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Induction of smectic behaviour in a carborane-containing mesogen. Tail fluorination of a three-ring nematogen and its miscibility with benzene analogues

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Partial tail fluorination of a nematic three-ring carborane mesogen, **1H**, induced smectic A (SmA) and smectic C (SmC) phases, leaving a narrow range nematic phase in **1F**. In contrast, fluorination of the benzene and bicyclo[2.2.2]octane analogues, **2H** and **3H**, eliminated their nematic behaviour, enhanced their respective SmC and SmA phases and induced SmA, smectic I (SmI) and smectic F (SmF) phases in **2F**. A binary phase diagram of **1F** with its non-fluorinated analogue **1H** shows nearly ideal miscibility. In the approximately equimolar mixture of **1F** and **2H** the SmC phase is expanded by 36 K, and in a mixture of **1F** and **2F** the SmA phase is stabilised by additional 37 K.

Keywords: tail fluorination; smectic phase induction; carborane mesogen

1. Introduction

Fluorination of alkyl chains in mesogenic compounds significantly enhances or induces smectogenic properties, whereas the nematic phases are often completely eliminated (*1–5*). This phenomenon, ascribed to microsegregation of the polar and semi-rigid fluorous fragments (*6*), has been exploited in the preparation of polar tilted phases (*7*), including orthoconic materials (*8–10*). Such compounds typically exhibit good miscibility with non-fluorinated mesogens and often improve their electro-optical properties (*7, 11, 12*).

Carborane-containing mesogens typically are nematogenic (*13*) and rarely exhibit smectic phases (*14–17*). Comparative studies of isostructural homologous series demonstrated that even long alkyl tail homologues maintain nematic properties or are exclusively nematic materials, whereas the carbocyclic analogues show onset of smectic behaviour and complete loss of nematic phases relatively early in the homologous series (*18–20*). This high tendency of carborane derivatives to exhibit nematogenic properties has been attributed to fivefold rotational symmetry of the carborane and, consequently, higher conformational flexibility of carborane derivatives (*18, 21, 22*). Recently, we became interested in induction of lamellar phases in carborane derivatives with the goal of using them as components of polar smectic materials (*23*). Therefore, we set out to investigate the effect of tail fluorination on mesogenic properties of carborane derivatives and on their behaviour in binary mixtures.

In this paper, we report studies of the effect of partial tail fluorination in **1H** (see Figure 1) on the mesophase structure and stability of **1F**. We contrast these results with those obtained for the benzene and bicyclo[2.2.2]octane analogues **2** and **3** (Figure 1). We also investigated the miscibility of the carborane derivative **1F** with its non-fluorinated analogue **1H** and benzene derivatives **2H** and **2F**.

2. Results

Synthesis

Mesogens **1**–**3** were prepared by esterification of carboxylic acid **4** with phenol **5**, **6** or **7**, respectively, using either thionyl chloride to generate the acid chloride (compound **1**) or dicyclohexylcarbodiimide (DCC, compounds **2** and **3**), as shown in Scheme 1. The preparation of phenols **5** (*24*) and **7** (*24*) and carboxylic acid **4F** (*25*) is described elsewhere.

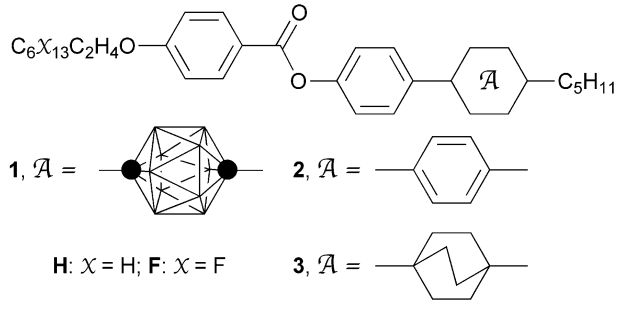

Figure 1. Molecular structures of mesogens **1**–**3**. In compound **1**, $\mathcal{A}$=1,12-dicarba-*closo*-dodecaborane (*p*-carborane) in which each vertex represents a BH fragment and each sphere is a carbon atom.

