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

Synthesis and mesophase behaviour of mesogens bearing omega, alpha, alpha-trihydroperfluoroalkoxy end tails

Bao-Quan Chen; Jian-Xun Wen

To cite this Article Chen, Bao-Quan and Wen, Jian-Xun(1999) 'Synthesis and mesophase behaviour of mesogens bearing omega, alpha, alpha-trihydroperfluoroalkoxy end tails', Liquid Crystals, 26: 8, 1135 — 1140
To link to this Article: DOI: 10.1080/026782999204165
URL: http://dx.doi.org/10.1080/026782999204165

LIQUID CRYSTALS, 1999, VOL. 26, NO. 8, 1135–1140

Synthesis and mesophase behaviour of mesogens bearing ω,α,α-trihydroperfluoroalkoxy end tails

BAO-QUAN CHEN and JIAN-XUN WEN*
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
354 Fenglin Road, Shanghai 200032, PR China

(*Received 23 December 1998; accepted 23 January 1999*)

One series of two-ring and two series of three-ring liquid crystal compounds, all containing ω,α,α-trihydroperfluoroalkoxy terminal tails, were prepared and characterized by IR, NMR, MS and elemental analysis. Their phase transition behaviour was investigated by DSC and polarizing optical microscopy. Biphenylene derivatives with the ω,α,α-trihydroperfluoroalkoxy end group form a stable smectic A phase. In the three-ring system, biphenylene ester compounds exhibit a smectic phase without a nematic phase. The compounds exhibit smectic A and smectic C phases when the terminal groups are intermediate length alkyl and fluorinated alkyl chains. Mesogens with fluorinated tails have a broader smectic C phase than the non-fluorinated mesogens.

1. Introduction

Fluorinated liquid crystals (LCs) have received great attention in the past decade due to unique properties such as low viscosity, low birefringence, and low conductivity. Laterally fluorinated LCs, where one or more fluorine atoms substitute the aromatic proton(s) in the core, have been widely studied, from their syntheses to their physical properties. These investigations show that variation in the position and number of fluorine atoms on LC molecules can cause great changes in the mesophase range, sequence of mesophases and electro-optical properties [1–11]. However, LC molecules containing fluoroalkyl chains as terminal groups are rarely studied because it is difficult to obtain fluoro-containing reagents. Most of the fluorinated LCs studied were ferroelectric LCs with a trifluoromethyl group or a fluorine bonding to a chiral carbon [12–15]. Thus far, the very limited studies on fluorinated LCs with perfluoroalkyl or highly fluorinated alkyl terminal chains indicate that smectic character is enhanced to some extent in such systems [16–22]. Therefore, we wished to study systematically fluorinated LCs possessing both step-growth alkyl and fluorinated alkyl end chains. In a previous paper [23], we reported a new kind of LC: 4-(1,1,7-trihydroperfluoroheptyloxycarbonyl)phenyl 4′-*n*-alkoxybiphenyl-4-carboxylates, some of which exhibit a broad smectic C phase and a very narrow smectic A phase. We now present recent results on similar fluorinated mesogens with an ω,α,α,-trihydroperfluoroalkoxy moiety.

