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

The synthesis and mesogenic behaviour of the first series of low molar mass thieno[3,2-b]thiophene-2-carboxylate ester-based mesogens

Raymond M. Gipson[a]; Paul Sampson[a]; Alexander J. Seed[a]
[a] Department of Chemistry, Kent State University, Kent, OH, USA

Online publication date: 12 January 2010

To cite this Article Gipson, Raymond M. , Sampson, Paul and Seed, Alexander J.(2010) 'The synthesis and mesogenic behaviour of the first series of low molar mass thieno[3,2-b]thiophene-2-carboxylate ester-based mesogens', Liquid Crystals, 37: 1, 101 — 108
To link to this Article: DOI: 10.1080/02678290903390965
URL: http://dx.doi.org/10.1080/02678290903390965

Liquid Crystals,
Vol. 37, No. 1, January 2010, 101–108

Taylor & Francis
Taylor & Francis Group

The synthesis and mesogenic behaviour of the first series of low molar mass thieno[3,2-*b*]thiophene-2-carboxylate ester-based mesogens

Raymond M. Gipson, Paul Sampson and Alexander J. Seed*

Department of Chemistry, Kent State University, Kent, OH 44242-0001, USA

(Received 14 August 2009; final form 6 October 2009)

The synthesis of a family of alkyl 5-(4-hexyloxyphenyl)thieno[3,2-*b*]thiophene-2-carboxylate liquid crystals is described. The synthetic methodology utilised includes a Fiesselmann synthesis of the thieno[3,2-*b*]thiophene core, and the first report of a completely regioselective α-bromination of the resulting thieno[3,2-*b*]thiophene-2-carboxylate ester. The target materials display enantiotropic smectic A phases with melting points and transition temperatures that are significantly higher than their phenyl analogues. The synthesis and mesomorphic behaviour of these new materials is reported and discussed.

Keywords: thieno[3,2-*b*]thiophene; esters; smectic A; high polarisability

1. Introduction

Highly polarisable rigid core units are often found in many different types of mesogenic structures that are utilised in electrooptic and all-optical applications. For example, high molecular polarisability is required for optical applications, including all-optical switches, spatial light modulation, organic field-effect transistors (OFETs), organic light emitting diodes (OLEDs), etc. Liquid crystals show great promise for use in OLED devices as macroscopic alignment of the director in the mesophase allows for the generation of anisotropic charge carrier mobility and polarised electroluminescence emission [1, 2]. Materials exhibiting glass transitions below the nematic phase are particularly valuable as they give excellent alignment, which is essential for high quantum efficiency. In addition, these glass transitions may help prevent crystallisation, thus increasing the lifetime of the device.

Like thiophene, the polarisable thieno[3,2-*b*]thiophene core is a compact heterocyclic unit that has a large number of π electrons per unit area (10 π electrons across 8 atoms). However, the thieno[3,2-*b*]thiophene core may be disubstituted at the 2 and 5 positions to give a completely linear unit unlike thiophene, which suffers from a bent-core structure whether 2,4- or 2,5-disubstituted [3]. These factors should lead to significantly enhanced mesophase thermal stability of thieno[3,2-*b*]thiophene mesogens when compared to analogous thiophene containing derivatives. In addition, when substituted with aromatic rings at the 2 and 5 positions of the thieno[3,2-*b*]thiophene core, it has been demonstrated that the interannular torsion angles are very small (for example, with 5-pyridyl it is 7.4°, and with 2-benzo[*d*]-1,3-thiazole it is 2.7° [4], which leads to extremely efficient conjugation across the molecular system. Small intermolecular π–π stacking distances between electron-donor and electron-acceptor intermolecular segments allows for effective charge carrier transfer perpendicular to the molecular plane [4]. Molecular roll (d_r) and pitch (d_p) distances have been shown [5] to be important for effective π-stacking and certain thieno[3,2-*b*]thiophenes have extremely small values of d_r with calculated electronic couplings that are almost double that of pentacene.

Thieno[3,2-*b*]thiophenes have seen relatively widespread use in the field of organic semiconductor, photovoltaic, and OLED-based applications [6–13]. In particular, it has been recently recognised that mesogenic thieno[3,2-*b*]thiophene-based polymers and low molar mass materials may exhibit exceptional carrier mobility and stability [14]. The alignment of such materials upon cooling from the isotropic phase through to the mesophase and into the crystal form has been shown to yield large highly ordered domains that are not obtained through solution deposition of non-mesogenic materials. Many other non-mesogenic thieno[3,2-*b*]thiophene-based systems have also been reported as non-linear optic chromophores [15], and for semiconductor application [9].

