

# Novel supramolecular liquid-crystalline complexes derived from 5-*n*-decyl-substituted thieno[3,2-*b*]thiophene-2- and thiophene-2-carboxylic acids

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A convenient route to thieno[3,2-*b*]thiophene-2-carboxyaldehyde (**1**) for the synthesis of new 5-*n*-decylthieno[3,2-*b*]thiophene-2-carboxylic acid (**10**) is described. A class of novel supramolecular liquid-crystalline complexes are formed starting from **10** or 5-*n*-decylthiophene-2-carboxylic acids and stilbazoles, through intermolecular hydrogen bonding.

The synthesis and characterization of hydrogen-bonded liquid crystals have recently drawn increasing attention.<sup>1</sup> By way of the molecular recognition and self-assembly of suitably functionalized similar or dissimilar molecules through hydrogen bonding, a variety of supramolecular liquid crystals can be constructed simply and spontaneously. Although many supramolecular liquid crystals formed by interaction of various hydrogen donors and acceptors have been reported, the use of heterocyclic carboxylic acid as a donor in this system hitherto remains unexplored. Here we report the preparation and characterization of a novel class of thieno[3,2-*b*]thiophene- and thiophene-containing supramolecular liquid-crystalline complexes (Fig. 1) where the 5-*n*-decylthieno[3,2-*b*]thiophene-2- or 5-*n*-decylthiophene-2-carboxylic acid<sup>2</sup> and *trans*-4-alkoxy-4'-stilbazoles<sup>3</sup> are used as building components.

A convenient route to thieno[3,2-*b*]thiophene-2-carboxyaldehyde (**1**)<sup>4</sup> from the available methyl 3-hydroxy-5,6-dihydrothieno[3,2-*b*]thiophene-2-carboxylate (**2**)<sup>7</sup> was developed for the synthesis of the required 5-*n*-decylthieno[3,2-*b*]thiophene-2-carboxylic acid (**10**) (Scheme 1). Treatment of **2** (24.4 mmol) with methanesulfonyl chloride (MsCl, 29.7 mmol) and triethylamine (64.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) at room temperature gave the mesylate **3**<sup>†</sup> as a solid in 98% yield after purification by flash chromatography (silica gel, hexane–ethyl acetate, 3 : 1). Reductive removal of the methanesulfonyl group from **3** to afford **5** was accomplished by treatment of **3** (7.2 mmol) with sodium iodide (36 mmol) and Zn–Ag (72

mmol) in anhydrous DMSO (20 mL) under nitrogen at 80 °C for 26 h, presumably *via* the iodo intermediate **4**.<sup>8</sup> After filtration, extraction (CHCl<sub>3</sub>), and purification by flash chromatography (silica gel, hexane–ethyl acetate, 15 : 1), methyl 5,6-dihydrothieno[3,2-*b*]thiophene-2-carboxylate (**5**)<sup>†</sup> was obtained as a solid in 80% yield. Reaction of **5** with LiAlH<sub>4</sub> (2.5 equiv.) in anhydrous diethyl ether afforded the crude alcohol **6**<sup>†</sup>, which was directly treated with an excess of MnO<sub>2</sub> (10 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> by stirring at room temperature for 24 h giving the aldehyde **1** in 91% overall yield from **5**. A smooth oxidation of the alcohol functionality as well as the dihydrothiophene ring occurred in one flask. The spectral data of **1** are identical with those previously reported.<sup>6</sup>

Synthesis of the new hydrogen-bonded donor **10** is straightforward as shown in Scheme 1 by sequential protection, alkylation and deprotection reactions wherein the crude intermediates **7** and **8** were used without purification.<sup>9</sup> Thus to a stirred solution of **7**<sup>6</sup> (1.88 mmol) in anhydrous THF (50 mL) and hexamethylphosphoramide (HMPA, 12.2 mmol) at –78 °C was added Bu<sup>n</sup>Li (1.98 mmol) dropwise. The reaction mixture was stirred at the same temperature for 1 h prior to the addition of *n*-iododecane (2.12 mmol). After stirring for another 1 h, the resultant mixture was allowed to warm gradually to –60 °C and quenched with aqueous THF. The crude product **8** was obtained by eluting the reaction mixture through a silica gel column (hexane–ethyl acetate, 5 : 1) to remove HMPA. Further treatment of **8** with a catalytic amount of tosylic acid (0.2 equiv.) in refluxing acetone for 4 h gave **9**<sup>†</sup> as a solid after purification by flash chromatography (silica gel, hexane–ethyl acetate, 35 : 1) (87% overall yield from **1**). It is noteworthy that the use of HMPA (6.5 equiv.) as a