2. Experimental

2.1. *Synthesis route*

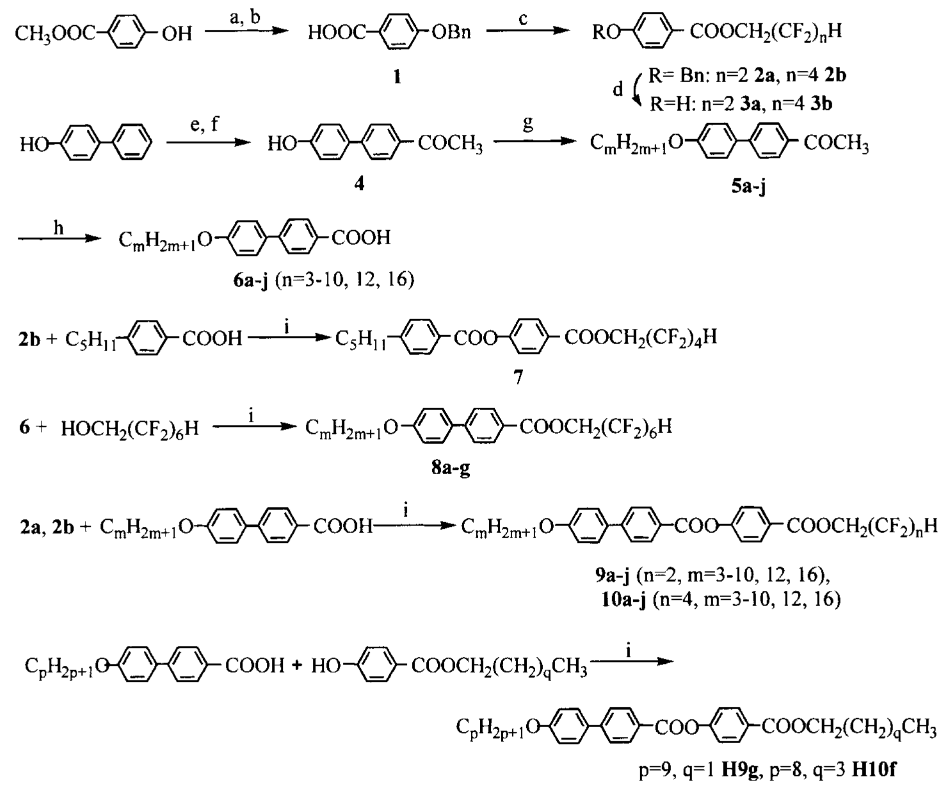
The paths to these fluorinated liquid crystals are outlined in the scheme. The synthesis of *p*-benzyloxybenzoic acid (**1**) was reported previously [23]. This protected acid was esterified with a fluorinated alcohol using dicyclohexylcarbodiimide (DCC) as dehydrating reagent and *N*,*N*-dimethylaminopyridine (DMAP) as catalyst in dry tetrahydrofuran (THF). The fluorinated intermediates obtained (**2a**, **2b**) were deprotected via hydrogenation by palladium on active carbon under H_2 to give fluorinated alkoxycarbonyl phenols (**3a**, **3b**). The 4-*n*-alkoxybiphenyl-4′-carboxylic acids (**6a–j**) were prepared in four steps using the method reported by Gray *et al.* [24, 25]. Then **6a–j** were allowed to react with **3a** and **3b** to give two series of target molecules (**9a–j**, **10a–j**). Compounds **6a–j** were esterified with the fluorinated alcohol 1,1,7-trihydroperfluoroheptanol, to offer a series of two-ring mesogens (**8a–g**). Additionally, esterification between **2b** and *p*-*n*-pentylbenzoic acid gave compound **7**.

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. ^{1}H 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 a FX-90Q (90 MHz) or Bruker 300AM instrument. For ^{19}F NMR spectra, the high field was

*Author for correspondence.

Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online ©1999 Taylor & Francis Ltd
http://www.tandf.co.uk/JNLS/lct.htm
http://www.taylorandfrancis.com/JNLS/lct.htm



Reagents and conditions: (a) C_2H_5ONa/C_2H_5OH, BnCl, r.t. to reflux; (b), *(i)* NaOH, C_2H_5OH/H_2O, overnight, *(ii)* 6N HCl ; (c) $H(CF_2)_nCH_2OH$ (n=2, 4), DCC, DMAP, THF, 0°C to r.t.; (d) Pd/C, ethyl acetate, H_2; (e) CH_3COCl, CS_2, $AlCl_3$, reflux; (f), (i) NaOH, C_2H_5OH/H_2O, (ii) 6N HCl; (g) NaH, n-$C_mH_{2m+1}Br$, DMF, 100°C; (h), *(i)* NaOBr, dioxane/ water, *(ii)* 6N HCl; (i) DCC, DMAP, THF.

Scheme.

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 [26, 27].

2.3. *4-Benzyloxybenzoic acid (**1**)*

The method of preparation of compound **1** was reported in a previous paper [23].