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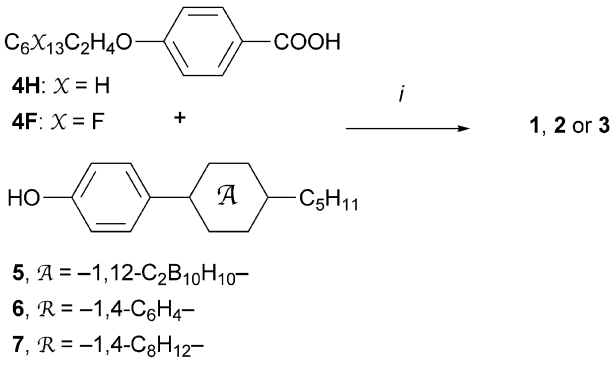


Scheme 1. Synthesis of mesogens **1**–**3**. (i): **1**, $SOCl_2$, Et_3N; **2** and **3**, DCC, DMAP, CH_2Cl_2.

Thermal analysis

The transition temperatures and associated enthalpies for compounds **1–3** are presented in Table 1. Phase structures were assigned by comparison with published textures for reference compounds and established trends in thermodynamic stability (*26–28*).

Carborane derivative **1H** exhibits only a nematic phase, whereas the benzene analogue **2H** displays a smectic C (SmC) phase and the bicyclo[2.2.2]octane **3H** a smectic A (SmA) phase in addition to the nematic phase. Partial fluorination of the octyloxy chain significantly increased the clearing temperatures for all three compounds, with a higher gain in stability for the carbocyclic derivatives (about 65 K), and induced (**1H**) or enhanced (**2H** and **3H**) smectic behaviour. Thus, partial fluorination of **1H** induced SmA and monotropic SmC phases in **1F**, which nearly completely replaced the nematic phase of **1H**. In comparison, partial fluorination of the carbocyclic derivatives **2H** and **3H** resulted in complete suppression of the nematic phase and significant enhancement of SmC (in **2F**) and SmA (in **3F**) phases. In the latter, the SmA phase was widen by 85 K and stabilised by 172 K relative to that in **3H**. In addition, fluorination induced a 70 K wide SmA phase and monotropic smectic I (SmI) and smectic F (SmF) phases in benzene analogue **2F**. The bicyclo[2.2.2]octane derivative **3F** exhibits also an ordered, orthogonal, enantiotropic phase below SmA phase, possible an E phase.

Binary phase diagrams

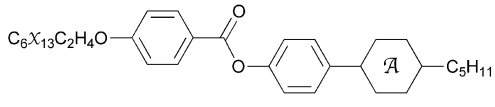
The effect of partial tail fluorination in carborane mesogen **1F** on miscibility with non-fluorinated and carbocyclic analogues was investigated in isobaric binary phase diagrams, as shown in Figure 2.

In general, the phase transitions change approximately linearly with respect to the composition of the mixture in all three diagrams. Most significant deviations from the linearity are observed for the SmA–isotropic transition temperatures in the **1F**–**2F** system (Figure 2(c)) and the SmC–mesophase (M) transition in the **1F**–**2H** system (Figure 2(b)). In both cases, the lower temperature phase is stabilised relative to the ideal linear relationship by as much as 36 K.

The phase diagram of the fluorinated and non-fluorinated carborane derivatives, **1F** and **1H** (Figure 2(a)), shows an almost linear change of transitions temperatures with concentration for the clearing (N–I) and melting (Cr–M) temperatures. The pure nematic behaviour of **1H** prevails in the binary mixture until about $x=0.4$ of **1F** at which point a monotropic SmC phase is detected and continues until $x=1.0$. At about $x=0.5$ (the equimolar mixture), a SmA phase is detected and it begins to gradually replace the nematic phase with increasing concentration of **1F**.