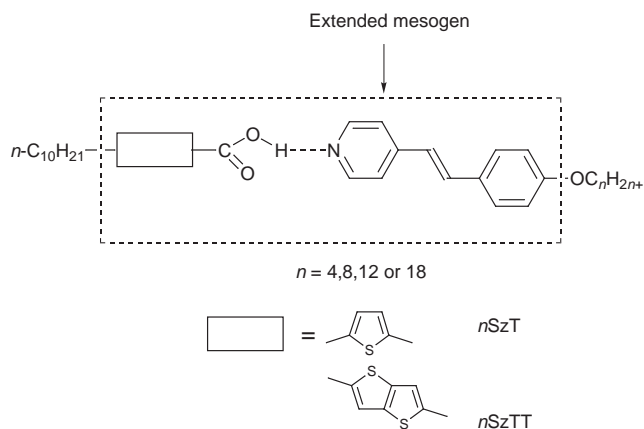
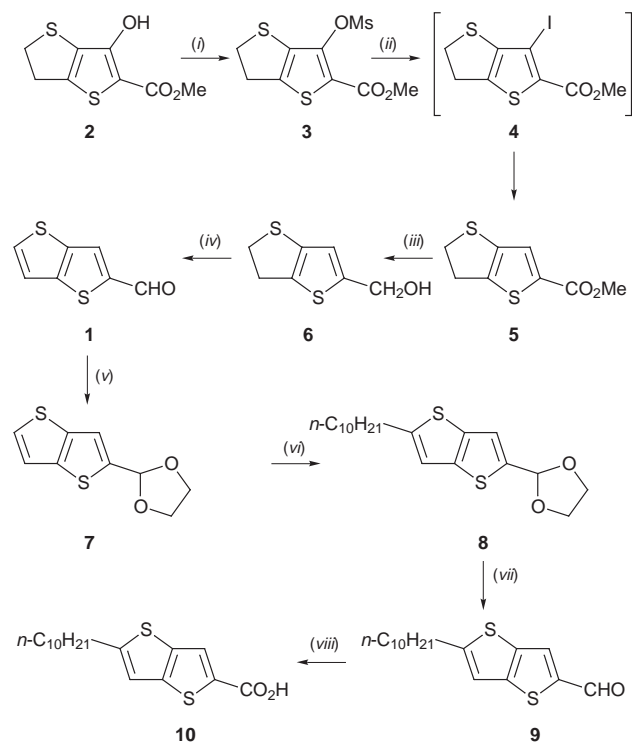


Fig. 1

<sup>†</sup> Compounds: **3**: mp 66–67 °C; <sup>1</sup>H NMR δ 3.26 (t, 2 H, *J* = 8 Hz), 3.34 (s, 3 H), 3.77 (t, 2 H, *J* = 8 Hz), 3.86 (s, 3 H); MS *m/z* 294 (*M*<sup>+</sup>, 100), 216, 215, 187, 184, 144, 100, 71. Exact mass calcd for C<sub>9</sub>H<sub>10</sub>O<sub>5</sub>S<sub>3</sub>: 293.9690; found: 293.9689; **5**: mp 55.5–56 °C; <sup>1</sup>H NMR δ 3.23 (t, 2 H, *J* = 8 Hz), 3.77 (t, 2 H, *J* = 8 Hz), 3.86 (s, 3 H), 7.46 (s, 1 H); MS *m/z* 200 (*M*<sup>+</sup>, 100), 169, 141, 140, 97, 69. Exact mass calcd for C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>S<sub>2</sub>: 199.9966; found: 199.9971; crude **6**: <sup>1</sup>H NMR δ 1.72 (t, 1 H, *J* = 5.9 Hz), 3.17 (t, 2 H, *J* = 8 Hz), 3.74 (t, 2 H, *J* = 8 Hz), 4.71 (d, 2 H, *J* = 5.9 Hz), 6.72 (s, 1 H); **9**: mp 40.5–41 °C; <sup>1</sup>H NMR δ 0.88 (t, 3 H, *J* = 6.8 Hz), 1.28 (br m, 14 H), 1.73 (m, 2 H), 2.91 (t, 3 H, *J* = 7.4 Hz), 7.01 (s, 1 H), 7.84 (s, 1 H), 9.91 (s, 1 H); MS *m/z* 308 (*M*<sup>+</sup>), 183, 182, 181 (100), 153. Exact mass calcd for C<sub>17</sub>H<sub>24</sub>O<sub>2</sub>S<sub>2</sub>: 308.1269; found: 308.1269; **10**: <sup>1</sup>H NMR δ 0.88 (t, 3 H, *J* = 7.1 Hz), 1.28 (br m, 14 H), 1.73 (m, 2 H), 2.91 (t, 3 H, *J* = 7.6 Hz), 6.99 (s, 1 H), 7.99 (s, 1 H); MS *m/z* 324 (*M*<sup>+</sup>), 199, 198, 197 (100), 175, 153, 149, 121, 90, 43, 41. Exact mass calcd for C<sub>17</sub>H<sub>24</sub>O<sub>2</sub>S<sub>2</sub>: 324.1218; found: 324.1231.