For a number of years we have been exploring new synthetic methodologies for the construction of flexible thieno[3,2-*b*]thiophene building blocks that may be incorporated into low molar mass mesogenic structures for potential use in optical applications, such as those described above. A detailed survey of the literature reveals that thieno[3,2-*b*]thiophene-containing mesogens have been reported a number of times

*Corresponding author. Email: aseed@kent.edu

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290903390965
http://www.informaworld.com

as polymeric derivatives (mostly poly(2,5-bis(3-alkylthiophen-2-yl) thieno[3,2-*b*]thiophenes and related systems) [14, 16–20], while only three reports exist for their incorporation in low molar mass materials [2, 6, 21].

The first synthetic approach to thieno[3,2-*b*]thiophene-based low molar mass mesogenic targets was reported by Tso *et al.* in 1998 [21]. The methodology used was very lengthy and unsuitable for the rapid and large-scale synthesis of flexible building blocks that we required. In 1997 Fuller *et al.* [22] reported the first large-scale and highly efficient synthesis of ethyl thieno[3,2-*b*]thiophene-2-carboxylate from the reaction of 3-bromothiophene-2-carbaldehyde with ethyl 2-mercaptoacetate and potassium carbonate (the Fiesselmann reaction). A number of related derivatives had been previously prepared by other authors using different bases to affect the ring closure [23–25].

The reaction of ethyl thieno[3,2-*b*]thiophene-2-carboxylate and related esters (esters with chains longer than two carbon atoms have not been reported in the literature) with electrophiles has not been evaluated [26], and we postulated that the thieno[3,2-*b*]thiophene ring would react at the α-position based on resonance delocalisation of the σ-complex. In order to generate the most flexible building block possible, we chose to incorporate a bromine atom at the α-position, which would enable us to carry out palladium-catalysed cross-coupling, halogen-metal exchange, etc., which would lead to a very broad synthetic utility.

This initial work has focused on an evaluation of the impact of the thieno[3,2-*b*]thiophene core on mesogenic behaviour, as studies in this area have yet to be carried out. This preliminary study focuses on the synthesis of a family of 5-(4-alkoxyphenyl)thieno[3,2-*b*]thiophene-2-carboxylate esters. The combination of aryloxy and carboxylate ester terminal groups was expected to confer high mesogenic thermal stability with Smectic A (SmA) and/or Smectic C (SmC) phases being exhibited.