The **1F**–**2H** binary mixture shows similar behaviour (Figure 2(b)). The temperatures for the N–I phase transition are approximately linearly dependent

Table 1. Transition temperatures (°C) and enthalpies (in parentheses, kJ mol^{-1}) for compounds **1–3** (Cr=crystal, Sm=smectic, N=nematic, I=isotropic). Monotropic transitions are shown in parentheses.



		1	2	3
X	A			
H		Cr 94 N 165 I (32.5) (1.3)	Cr 102 SmC 123 N 182 I (24.0) (1.0) (1.5)	Cr 101 SmA 108 N 216 I (18.6) (0.5) (1.0)
F		Cr[a] 128 (SmC 120)[b] SmA 189 N 193 I (23.2) (4.2)[c]	Cr 113 (SmF 97 SmI 111) SmC 178 SmA 248 I (24.4) (0.2) (1.0) (0) (9.6)	Cr 141 X 188 SmA 280 I (27.8) (3.2) (10.5)

[a] Crystalline polymorphs Cr_1 69 Cr_2 87 Cr_3. [b] Microscopic observation. [c] Combined enthalpy for SmA–N and N–I transitions.

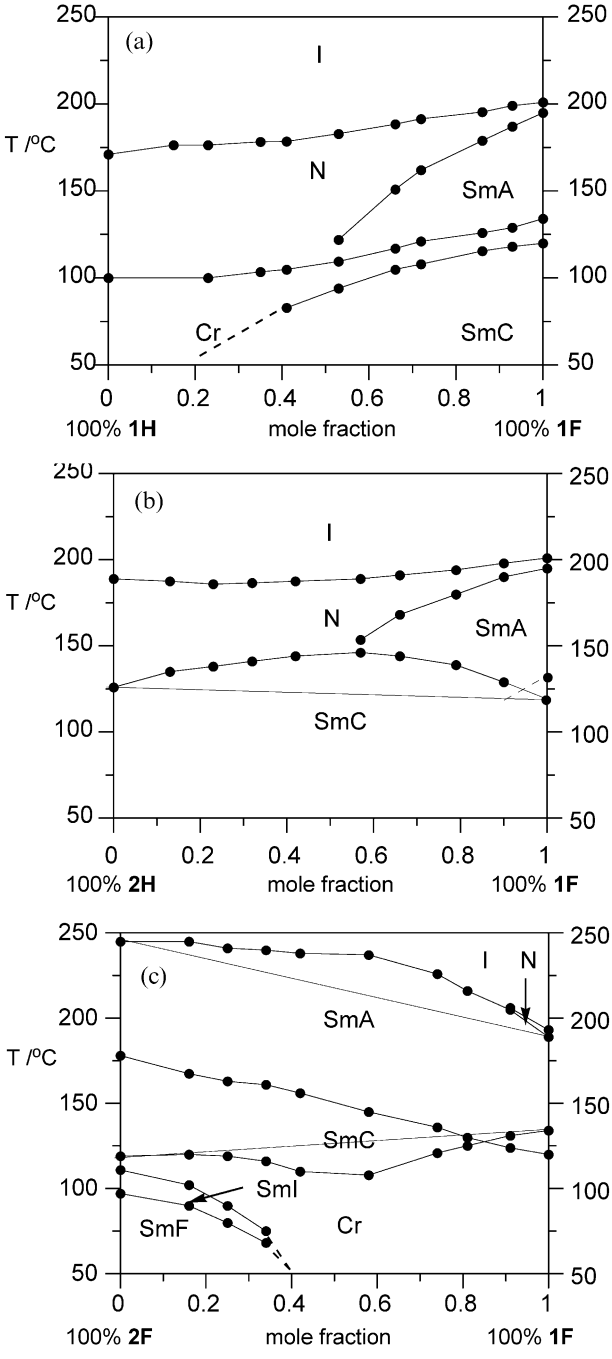


Figure 2. Binary phase diagrams for carborane **1F** with (a) carborane **1H**, (b) benzene analogue **2H** and (c) benzene analogue **2F** (Cr=crystal, Sm=smectic, N=nematic, I=isotropic). The lines are guides to the eye.