**Scheme 1** Reagents and conditions (i)  $\text{MSCl}$ ,  $\text{Et}_3\text{N}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ; (ii)  $\text{NaI}$ ,  $\text{Zn-Ag}$ ,  $\text{DMSO}$ ,  $80^\circ\text{C}$ ; (iii)  $\text{LiAlH}_4$ ,  $\text{Et}_2\text{O}$ ,  $25^\circ\text{C}$ ; (iv)  $\text{MnO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ; (v)  $\text{HOCH}_2\text{CH}_2\text{OH}$ ,  $\text{TsOH}$ ,  $\text{C}_6\text{H}_6$ , reflux; (vi)  $\text{Bu}^n\text{Li}$ ,  $n\text{-C}_{10}\text{H}_{21}\text{I}$ ,  $\text{THF}$ ,  $\text{HMPA}$ ,  $-78$ – $60^\circ\text{C}$ ; (vii)  $\text{TsOH}$ , acetone, reflux; (viii)  $\text{Ag}_2\text{O}$ ,  $\text{Et}_2\text{O}$ – $\text{MeOH}$ ,  $0$ – $25^\circ\text{C}$

cosolvent for the alkylation of **7** is crucial. In the absence of HMPA, less than 10% of the alkylated product **8** was obtained under the reaction conditions. Oxidation of **9** was carried out by treatment of an ethereal solution of **9** (1.2 mmol in 40 mL ether) with the vigorously stirred semisolid  $\text{Ag}_2\text{O}^{10}$  (prepared from 2.85 mmol aq.  $\text{AgNO}_3$  and 5.61 mmol aq.  $\text{NaOH}$ ) at  $0^\circ\text{C}$  for 10 min prior to the addition of 20 mL  $\text{MeOH}$ . The reaction mixture was stirred at room temperature for another 3 h. The silver suspension was removed by filtration and washed with hot water. The cold filtrate was acidified with concentrated hydrochloric acid precipitating the acid **10**† (90% yield), which was further purified by recrystallization from 95%  $\text{EtOH}$ .

The two novel classes of hydrogen-bonded liquid-crystalline mesogens  $n\text{SzTT}$  and  $n\text{SzT}$  (Fig. 1) containing three different aromatic rings within the extended rigid core are simply prepared by the slow evaporation of a tetrahydrofuran solution of **10** (TT) or 5- $n$ -decylthiophene-2-carboxylic acid (T) and *trans*-4-alkoxy-4'-stilbazole in a 1 : 1 molar ratio. Their phase-transition temperature ranges are listed in Table 1.

All new hydrogen-bonded complexes  $n\text{SzTT}$  and  $n\text{SzT}$  ( $n = 4, 8, 12$  or  $16$ ) are found to behave as one single component and exhibit different mesomorphic properties from their original constituents. As indicated in the Table 1, the new hydrogen donor **10** (TT) exhibits both smectic C and nematic (N) phases.<sup>11</sup> *Trans*-4-alkoxy-4'-stilbazoles ( $n\text{Sz}$ ,  $n = 4, 8, 12$  or  $16$ ) are known to have narrow ranges of smectic B and E phases<sup>3b</sup> while the 5- $n$ -decylthiophene-2-carboxylic acid (T) itself is nonmesogenic.<sup>2</sup> However, only the smectic A ( $S_A$ ), smectic C and two unidentified smectic X and X' ( $S_X$  and  $S_{X'}$ ) phases are observed for complexes  $n\text{SzTT}$  and  $n\text{SzT}$ , and the  $n\text{SzTT}$  ( $n = 4, 8, 12$  or  $16$ ) series possess neither

**Table 1** Phase-transition temperatures<sup>a</sup> of hydrogen-bonded complexes  $n\text{SzTT}$  and  $n\text{SzT}$  from a 1 : 1 molar ratio of *trans*-4-alkoxy-4'-stilbazoles ( $n\text{Sz}$ ) with 5- $n$ -decylthiophene-2-carboxylic acid (TT) or 5- $n$ -decylthiophene-2-carboxylic acid (T)