2. Synthesis

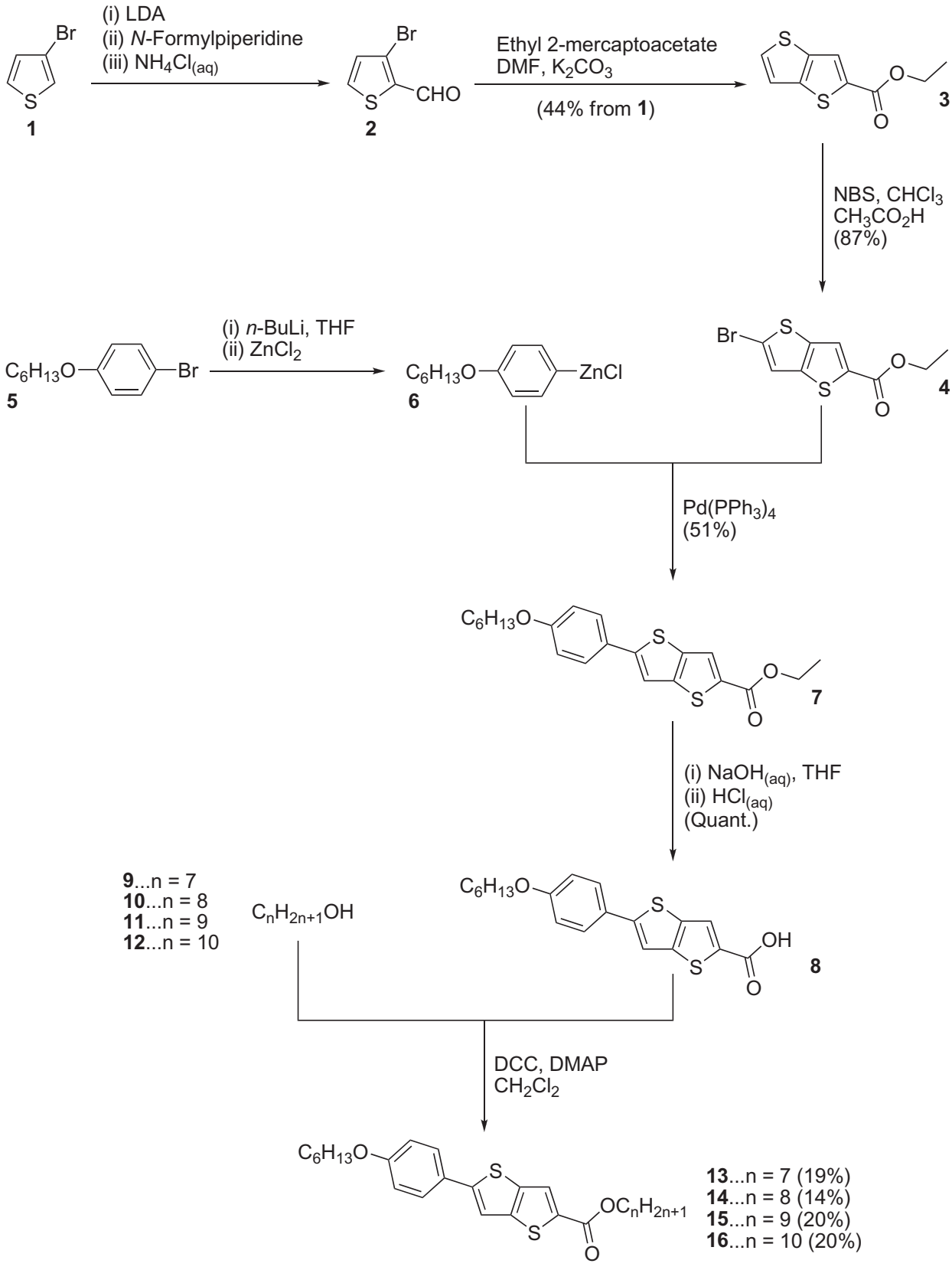
The preparation of alkyl 5-(4-alkoxyphenyl)thieno[3,2-*b*]thiophene-2-carboxylates **13–16** is depicted in Scheme 1. 3-Bromothiophene (**1**) was deprotonated at the more acidic α-position (ortho to bromine) using lithium diisopropylamide (LDA) followed by reaction with *N*-formylpiperidine and hydrolysis. The resulting crude aldehyde was then subjected to a tandem S_NAr/aldol condensation (Fiesselmann reaction) to afford ethyl thieno[3,2-*b*]thiophene-2-carboxylate **3** according to the procedure described by Fuller *et al.* [22].

To the best of our knowledge, bromination of alkyl thieno[3,2-*b*]thiophene-2-carboxylate esters has not been performed prior to this publication. In general, electrophilic aromatic substitution of thieno[3,2-*b*]thiophenes is a very under-developed area with few significant publications [26–28]. However, from the limited number of studies in the literature, it is clear that the parent thieno[3,2-*b*]thiophene is more reactive than thiophene and that the α:β regioselectivity is approximately 1000:1 [27]. Resonance arguments suggested that electrophilic aromatic substitution on these carboxylate ester derivatives would take place at the unsubstituted α-position with high levels of regioselectivity. Using related thienyl and thieno[3,2-*b*]thiophene substrates [29–32] as model systems we chose to brominate **3** using *N*-bromosuccinimide in a mixed solvent system (chloroform/acetic acid, 1:1). Under these conditions the bromination of **3** was achieved with complete α-regioselectivity in 87% yield. The sparingly soluble nature of brominated product **4** in numerous organic solvents (including diethyl ether, ethyl acetate, and petroleum ether), necessitated its purification by filtering through a short plug of silica gel followed by recrystallisation from dichloromethane/petroleum ether. Silica gel chromatography resulted in product streaking and was abandoned. Unlike the parent 2-bromothieno[3,2-*b*]thiophene, which is known to decompose within a few hours at room temperature [32], **4** proved to be perfectly stable at room temperature. Palladium-catalysed Negishi coupling [33] of **4** with arylzinc chloride **6** gave a 50% yield of **7**. The Negishi method was selected as the method of choice due to the exceptional tolerance of arylzinc chlorides/bromides to a wide variety of sensitive functional groups including esters; thieno[3,2-*b*]thiophenes have been previously cross-coupled under Stille [4, 7–9, 11, 12], Suzuki-Miyaura [6] and Sonogashira [34] conditions. Once again, this material (**7**) has relatively low solubility and chromatography had to be carried out on a small scale with relatively large quantities of silica gel (a minimum of 100 g of silica gel per gram of crude **7**). Ester **7** was then subjected to basic hydrolysis to give carboxylic acid **8**. Finally, acid **8** was subjected to esterification with alcohols **9–12** using *N*,*N*'-dicyclohexylcarbodiimide (DCC)/4-(*N*,*N*-dimethylamino)pyridine (DMAP) [35] to afford targets **13–16**. These longer chain esters proved to be much more soluble in organic solvents and were easily purified by column chromatography followed by recrystallisation.