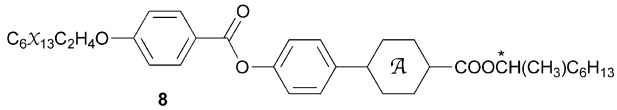
on the mole fraction x, and the SmA phase of **1F** starts to gradually replace the nematic phase at the approximately equimolar composition of the mixture. Interestingly, the SmC phase is expanded at the expense of the higher temperature phase (nematic and later SmA). The maximum stabilisation of the SmC phase by 36 K was found for the equimolar mixture (x=0.5).

The phase diagram of the two fluorinated derivatives **1F** and **2F** (Figure 2c) is the richest among the three shown in Figure 2. Addition of the carborane derivative **1F** destabilised all phases displayed by **2F**. Thus, the monotropic SmI and SmF phases of **2F** disappear quickly with increasing concentration of **1F** and are not observed above the mole fraction $x>0.4$. Only the SmC–SmA transition changes linearly with increasing concentration of **1F**. Interestingly, the Cr–SmC transition is suppressed by 18 K and the SmA–I transition is expanded by 37 K for the mole fraction of about x=0.6 of **1F** relative to the linear relationship.

3. Discussion and conclusions

Results in Table 1 show that carborane derivatives **1** have lower mesophase stability and less smectogenic character than the carbocyclic derivatives **2** and **3**. This is in agreement with the results of other comparative studies for series of isostructural mesogens (*13, 16, 17, 22, 24*). The induction of smectic behaviour in **1H** by tail-fluorination is less effective than that in carbocyclic derivatives **2H** and **3H**, which is consistent with results for **8** (Figure 3) (*23*), chiral analogues of **1** and **2**. Thus, in both carborane derivatives only SmA enantiotropic phases were induced by fluorination, and no broad-range enantiotropic SmC behaviour characteristic for the benzene analogues was observed. The bicyclo[2.2.2]octane derivatives shares some characteristics of both molecular systems. Thus, compound **3H** exhibits a broad-range nematic phase, and no enantiotropic tilted phases were found in the fluorinated analogue **3F**. On the other hand, tail fluorination enhances the mesophase stability for the bicyclo[2.2.2]octane and benzene derivatives to similar extent (about 65 K), which is accompanied by complete loss of the nematic phase.

Investigation of binary phase diagrams demonstrated nearly ideal miscibility of the fluorinated carborane mesogen **1F** with its close analogues **1H** and **2**. This finding is consistent with our previous results for phase diagrams of non-fluorinated carborane mesogens with carbocyclic derivatives (*14, 15, 29*). Notably, the SmA phase in the binary mixture of **1F** and **2F** and the SmC phase in the **1F**–**2H** binary



8

X = H, F; A = –1,12-$C_2B_{10}H_{10}$–, –C_6H_4–

Figure 3. Structure of chiral analogues of compounds **1** and **2**.

system were significantly expanded by about 36 K. A similar expansion of SmC (*15*) and E (*14*) phases was observed before, and ascribed to quadrupolar (*21*) interactions between the carborane and biphenyl fragments (*14*). Such enhancement of smectic phases is desired for formulation of polar mesogenic materials.

Overall results demonstrate that partially fluorinated carboranes, such as **1F**, are compatible with carbocyclic compounds and are promising for applications as functional additives to polar smectic materials.

4. Experimental details

General

Optical microscopy and phase identification was performed using a PZO "Biolar" polarised microscope equipped with a HCS250 Instec hot stage. Thermal analysis was obtained using a TA Instruments 2920 differential scanning calorimeter (DSC). Transition temperatures (onset) and enthalpies were obtained using small samples (1–2 mg) and a typical heating rate of 5 K min^{-1} under a flow of nitrogen gas. For DSC and microscopic analyses, each compound was additionally purified by dissolving in CH_2Cl_2, filtering to remove particles and recrystallisation. The resulting crystals were dried in vacuum overnight at ambient temperature.