<b>TT</b>	K	$\frac{80.6(20.0)}{70.1(17.3)}$	$\xrightarrow{S_X}$	$\frac{130.2(34.1)}{118.2(36.4)}$	$\xrightarrow{S_C}$	$\frac{136.4(0.6)}{130.8(2.1)}$	$\xrightarrow{N}$	$\frac{168.3(9.0)}{164.6(8.1)}$	I
<b><math>n\text{SzTT}</math></b>									
( $n = 4$ )	K	$\frac{77.5(22.0)}{36.0(6.3)}$	$\xrightarrow{K'}$	$\frac{90.5(10.7)}{67.5(0.8)}$	$\xrightarrow{S_C}$	$\frac{102.0(b)}{101.0(b)}$	$\xrightarrow{S_A}$	$\frac{183.0(19.3)}{179.9(18.3)}$	I
( $n = 8$ )	K	$\frac{80.1(7.3)}{73.3(3.9)}$	$\xrightarrow{S_X}$	$\frac{104.1(0.9)}{101.4(1.5)}$	$\xrightarrow{S_C}$	$\frac{172.3(b)}{171.5(b)}$	$\xrightarrow{S_A}$	$\frac{181.9(17.3)}{178.6(18.1)}$	I
( $n = 12$ )	K	$\frac{53.8(2.0)}{85.0(3.8)}$	$\xrightarrow{K'}$	$\frac{88.5(4.1)}{119.4(6.2)}$	$\xrightarrow{S_C}$	$\frac{179.6(29.4)}{176.6(29.0)}$			I
( $n = 16$ )	K	$\frac{78.4(3.7)}{55.5(4.4)}$	$\xrightarrow{S_X}$	$\frac{119.1(7.5)}{115.9(7.2)}$	$\xrightarrow{S_C}$	$\frac{176.7(33.1)}{173.0(30.9)}$			I
<b><math>n\text{SzT}</math></b>									
( $n = 4$ )	K	$\frac{61.7(25.9)}{54.7(0.9)}$			$\xrightarrow{S_A}$	$\frac{132.3(18.3)}{128.1(18.8)}$			I
( $n = 8$ )	K	$\frac{60.6(42.2)}{25.3(40.9)}$	$\xrightarrow{S_X}$	$\frac{86.2(3.9)}{83.0(3.9)}$	$\xrightarrow{S_C}$	$\frac{110.0(b)}{108.0(b)}$	$\xrightarrow{S_A}$	$\frac{136.8(22.1)}{133.1(20.8)}$	I
( $n = 12$ )	K	$\frac{40.5(23.2)}{25.0(20.9)}$	$\xrightarrow{S_X'}$	$\frac{53.3(4.5)}{28.0(8.4)}$	$\xrightarrow{S_X}$	$\frac{102.2(7.9)}{98.8(8.5)}$	$\xrightarrow{S_C}$	$\frac{135.7(24.6)}{131.7(24.7)}$	I
( $n = 16$ )	K	$\frac{73.6(52.4)}{42.3(34.3)}$	$\xrightarrow{S_X}$	$\frac{105.5(10.9)}{101.8(11.2)}$	$\xrightarrow{S_C}$	$\frac{132.3(24.3)}{128.0(24.1)}$			I

<sup>a</sup> Phase-transition temperatures ( $^\circ\text{C}$ ) and the corresponding enthalpies ( $\text{J g}^{-1}$ , in parentheses) were determined by the second heating and cooling scans (heating and cooling rate of  $10^\circ\text{C min}^{-1}$ ) of differential scanning calorimetry using a Perkin Elmer DSC-7 calorimeter; abbreviations: K and K' = crystalline phases,  $S_X$  = unidentified smectic phase, I = isotropic liquid. <sup>b</sup> The enthalpy was too small to be detected by DSC and the phase-transition temperature was assigned by polarizing optical microscopy.

the nematic nor the smectic B and E phases. In contrast to the pure dimeric acids TT and T, the smectic A phase is apparently introduced in both complexes *nSzTT* and *nSzT* by the hydrogen-bonded interaction between the acid and stilbazole components. In addition, this interaction suppresses the nematic phase displayed by the dimeric acid TT. It is noted that the ranges of smectic A phase become wider for both *nSzTT* and *nSzT* bearing shorter alkoxy tails of the stilbazole moieties, and the smectic A phase disappears (replaced by the smectic C phase) for those with longer alkoxy chains (12*SzTT*, 16*SzTT*, 12*SzT* and 16*SzT*). Significantly, the tilted layered (smectic C) phase is stabilized (*i.e.* with a wider range of the *S<sub>C</sub>* phase) by the binary extended core, and the complex 8*SzTT* has the widest range of the *S<sub>C</sub>* phase (~68 °C) in both series. Such a trend is consistent with that of similar benzenoid homologues of thermotropic mesogens.<sup>12</sup>

