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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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 SmI (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, A=1,12-dicarba-closo-dodecaborane (p-carborane) in which each vertex represents a BH fragment and each sphere is a carbon atom.
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 derivative 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>
<thead>
<tr>
<th>X</th>
<th>A</th>
<th>Cr 94 N 165 I (32.5) (1.3)</th>
<th>Cr 102 SmC 123 N 182 I (24.0) (1.0) (1.5)</th>
<th>Cr 101 SmA 108 N 216 I (18.6) (0.5) (1.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Cr 128 SmC 120</td>
<td>Cr 113 SmF 97 SmI 111</td>
<td>Cr 141 X 188 SmA 280 I (27.8) (3.2) (10.5)</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>189 N 193 I</td>
<td>SmC 178 SmA 248 I</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.

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

![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.](image)

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 (\( x = 0.5 \)).

![Figure 3. Structure of chiral analogues of compounds 1 and 2.](image)
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 enthalpy changes 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 CH2Cl2, 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 CH2Cl2, 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-octoxybenzoate (1H).

A solution of crude acid chloride, prepared from acid 4H (50 mg, 0.20 mmol) and SOCl2, phenol 5 (24 mg, 0.20 mmol), and Et3N (28 μl, 0.20 mmol) in CH2Cl2 was stirred at ambient temperature. The crude product was passed through a silica gel plug and recrystallised from heptane. 1H NMR (300 MHz): δ 0.84 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.6 Hz, 3H), 1.09–1.13 (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 C28H33B10F13O3, C 43.53, H 4.30%; found, C 43.53, H 4.35%.

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. 1H NMR (300 MHz): δ 0.84 (t, J = 7.1 Hz, 3H), 1.09–1.25 (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), 7.53 (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): 1733 (C=O), 2611 (B–H). Elemental analysis: calculated for C28H46B10O3, C 62.42, H 8.61%; found, C 62.21, H 8.35%.

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

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). 1H 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, J1 = 18.4 Hz, J2 = 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). \(^\text{1}H\) NMR: \(\delta 0.89\) (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 54.40, H 3.85; found, C 54.68, H 3.81%.

References