3. Results and discussion

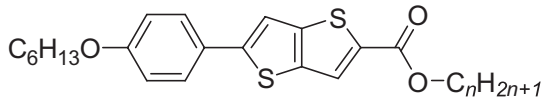
3.1 Transition temperatures

The transition temperatures of the targeted alkyl 5-(4-hexyloxyphenyl)thieno[3,2-*b*]thiophene-2 carboxylates (**13–16**) [36] are shown in Table 1. The transition



Scheme 1. Synthetic route to alkyl 5-(4-hexyloxyphenyl)thieno[3,2-*b*]thiophene-2-carboxylates **13**–**16**.

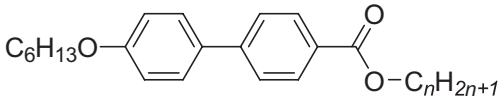
Table 1. Transition temperatures and associated enthalpies (kJ mol^{-1}) of alkyl 5-(4-hexyloxyphenyl)thieno[3,2-*b*]thiophene-2-carboxylates **13**–**16**.



n	Compound	Cryst		SmA		Iso Liq	Recryst.
7	**13**	•	140.1 *(22.31)*	•	164.2 *(10.48)*	•	132.5
8	**14**	•	136.3 *(22.46)*	•	160.7 *(11.41)*	•	129.8
9	**15**	•	133.5 *(20.39)*	•	157.2 *(10.86)*	•	128.2
10	**16**	•	131.1 *(26.73)*	•	154.2 *(14.79)*	•	127.8

Italicised numbers in parentheses are associated transition temperature enthalpies (kJ mol^{-1}).

Table 2. Transition temperatures of alkyl 4'-hexyloxybiphenyl-4-ylcarboxylates **17**–**20** synthesised by Goodby and Gray [37].



n	Compound	Cryst	SmB		SmA		Iso Liq	Recryst.
7	**17**	•	76	[• 57]	•	84	•	64
8	**18**	•	74	(• 56)	•	82	•	54
9	**19**	•	71	(• 55)	•	80	•	53
10	**20**	•	59	(• 54.5)	•	78	•	51

( ) Indicates a monotropic phase.
[ ] Indicates a virtual transition temperature.

temperatures for the analogous alkyl 4'-hexyloxybiphenyl-4-ylcarboxylates (**17**–**20**) [37] are shown in Table 2.

All of the target 5-(4-hexyloxyphenyl)thieno[3,2-*b*]thiophene-2 carboxylates display enantiotropic SmA phases. The melting points and clearing points are all found to gradually decrease as the length of the terminal alkyl chain increases.

3.1.1 Comparison of the thieno[3,2-b]thiophene and benzene cores

The trends between the two series of thieno[3,2-*b*]thiophene and benzene-containing derivatives are remarkably similar. Like their thieno[3,2-*b*]thiophene counterparts, the benzene derivatives have melting and clearing points that decrease with increasing length of the terminal alkyl chain. The thieno[3,2-*b*]thiophene derivatives have melting points that are considerably higher than those of the phenyl analogues (compare **13** and **17** [increase of 64°C], **14** and **18** [increase of 62°C], **15** and **19** [increase of 63°C] and **16** and **20** [increase of 72°C]).

Both sets of compounds display enantiotropic SmA phases with the SmA–isotropic liquid (Iso Liq) phase transitions being observed to decrease as the terminal alkyl chain length increases. Again the clearing points (SmA–Iso Liq in all cases) are considerably higher for the thieno[3,2-*b*]thiophene series (compare **13** and **17** [increase of 80°C], **14** and **18** [increase of 79°C], **15** and **19** [increase of 77°C] and **16** and **20** [increase of 76°C]).