2.4. *1,1,3-Trihydroperfluoropropyl hydroxybenzoate (**3a**)*

To a mixture of compound **1** (1.347 g, 6.13 mmol) and 2,2,3,3-tetrafluoropropanol (0.89 g, 6.7 mmol) in THF (25 ml) cooled in an ice bath, was added DCC (1.77 g, 8.5 mmol) followed by a catalytic amount of DMAP. The resulting mixture was stirred under dry conditions while warming to room temperature. Thin layer chromatography (TLC) was used to monitor the reaction. After completion, the precipitate was filtered off and THF was evaporated. The residue was purified by flash chromatography on a silica gel column using petroleum ether/ethyl acetate (20/1) as eluent, and then by recrystallization from methanol to give white crystals (**2a**, 1.702 g, 81%). This product was dissolved in ethyl acetate (25 ml) containing 0.03 g of palladium on active carbon. The mixture was stirred under a hydrogen atmosphere at room temperature for 6.5 h to remove the benzyl protection. This gave colourless crystals of **3a**. Yield 1.34 g (79%). ^1H NMR (90 MHz, $CDCl_3$/TMS) δ: 4.97 (t, $J=13.9$ Hz, 2H, OCH_2), 6.22 (tt, $J_1=52.2$ Hz, $J_2=5.4$ Hz, CF_2H), 6.68 (s, 1H, OH), 7.06 (d, $J=8.8$ Hz, 2H, aromatic H), 8.12 (d, $J=8.8$ Hz, 2H, aromatic H). ^{19}F NMR (60 MHz, $CDCl_3$/TFA) δ: 25.8 (m, 2F), 60.6 (d, $J=5$ Hz, 2F). IR (KBr disc, cm^{-1}): 3430 (O–H), 1706 (C=O), 1609, 1594 (aromatic C=C), 1288, 1234, 1172, 1142 (ether C–O–C), 857, 766 (aromatic C–H, out-of-face).

2.5. *p-n-Alkoxybiphenyl carboxylic acids (**6a–j**, m = 3–10, 12, 16)*

The *p-n*-alkoxybiphenyl carboxylic acid (**6a–j**) were prepared in four steps using the procedure reported by Gray *et al.* [24, 25].

2.6. *1,1,5-Trihydroperfluoropentyl p-(p-n-pentylphenylcarboxyl)benzoate (**7**)*

The esterification of compound **2b** with *p-n*-pentylphenylcarboxylic acid was carried out in THF with DCC in the presence of catalytic DMAP by a procedure similar to that described for **2a**. ^{1}H NMR (90 MHz, $CDCl_3$/TMS) δ: 0.79–2.00 (m, 9H, alkyl H), 2.70 (m, 2H, $C\underline{H}_2$–Ar), 4.84 (t, $J = 13$ Hz, 2H, OCH_2), 6.05 (tt, $J_1 = 52$ Hz, $J_2 = 5.2$ Hz, 1H, CF_2H), 6.84–8.35 (m, 8H, aromatic H). ^{19}F NMR (60 MHz, $CDCl_3$/TFA) δ: 42.6 (t, $J = 13$ Hz, 2F, CH_2CF_2), 48.3 (m, 2F), 53.2 (m, 2F), 60.4 (m, 2F). IR (KBr disc, cm^{-1}): 2932, 2859 (C–H), 1735 (C=O), 1604, 1507 (aromatic C=C), 1216, 1168 (C–O–C), 858, 763 (aromatic C–H, out-of-face). MS (*m/z*, abundance): 175 (C_5H_{11}–C_6H_4–CO^+, 100%), 527 (M^+, weak). Elemental analysis: found, C 53.21, H 3.91, F 28.07; calculated (for $C_{24}H_{21}F_8O_4$), C 53.24, H 3.91, F 28.67%.

2.7. *1,1,7-Trihydroperfluoroheptyl p-n-alkoxybiphenyl carboxylates (**8a–g**, m = 3–10)*

The esterification of 1,1,7-trihydroperfluoroheptanol with compounds **6a–j** was carried out in THF with DCC in the presence of catalytic DMAP by a similar procedure (step c) as described for **2a** to give compounds **8a–j**. All the resulting compounds gave good spectral data to support the corresponding structures. For example, compound **8a** has the following spectral data: ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ: 1.00 (t, $J = 6$ Hz, 3H, CH_3), 1.32–2.00 (m, 4H, alkyl H), 4.00 (t, $J = 6$ Hz, 2H, OCH_2), 4.90 (t, $J = 13$ Hz, 2H, CH_2CF_2), 6.05 (tt, $J_1 = 52$ Hz, $J_2 = 5.2$ Hz, 1H, CF_2H), 7.20 (d, $J = 10$ Hz, 2H, aromatic H), 7.53–7.80 (m, 4H, aromatic H), 8.16 (d, $J = 10$ Hz, aromatic H). ^{19}F NMR (300 MHz, $CDCl_3$/TFA) δ: 42.5 (t, $J = 11.7$ Hz, 2F), 45.5 (m, 2F), 46.3 (m, 4F), 52.5 (m, 2F), 60.1 (d, $J = 52$ Hz, 2F). IR (KBr disc, cm^{-1}): 2938, 2874 (C–H), 1732 (C=O), 1604, 1580 (aromatic C=C), 1202, 1143 (C–O–C), MS (*m/z*, abundance): 197 (HO–C_6H_4–C_6H_4–CO^+, 100%), 528 (HO–C_6H_4–C_6H_4–$COOCH_2(CF_2)_6H$, 89.2%), 584 (M^+, 43%). Elemental analysis: found, C 49.65, H 3.03, F 38.35; calculated (for $C_{24}H_{20}F_{12}O_3$), C 49.33, H 3.45, F 39.01%.

