2 H, J = 6 Hz, OCH_2), 0·8–2·0 (m, 15 H, $(CH_2)_6CH_3$), (m, 11 H, $(CH_2)_4CH_3$); ^{19}F NMR ($CDCl_3$) δ 60·1 (d, 2 F, J = 18·8 Hz), 79·5 (d, 2 F, J = 18·8 Hz); IR (KBr, cm^{-1}) 2900, 2850, 1745, 1610, 1590, 1480, 1400, 1280, 1250, 1160, 1095, 1080, 1015, 880, 840, 825; Elemental analysis (per cent): Calculated C 75·57, H 6·30, Cl 7·71; found C 75·32, H 6·32, Cl 7·34, MS(*m/z*) 460 ($M^+ - 1$).

3. Results and discussion

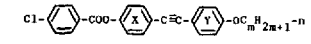
The series **A**, **B** and **C** homologues prepared are shown in the table. The transition temperatures, enthalpy changes (ΔH) and phase temperature ranges (ΔT) for these compounds are also listed in the table. In the figure, the transition temperatures for series **A** and **B** are plotted as a function of the carbon chain length in the *n*-alkoxy substituent.

In series **A**, when m = 4–9, each of the homologues exhibits an enantiotropic nematic phase. The clearing points decrease from 186·3°C to 162·3°C with increasing alkoxy chain length. For series **B**, the perfluorophenyl was present in a different position of the core unit. When m = 4–8, the homologues exhibit the enantiotropic nematic phase with the clearing points dropping from 213·6°C to 179·7°C. Compound **B-9** shows a monotropic smectic C phase as well as an enantiotropic nematic phase with a clearing point of 173·0°C. Compound **C-8**, a non-fluorinated homologues of series **A** and **B**, exhibits an enantiotropic nematic phase and monotropic smectic C phase with a high melting point (132·6°C) and a high clearing point (218·0°C).

The melting enthalpy for compounds **A-4**–**A-9** and **B-4**–**B-9** varies from 50–65 J g^{-1} and the nematic to isotropic transition average enthalpy is 2·06 J g^{-1}. The melting enthalpy for **C-8** is 96·95 J g^{-1} and the nematic to isotropic transition enthalpy is 2·27 J g^{-1}. The nematic to smectic enthalpy values for compounds **B-9** and **C-8** were too small to be measured.

The comparison of compounds of series **A** with series **B** give information about the effect of the different position of the perfluorophenyl group on the mesomorphic properties. The perfluorophenyl in series **A** is at the centre of the core unit whereas in series **B** it is at the side of the core unit in molecule. Firstly, the centre perfluorophenyl

Phase transition temperatures for compounds **A4–9**, **B4–9** and **C-8**.



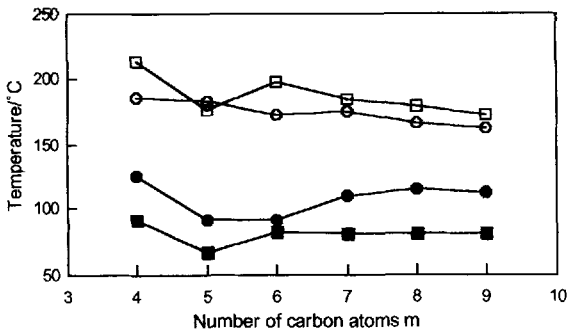
A X = F, Y = H, m = 4, 5, 6, 7, 8, 9.
B X = H, Y = F, m = 4, 5, 6, 7, 8, 9.
C X = H, Y = H, m = 8.

Compound	m	C–N/°C	N–I/°C	ΔT_N/°C	N–S_C/°C	ΔT_{S_C}/°C	N/S_C–C/°C
A-4	4	125·4 [52·19]	186·3 [1·62]	60·9			99·4
A-5	5	91·6 [67·28]	183·2 [2·71]	91·6			60·6
A-6	6	91·3 [67·60]	173·0 [4·40]	81·7			64·9
A-7	7	109·6 [64·96]	175·2 [2·38]	65·6			65·3
A-8	8	115·2 [61·00]	167·0 [2·02]	51·8			84·9
A-9	9	112·2 [56·48]	162·3 [1·84]	50·1			76·7
B-4	4	91·2 [62·92]	213·6 [1·63]	122·4			68·0
B-5	5	66·8 [39·39]	177·0 [0·98]	110·2			55·8
B-6	6	82·3 [68·01]	197·8 [1·38]	115·5			59·7
B-7	7	80·6 [80·15]	185·2 [1·90]	104·6			56·9
B-8	8	80·8 [47·34]	179·7 [1·38]	98·9			58·0
B-9	9	80·5 [69·39]	173·0 [1·73]	92·5	(73·6)†	16·6	57·0
C-8	8	132·6 [96·95]	218·0 [2·27]	85·4	(137·5)†	35·8	101·7

( ) Indicates a monotropic phase transition; [ ], ΔH values in J g^{-1}.
† ΔH value too small to be measured.

group position tends to promote nematic phase behaviour whereas the side perfluorophenyl group position favours smectic C phase formation, providing that the alkoxy chain is long enough. Compound **B-9** exhibits a monotropic smectic phase beside the enantiotropic nematic phase. Only compound **A-9** exhibited an enantiotropic nematic phase. Furthermore, the clearing points of series **B** are higher than series **A**, and the melting points lower. So the nematic thermal range of series **B** is larger than that of series **A**. The average increment of ΔT_N is 40·4°C. These phenomena indicate that the side perfluorophenyl group position favors mesomorphic properties of the liquid crystalline state.

Also, in the equivalent comparison of compounds **A-8**, **B-8** and **C-8**, the melting and clearing points are reduced when the perfluorophenyl group was introduced into the molecule. For **A-8** to **C-8**, the melting points drops from 132·5°C to 115·2°C and the clearing points drops from 218·0°C to 167·0°C. For compound **B-8** to **C-8**, the melting point drops from 132·6°C to 80·8°C and the clearing point drops from 218·0°C to 179·7°C. In addition, the mesomorphic thermal range is still large for the fluorinated homologues. The nematic thermal ranges are from 50·1°C to 122·4°C for the prepared compounds. Moreover, compounds **A-8** show an enantiotropic nematic phase without the smectic C phase but compound **C-8** exhibits a monotropic smectic C phase. Thus, when fluorine is introduced into the benzoate-tolane liquid crystal with a chlorine substituent, the liquid crystal exhibits a nematic phase rather than a smectic phase.



The transition temperatures of series **A** (circles) and **B** (squares) as a function of the length of the *n*-alkoxy chain length, m. Melting points and clearing points are shown as filled and open symbols, respectively.

4. Conclusions

Three homologous series of 4-chloro-substituted benzoate-tolanes were prepared. Thermal optical microscopy and DSC show that these compounds were liquid crystalline. Each homologue exhibits a wide range of nematic phase and two homologues have a monotropic smectic C phase. The introduction of a perfluorophenyl group into the liquid crystal reduces the clearing and melting points. The central perfluorophenyl group position series present stable a nematic phase and the side perfluorophenyl group position series have a tendency to form a smectic C phase when the carbon chain of *n*-alkoxy substitutent is long enough.

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