Binary mixtures were prepared by dissolving both components in small amounts of dry CH_2Cl_2, subsequent evaporation of the solvent and drying the resulting homogenous material at 70°C for several hours. Transition temperatures of the mixtures were taken as the upper limit of the biphasic regions observed by optical microscopy.

Synthesis

4-(12-Pentyl-p-*carboran-1-yl)phenyl 4-octyloxybenzoate (**1H**).*

A solution of crude acid chloride, prepared from acid **4H** (50 mg, 0.20 mmol) and $SOCl_2$, phenol **5** (*24*) (61 mg, 0.20 mmol), and Et_3N (28 μl, 0.20 mmol) in CH_2Cl_2 was stirred at ambient temperature. The crude product was passed through a silica gel plug and recrystallised from heptane. ^{1}H NMR (300 MHz): δ 0.84 (t, J=7.3 Hz, 3H), 0.89 (t, J=7.6 Hz, 3H), 1.09–1.32 (m, 14H), 1.44–1.50 (m, 2H), 1.6–3.5 (brm, 10H), 1.65 (t, J=8.0 Hz, 2H), 1.81 (quint, J=7.1 Hz, 2H), 4.03 (t, J=6.5 Hz, 2H), 6.95 (d, J=8.7 Hz, 2H), 6.99 (d, J=8.6 Hz, 2H), 7.24 (d, J=8.6 Hz, 2H), 8.08 (d, J=8.7 Hz, 2H). IR (film, cm^{-1}): 1731 (C=O), 2602 (B–H). Elemental analysis: calculated for $C_{28}H_{46}B_{10}O_3$, C 62.42, H 8.61; found, C 62.21, H 8.35%.

4-(12-Pentyl-p-*carboran-1-yl)phenyl 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)benzoate (**1F**).*

Acid **4F** (*25*) (75 mg, 0.30 mmol) was reacted with phenol **5** (78 mg, 0.20 mmol) as described in the synthesis of **1H**. Colourless needles were obtained upon recrystallisation from heptane. ^{1}H NMR (300 MHz): δ 0.84 (t, J=7.1 Hz, 3H), 1.09–1.25 (m, 6H), 1.65 (t, J=8.0 Hz, 2H), 2.68 (tt, J_1=18.4 Hz, J_2=6.8 Hz, 2H), 4.36 (t, J=6.7 Hz, 2H), 6.97 (d, J=8.9 Hz, 2H), 7.00 (d, J=8.8 Hz, 2H), 7.25 (d, J=8.6 Hz, 2H), 8.12 (d, J=8.9 Hz, 2H). IR (film, cm^{-1}): 1733 (C=O), 2611 (B–H). Elemental analysis: calculated for $C_{28}H_{33}B_{10}F_{13}O_3$, C 43.53, H 4.30; found, C 43.53, H 4.35%.

*4′-Pentylbiphenyl-4-yl 4-octyloxybenzoate (**2H**).*

Acid **4H** (50 mg, 0.20 mmol), phenol **6** (48 mg, 0.20 mmol), DCC (52 mg, 0.25 mmol) and DMAP (3 mg) were stirred in CH_2Cl_2 (10 ml) for 18 h. The reaction mixture was condensed and loaded directly onto a silica gel column. The column was eluted with a hexane/AcOEt mixture (3:1 ratio) to give 81 mg (86% yield) of ester **2H**, which was further purified by recrystallisation from isooctane (colourless needles). ^{1}H NMR (400 MHz): δ 0.92 (t, J=7.0 Hz, 3H), 0.93 (t, J=6.7 Hz, 3H), 1.29–1.40 (m, 12H), 1.50 (quint, J=7.2 Hz, 2H), 1.68 (quint, J=7.4 Hz, 2H), 1.84 (quint, J=7.0 Hz, 2H), 2.66 (t, J=7.7 Hz, 2H), 4.06 (t, J=6.6 Hz, 2H), 7.00 (d, J=8.9 Hz, 2H), 7.27 (d, J=8.6 Hz, 2H), 7.28 (d, J=8.6 Hz, 2H), 7.53 (d, J=8.0 Hz, 2H), 7.64 (d, J=8.6 Hz, 2H), 8.19 (d, J=8.8 Hz, 2H). IR (film, cm^{-1}): 1726 (C=O). Elemental analysis: calculated for $C_{32}H_{40}O_3$, C 81.32, H 8.53; found, C 81.43, H. 8.55%.