2.8. *4-(1,1,3-Trihydroperfluoropropyloxycarbonyl)phenyl 4′-n-alkoxybiphenyl-4-carboxylates (**9a–j**, n = 2, m = 3–10, 12, 16)*

Compounds **9a–j** were prepared from compound **3a** and compounds **6a–j** by a similar procedure (step c) as described for **2a**. All the resulting compounds gave good spectral data to support the corresponding structures. For example, compound **9a** ($n = 2$, $m = 3$) has following spectral data: ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ: 1.03 (t, $J = 7.2$ Hz, 3H, CH_3), 1.62–1.93 (m, 2H, CH_2), 3.99 (t, $J = 5.5$ Hz, 2H, OCH_2), 4.80 (t, $J = 13$ Hz, 2H, CH_2CF_2), 6.47 (tt, $J_1 = 52$ Hz, $J_2 = 5$ Hz, 1H, CF_2H), 6.89 (d, $J = 9$ Hz, 2H, aromatic H), 7.33–7.83 (m, 6H, aromatic H), 8.02–8.23 (m, 4H, aromatic H). ^{19}F NMR (300 MHz, $CDCl_3$/TFA) δ: 48.0 (m, 2F), 62.0 (d, $J = 6.2$ Hz, 2F), IR (KBr disc, cm^{-1}), 2977 (C–H), 1724 (C=O), 1603 (aromatic C=C), 1209, 1195, 1165 (C–O–C), 829, 768 (aromatic C–H, out-of-face). MS (*m/z* abundance): 239 (C_3H_7O–C_6H_4–CO^+, 100%), 490 (M^+, 5%). Elemental analysis: found, C 63.87, H 4.61, F 15.21; calculated (for $C_{26}H_{22}F_4O_5$), C 63.37, H 4.52, F 15.49%.

2.9. *4-(1,1,5-Trihydroperfluoropentyloxycarbonyl)phenyl 4′-n-alkoxybiphenyl-4-carboxylates (**10a–j**, n = 4, m = 3–10, 12, 16)*

Compounds **10a–j** were prepared from compound **3b** and compounds **6a–j** by a similar procedure (step c) as described for **2a**. All the resulting compounds gave good spectral data to support the corresponding structures. For example, compound **10a** ($n = 4$, $m = 3$) has following spectral data: ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ: 1.07 (t, $J = 7$ Hz, 3H, CH_3), 1.81 (q, $J = 5.2$ Hz, 2H, CH_2), 3.96 (t, $J = 5.5$ Hz, 2H, OCH_2), 4.80 (t, $J = 13.5$ Hz, 2H, CH_2CF_2), 6.03 (tt, $J_1 = 52$ Hz, $J_2 = 5$ Hz, 1H, CF_2H), 6.96 (d, $J = 9$ Hz, 2H, aromatic H), 7.15–7.76 (m, 6H, aromatic H), 8.03–8.30 (m, 4H, aromatic H). ^{19}F NMR (300 MHz, $CDCl_3$/TFA) δ: 41.2 (m, 2F), 47.0 (m, 2F), 51.8 (m, 2F), 51.9 (m, 2F). IR (KBr disc, cm^{-1}), 2934 (C–H), 1724 (C=O), 1604 (aromatic C=C), 1166, 1118, 1076 (C–O–C), 828, 768 (aromatic C–H, out-of-face). MS (*m/z*, abundance): 239 (C_3H_7O–C_6H_4–C_6H_4–CO^+, 100%), 590 (M^+, 1%). Elemental analysis: found, C 56.84, H 3.86, F 25.82; calculated (for $C_{28}H_{22}F_8O_5$), C 56.96, H 3.75, F 25.74%.