It is also interesting that the new supramolecular liquid-crystalline complexes *nSzT* having a kinked molecular structure exhibit stable mesophases similar to those of the more rod-like complexes *nSzTT*, although with relatively narrow mesophase ranges and lower transition temperatures. This phenomenon is comparable with that of similar benzenoid supramolecular liquid-crystalline complexes having an angular structure.<sup>13</sup> It might be attributable to the reduced packing efficiency of the nonlinear configuration in the *nSzT* series.

In summary, we report herein a convenient synthesis of thieno[3,2-*b*]thiophene-2-carboxyaldehyde (**1**) as the precursor to 5-*n*-decylthieno[3,2-*b*]thiophene-2-carboxylic acid (**10**). Novel supramolecular liquid crystals *nSzTT* and *nSzT* are readily formed from **10** or 5-*n*-decylthiophene-2-carboxylic acid and stilbazoles through intermolecular hydrogen bonding. The present results suggest that the use of suitable heterocyclic acids as hydrogen-bonded donors could be of value in the design of new supramolecular liquid crystals.

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## References

- 1 For a recent review, see C. M. Paleos and D. Tsiourvas, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1696.
- 2 H. Wynberg and A. Logothetis, *J. Am. Chem. Soc.*, 1956, **78**, 1958.
- 3 (a) D. W. Bruce, D. A. Dunmur, E. Lalinde, P. M. Maitlis and P. Styring, *Liq. Cryst.*, 1988, **3**, 385. (b) H. C. Lin, L. L. Lai, Y. S. Lin, C. Tsai and R. C. Chen, *Mol. Cryst. Liq. Cryst.*, 1998, in the press.
- 4 The established routes to **1** involving either formylation of thieno[3,2-*b*]thiophene<sup>5</sup> or intramolecular cyclization of a 2,3-substituted thiophene<sup>6</sup> suffered the limitations of low overall yield and/or delicate synthetic operations.
- 5 Y. A. L. Gol'dfarb, V. P. Litvinov and S. Ozolin, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1965, 510; V. P. Litvinov and Y. A. L. Gol'dfarb, *Chemistry of Thienothiophenes*, in *Advanced Heterocyclic Chemistry*, eds. A. R. Katritzky and A. J. Boulton, Academic Press, New York, 1976, **19**, 123.
- 6 J. D. Prugh, G. D. Hartman, P. J. Mallorga, B. M. McKeever, S. R. Michelson, M. A. Murcko, H. Schwam, R. L. Smith, J. M. Sondey, J. P. Springer and M. F. Sugrue, *J. Med. Chem.*, 1991, **34**, 1805.
- 7 R. Donoso, P. J. de Urries and J. Lissavetzky, *Synthesis*, 1992, 526.
- 8 Y. Fujimoto and T. Tatsuno, *Tetrahedron Lett.*, 1976, 3325. The use of Zn-Ag instead of the zinc powder in our system greatly improved the yield of **5** (from 55% to 80%).
- 9 Ketals **7** and **8** are stable enough on silica gel and can be isolated by flash chromatography (silica gel, EtOAc-hexane, 1 : 25 for **7**, 1 : 35 for **8**).
- 10 E. Campaigne and M. LeSuer, *Org. Syntheses Coll. Vol. IV*, 1963, 919.
- 11 For several carboxylic acids with mesogenic properties due to the dimeric acid association through hydrogen bonding, see ref. 1.
- 12 L. J. Yu, *Liq. Cryst.*, 1993, **14**, 1303.
- 13 M. Willis, K. J. Price, H. Adams, G. Ungar and D. W. Bruce, *J. Mater. Chem.*, 1995, **5**, 2195; D. J. Price, K. Willis, T. Richardson, G. Ungar and D. W. Bruce, *J. Mater. Chem.*, 1997, **7**, 883; T. Kato, H. Adachi, A. Fujishima and J. M. J. Frechet, *Chem. Lett.*, 1992, 265; K. Willis, J. E. Luckhurst, D. J. Price, J. M. J. Frechet, J. Kihara, T. Kato, G. Ungar and D. W. Bruce, *Liq. Cryst.*, 1996, **21**, 585.

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