*4′-Pentylbiphenyl-4-yl 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)benzoate (**2F**).*

A reaction of acid **4F** (*25*) (52 mg, 0.11 mmol) with phenol **6** (29 mg, 0.12 mmol) as described for the preparation of **2H** gave 61 mg (yield 81%) of ester **2F**, which was further purified by recrystallisation from MeCN followed by isooctane/toluene (colourless microcrystals). ^{1}H NMR (400 MHz): δ 0.91 (t, J=6.9 Hz, 3H), 1.34–1.38 (m, 4H), 1.66 (quin, J=7.6 Hz, 2H), 2.65 (t, J=7.7 Hz, 2H), 2.69 (tt, J_1=18.4 Hz, J_2=6.7 Hz, 2H), 4.38 (t, J=6.7 Hz, 2H), 7.01 (d, J=9.0 Hz, 2H), 7.26 (d, J=8.6 Hz, 4H), 7.51 (d, J=8.2 Hz, 2H), 7.62 (d, J=8.6 Hz, 2H), 8.19 (d, J=8.9 Hz, 2H). IR (film, cm^{-1}): 1737 (C=O).

Elemental analysis: calculated for $C_{32}H_{27}F_{13}O_3$, C 54.40 H 3.85; found, C 54.68, H 3.81%.

*4-(4-Pentylbicyclo[2.2.2]oct-1-yl)phenyl 4-octyloxybenzoate (**3H**).*

A reaction of acid **4H** (125 mg, 0.5 mmol) with phenol **7** (*24*) (123 mg, 0.5 mmol) as described for the preparation of **2H** gave 250 mg (yield 89%) of ester **3H**, which was further purified by double recrystallisation from isooctane (white flakes). ^{1}H NMR: δ 0.89 (t, J=6.8 Hz, 6H), 1.07–1.40 (m, 16H), 1.45–1.53 (m, 8H), 1.78–1.86 (m, 8H), 4.04 (t, J=6.5 Hz, 2H), 6.96 (d, J=8.8 Hz, 2H), 7.10 (d, J=8.7 Hz, 2H), 7.35 (d, J=8.6 Hz, 2H), 8.13 (d, J=8.8 Hz, 2H). Elemental analysis: calculated for $C_{34}H_{50}O_3$, C 80.58, H 9.94; found, C 80.84, H 9.66%.

*4-(4-Pentylbicyclo[2.2.2]oct-1-yl)phenyl 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)benzoate (**3F**).*

The ester was obtained in 82% yield as described for **2F** and purified by recrystallisation from isooctane, followed by CH_2Cl_2/EtOAct, and then by MeCN/toluene. ^{1}H NMR: δ 0.89 (t, J=6.8 Hz, 3H), 1.06–1.35 (m, 8H), 1.45–1.53 (m, 6H), 1.78–1.86 (m, 6H), 2.68 (tt, J_1=18.3 Hz, J_2=6.3 Hz, 2H), 4.36 (t, J=6.7 Hz, 2H), 6.90 (d, J=8.3 Hz, 2H), 7.10 (d, J=8.2 Hz, 2H), 7.36 (d, J=8.2 Hz, 2H), 8.16 (d, J=8.3 Hz, 2H). Elemental analysis: calculated for $C_{34}H_{35}F_{13}O_3$, C 55.29, H 4.78; found, C 55.43, H 4.89%.

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