2.10. *4-Propyloxycarbonylphenyl 4′-n-nonyloxybiphenyl-4-carboxylates (**H9g**, p = 9, q = 1)*

Compound **H9g** was prepared from nonyl 4-hydroxybenzoate and compound **6g** by a similar procedure (step c) as described for **2a**. ^{1}H NMR (90 MHz, $CDCl_3$/TMS) δ: 0.76–2.00 (m, 26H, alkyl H), 4.00 (t, $J = 6$ Hz, 2H, OCH_2), 4.32 (t, $J = 6$ Hz, 2H, OCH_2), 6.99 (d, $J = 8.8$ Hz, 2H, aromatic H), 7.32 (d, $J = 8.8$ Hz, 2H, aromatic H), 7.38–7.79 (m, 4H, aromatic H), 8.06–8.42 (m, 4H, aromatic H). IR (KBr disc, cm^{-1}), 2924, 2853 (C–H), 1734 (C=O), 1602, 1500, 1498 (aromatic C=C), 1167, 1116, 1078 (C–O–C), 830, 768 (aromatic C–H, out-of-face). MS (*m/z*, abundance): 323

($C_9H_{19}O$–C_6H_4–C_6H_4–CO^+, 100%), 502 (M^+, 2%). Elemental analysis: found, C 76.49, H 7.90, calculated (for $C_{32}H_{38}O_5$), C 76.46, H 7.62%.

2.11. *4-Pentyloxycarbonylphenyl 4′-n-octyloxybiphenyl-4-carboxylates (**H10f**, p = 8, q = 3)*

Compound **H10f** was prepared from octyl-4-hydroxybenzoate and compound **6f** by a similar procedure (step c) as described for **2a**. ^{1}H NMR (90 MHz, $CDCl_3$/TMS) δ: 0.75–2.00 (m, 26H, alkyl H), 3.98 (t, $J = 6$ Hz, 2H, OCH_2), 4.30 (t, $J = 6$ Hz, 2H, OCH_2), 7.00 (d, $J = 8.8$ Hz, 2H, aromatic H), 7.32 (d, $J = 8.8$ Hz, 2H, aromatic H), 7.42–7.80 (m, 4H, aromatic H), 8.04–8.35 (m, 4H, aromatic H). IR (KBr disc, cm^{-1}), 2953, 2929, 2856 (C–H), 1725 (C=O), 1603, 1500, 1497 (aromatic C=C), 1165, 1117, 1075 (C–O–C), 830, 768 (aromatic C–H, out-of-face). MS (*m/z*, abundance): 309 ($C_8H_{17}O$–C_6H_4–C_6H_4–CO^+, 100%), 516 (M^+, 1%). Elemental analysis: found, C 76.73, H 8.01, calculated (for $C_{33}H_{40}O_5$), C 76.71, H 7.80%).

3. Results and discussion

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

As mentioned at the beginning, our target is to synthesize mesogens with a wide smectic C phase (SmC) by incorporating terminal highly-fluorinated alkyl chains. Therefore, compound **7** was synthesized at first. We hoped this rod-like molecule with two benzoate rings would possess liquid crystallinity. After characterization by DSC and POM it was seen that this compound does not have liquid crystallinity; it melts at 48.7°C. The reason may be that the core ester linkage destroys the conjugation of the two aromatic rings. Thereafter, a series of biphenyl compounds **8** were synthesized for investigation. Their phase transition temperatures are summarized in table 1. Compounds **8a–f** show a simple mesophase sequence. The smectic A (SmA) mesophases are relatively narrow. The mesophase ranges decrease as the alkyl chain grows from 4 to 10 methylene units, as shown in figure 1. Compound **8g**, with a decanyl terminal chain, are no longer liquid crystal. The six compounds **8a–f** of this series exhibit only a smectic phase; we ascribe this to a higher interaction between fluorinated alkyl chains than between hydrocarbon chains. Since none of the compounds **8** possesses the expected smectic C phase, our work progressed to the synthesis of mesogens with three aromatic rings as rigid LC cores, which we expected would give smectic C mesogens.

Table 1. Transition temperatures of compounds **8a–g**. Cr = crystal, SmA = smectic A, I = isotropic, Recr = recrystal phases.

Compounds	*m*	Transition temperatures/°C
8a	4	Cr 90.9 SmA 111.2 I 109.3 SmA 73.2 Recr
8b	5	Cr 79.1 SmA 97.4 I 95.7 SmA 64.3 Recr
8c	6	Cr 76.3 SmA 92.5 I 89.6 SmA 62.2 Recr
8d	7	Cr 71.8 SmA 85.2 I 83.6 SmA 59.0 Recr
8e	8	Cr 74.3 SmA 8.12 I 79.9 SmA 64.1 Recr
8f	9	Cr 79.1 SmA 81.9 I 77.7 SmA 70.3 Recr
8g	10	Cr 71.1 I 65.4 SmA 62.6 Recr

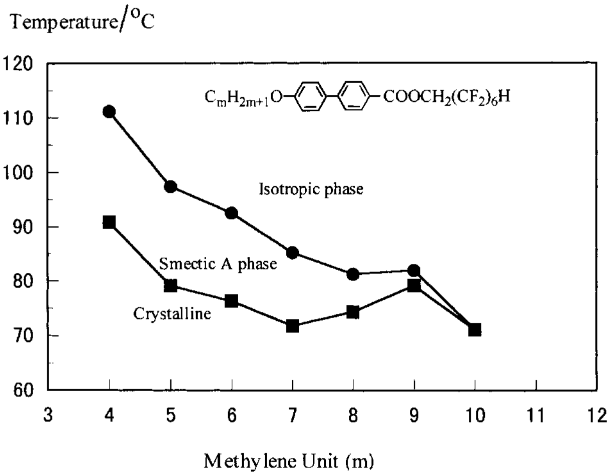


Figure 1. Transition behaviour of compounds **8a–g**: dependence of transition temperatures on the number (*m*) of methylene units of the non-fluorinated chain. Crystalline–smectic A (■), smectic A–isotropic (●).

The three-ring mesogens comprise the two series of compounds **9a–j** and **10a–j**. As summarized in tables 2 and 3, these compounds show smectic phases without a nematic phase. The series of compounds **9a–j** show only a SmA phase whose range varies with change in length of the alkyl chain. A short or long alkyl chain is

Table 2. Transition temperatures of compounds **9a–j** ($n = 2$) and **H9g**. Cr = crystal, SmA = smectic A, I = isotropic, Recr = recrystal phases.

Compounds	*m*	Transition temperatures/°C
9a	3	Cr 166.8 SmA 238.4 I 235.0 SmA 143.5 Recr
9b	4	Cr 147.5 SmA 234.7 I 231.4 SmA 116.1 Recr
9c	5	Cr 134.1 SmA 225.6 I 222.4 SmA 100.7 Recr
9d	6	Cr 117.5 SmA 216.8 I 213.1 SmA 87.9 Recr
9e	7	Cr 113.5 SmA 209.4 I 206.6 SmA 89.4 Recr
9f	8	Cr 115.4 SmA 185.1 I 184.6 SmA 111.3 Recr
9g	9	Cr 113.8 SmA 196.2 I 193.1 SmA 92.0 Recr
9h	10	Cr 106.5 SmA 195.2 I 192.3 SmA 93.8 Recr
9i	12	Cr 110.7 SmA 188.5 I 185.0 SmA 97.8 Recr
9j	16	Cr 102.2 SmA 149.7 I 148.6 SmA 84.4 Recr
H9g	9	Cr 92.4 SmA 212.0 I 207.5 SmA 85.7 Recr

Table 3. Transition temperatures of compounds **10a–j** ($n = 4$) and **H10f**. Cr = crystal, SmA = smectic A, I = isotropic, SmC = smectic C, and Recr = recrystal phases.

Compounds	*m*	Transition temperatures/°C
10a	3	Cr 160.3 SmA 234.9 I 228.6 SmA 143.5 Recr
10b	4	Cr 143.5 SmA 236.6 I 234.1 SmA 124.2 Recr
10c	5	Cr 134.8 SmA 224.1 I 221.4 SmA 109.1 SmC 104.1 Recr
10d	6	Cr 105.2 SmA 215.1 I 212.1 SmA 99.4 SmC 81.4 Recr
10e	7	Cr 104.4 SmC 132.9 SmA 200.9 I 197.8 SmA 89.7 SmC 78.8 Recr
10f	8	Cr 106.4 SmC 179.4 SmA 197.9 I 195.3 SmA 176.6 SmC 89.0 Recr
10g	9	Cr 111.7 SmC 173.8 SmA 189.4 I 186.9 SmA 171.0 SmC 90.8 Recr
10h	10	Cr 107.3 SmC 171.8 SmA 185.8 I 183.4 SmA 169.4 SmC 84.7 Recr
10i	12	Cr 101.2 SmC 160.9 SmA 177.6 I 175.2 SmA 158.6 SmC 78.6 Recr
10j	16	Cr 96.5 SmA 150.3 I 149.3 SmA 88.8 Recr
H10f	8	Cr 90.5 SmA 201.7 I 197.5 SmA 87.5 Recr

disadvantageous to the formation of wide smectic phases, as shown in figure 2. Comparing the mesophase ranges between fluorinated mesogen **9g** with non-fluorinated **H9g**, we find that 2,2,3,3-tetrafluoropropyl in place of the propyl chain lowers the stability of the mesophase and lowers the melting point by 5.8°C.

Compounds **10a–j** ($n = 4$) present a different behaviour with increasing length of alkyl chain. The influence of the alkyl chain length (methylene units, $m = 3$–10, 12, 16) on the phase behaviour is illustrated in figure 3. Some members of this series can form both SmC and SmA phases. The mesogens with a short alkyl chain ($m = 3, 4$) exhibit only the SmA phase, although the phase ranges are relatively broad. When the alkyl chain length is $m = 5$ or 6, the mesogens form a monotropic SmC phase besides a SmA phase. With continuing increase of alkyl chain length ($m = 7$–12), the mesogens show enantiotropic SmA and SmC phases. But with further lengthening of the hydrocarbon end chain to 16, mesogen **10j** forms only a SmA phase, as do **10a** and **10b**. In this series, a short or very long alkyl chain is thus disadvantageous to the formation of SmC phase. By POM, all compounds **10** exhibit the SmA phase typical focal-conic textures and the SmC phase broken focal-conic textures.

The non-fluorinated mesogen **H10f** possesses a single SmA phase, although its range is broader than that of the fluorinated analogue **10f**. Thus, the introduction of a fluoroalkyl chain decreases the stability of the mesophase but benefits the formation of a tilted smectic phase.

Transition temperatures decrease with increasing length of end alkyl chain, as shown in figure 3. The SmC ranges of mesogens **10f–10i** span most of the mesophase ranges. There are no higher order phases except for the SmC phase at low temperatures.

To summarize, this investigation, together with our previous study [23] on mesogens with highly fluorinated end chains, reveals that mesogens containing a fluorinated

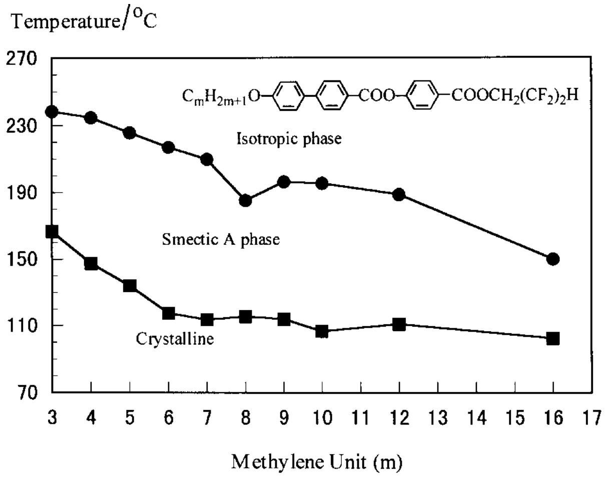


Figure 2. The transition behaviour of compounds **9a–j**: dependence of transition temperatures on the number (m) of methylene units of the non-fluorinated chain. Crystalline–smectic A (■), smectic A–isotropic (●).

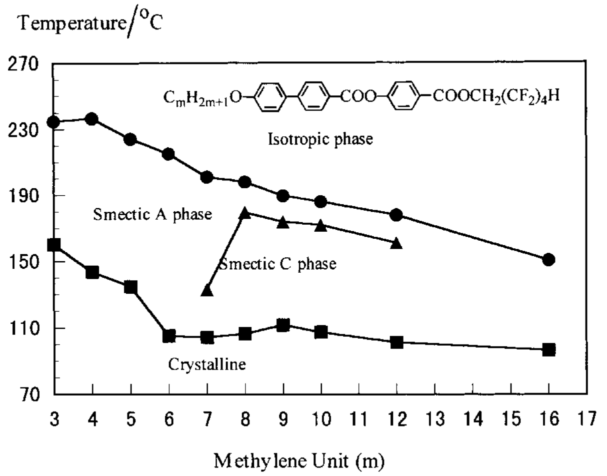


Figure 3. The transition behaviour of compounds **10a–j**: dependence of transition temperatures on the number (m) of methylene units of the non-fluorinated chain. Crystalline–smectic A or C (■), smectic C–smectic A (▲), smectic A–isotropic (●).

alkyl group form smectic phase following a '5+6' rule; that is, the two end tails are longer than 5 and 6 carbon atoms, respectively. Mesogens with intermediate length alkyl and fluorinated alkyl groups form broader smectic C phases than the non-fluorinated mesogens.

We gratefully acknowledge the financial support of National Natural Science Foundation of China.

References

[1] Gray, G. W., Hird, M., Lacey, D., and Toyne, K. J., 1989, *J. chem. Soc., Perkin Trans. II*, 2041.

[2] Gray, G. W., Hird, M., Lacey, D., and Toyne, K. J., 1990, *Mol. Cryst. liq. Cryst.*, **191,** 1.

[3] Nabor, M. F., Nguyen, H. T., Destrade, C., and Marcerou, J. P.., 1991, *Liq. Cryst.*, **10,** 785.

[4] Pugh, C., Andersson, S. K., and Percec, V., 1991, *Liq. Cryst.*, **10,** 229.

[5] Loubser, C., Wessels, P. L., Strying, P., and Goodby, J. W., 1994, *J. mater. Chem.*, **4,** 71.

[6] Wen, J. X., Tian, M. Q., and Chen, Q., 1994, *Liq. Cryst.*, **16,** 445.

[7] Xu, Y. L., Chen, Q., and Wen, J. X., 1994, *Mol. Cryst. liq., Cryst.*, **21,** 65.

[8] Xu, Y., Wang, W., Chen, Q., and Wen, J., 1996, *Liq. Cryst.*, **21,** 65.

[9] Wen, J., Tian, M., and Chen, Q., 1994, *J. Fluorine Chem.*, **68,** 117.

[10] Reiffenrath, V., Finkenzeller, U., Poetsch, E., Rieger, B., Coates, D., and Merok, E., 1990, *SPIE Proc.*, **1257,** 84.

[11] Wand, M. D., Vohra, R., and Monahan, S., 1993, *Liq. Cryst.*, **15,** 269.

[12] Wand, M. D., Vohra, R., Thurmes, W., Walba, D. M., Geelhaar, T., and Littwitz, B., 1991, *SPIE Proc.*, **1455,** 97.

[13] Fukuda, A., Takanishi, Y., Isozaki, T., Ishikawa, K., and Takezoe, H., 1994, *J. mater. Chem.*, **4,** 997.

[14] Shiratoki, N., Yoshizawa, A., Nishiyama, I., Fukumasa, M., Yokoyama, A., Hirai, T., and Yamane, M., 1991, *Mol. Cryst. liq. Cryst.*, **199,** 129.

[15] Saitoh, G., Nakamura, T., Suzuki, M., Satoh, M., Yoshio, K., and Watanabe, T., 1993, *Liq. Cryst.*, **14,** 1753.

[16] Janulis, E. P., Osten, D. W., Radcliffe, M. D., Novack, J. C., Tristrani-Kendra, M., Epstein, K. A., Keyes, M., Johnson, G. C., Savu, P. M., and Spawn, T. D., 1992, *SPIE Proc.*, **1665,** 146.

[17] Lobko, T. A., Ostruvskii, B. I., Pavluchenko, A. I., and Sulianov, S. N., 1993, *Liq. Cryst.*, **15,** 361.

[18] Twieg, R., Betterton, K., Dipietro, R., Gravert, D., Nguyen, C., Nguyen, H. T., Babeau, A., and Destrade, Y., 1991, *SPIE Proc.*, **1455,** 81.

[19] Janulis, E. P. Jr., Novack, J. C., Papapolymerou, G. A., Tristani-Kendra, M., and Huffman, W. A., 1988, *Ferroelectrics*, **85,** 375.

[20] Vilaita, P. M., and Weiss, R. D., 1992, *Liq. Cryst.*, **12,** 531.

[21] Tournilhac, F. G., Bosio, L., Simon, J., Blinov, L. M., and Yablonsky, S. V., 1993, *Liq. Cryst.*, **14,** 405.

[22] Gorria, P., Nguyen, H. T., Twieg, R. J., Betterton, K., and Sigaud, G., 1994, *Liq. Cryst.*, **21,** 523.

[23] Chen, B.-Q., Yang, Y.-G., and Wen, J.-X., 1998, *Liq. Cryst.*, **24,** 539.

[24] Gray, G. W., Hartley, T. B., and Jones, B., 1955, *J. chem. Soc.*, 1412.

[25] Xie, M.-G., Peng, M.-S., Jiang, Q., Hu, Z.-L., and Wang, X.-J., 1996, *Liq. Cryst.*, **21,** 461.

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

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