The longer chain benzene derivatives (**18**–**20**) have the additional feature of a monotropic Smectic B (SmB) phase, whereas the thieno[3,2-*b*]thiophenes do not exhibit any higher ordered smectic phases.

4. Conclusions

We have synthesised the first family of mesogenic thieno[3,2-*b*]thiophene-2-carboxylate ester-based mesogens. The synthetic pathway to the targets included the first report of an electrophilic aromatic substitution reaction (bromination) on a thieno[3,2-*b*]thiophene-2-carboxylate ester. The reaction proceeded with complete α-regioselectivity in high yield.

The thieno[3,2-*b*]thiophene-based compounds exhibit enantiotropic SmA phases and their melting and clearing points are significantly higher than for the analogous phenyl-containing compounds reported by Goodby and Gray [37]. Ongoing studies are underway to optimise the synthetic procedures and to further study the structure–property relationships of thieno[3,2-*b*]thiophene-containing mesogens.

5. Experimental

Confirmation of the structures of the products was obtained by ^{1}H (400 MHz) and ^{13}C (100 MHz) nuclear magnetic resonance (NMR) (Bruker Avance 400 MHz spectrometer using Topspin version 1.3 software) in $CDCl_3$ with tetramethylsilane as the internal standard. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA, USA).

The transition temperatures of the final products were determined by polarising optical microscopy using a Laborlux 12 POLS polarising microscope combined with a Mettler FP82HT Hot Stage and a Mettler FP90 Central Processor. Differential scanning

calorimetry (DSC) measurements were performed using a TA Instruments Differential Scanning Calorimeter 2920 at a heating and cooling rate of 5°C min^{-1} with indium as the internal standard.

Thin layer chromatography (TLC) was carried out using Whatman brand aluminium-backed plates (250 μm thick layer of 60 Å silica gel with an ultraviolet (UV) 254 nm fluorescence indicator). Column chromatography (flash) was carried out using Silicycle brand ultra pure silica gel silia*Flash*® P60 60 Å, 40–63 μm (230–400 mesh) particle size silica.

Anhydrous tetrahydrofuran (THF) was obtained by distillation over sodium with sodium benzophenone ketyl being used as the indicator. The petroleum ether was redistilled prior to use and zinc chloride was dried in an oven at 140°C. Dichloromethane was dried over activated 4 Å molecular sieves. All other chemicals were used as received.

The syntheses of compounds **2** [22], **3** [22] and **5** [38] have been reported previously.

5.1 3-Bromothiophene-2-carbaldehyde (2)

Compound **2** was prepared following the procedure reported by Fuller *et al.* [22] using anhydrous diisopropylamine (23 ml, $d = 0.722$ g ml^{-1}, 0.16 mol), *n*-butyllithium (10 M in hexanes, 14.7 ml, 0.15 mol), **1** (24.00 g, 147.2 mmol) and *N*-formylpiperidine (16.4 ml, $d = 1.019$ g ml^{-1}, 148 mmol). The reaction mixture was stirred at room temperature for 3 h. The isolated crude product was used in the next step without purification. Crude yield: 28.81 g. ^{1}H NMR ($CDCl_3$) δ 7.16 (1H, d, $J = 5.2$ Hz), 7.72 (1H, dd, $J = 1.6$ Hz, 5.2 Hz), 10.00 (1H, d, $J = 1.6$ Hz).

5.2 Ethyl thieno[3,2-b]thiophene-2-carboxylate (3)

A solution of **2** (4.68 g, 24.5 mmol) in dimethylformamide (DMF) (15 ml) was slowly added to a stirred mixture of ethyl 2-mercaptoacetate (3.00 g, 25.0 mmol), potassium carbonate (5.00 g, 36.2 mmol) and DMF (50 ml) at room temperature. The reaction mixture was stirred at room temperature for an additional two days (TLC analysis revealed a complete reaction). The potassium salts were filtered off and the red filtrate was diluted with dichloromethane (300 ml) and washed with water (3 × 100 ml). The combined organic fractions were dried (magnesium sulfate) and the drying agent was removed using vacuum filtration. The filtrate was concentrated under vacuum to afford an orange liquid that was purified by column chromatography (silica gel/10% diethyl ether in petroleum ether). A transparent orange liquid was obtained that slowly solidified on standing. Recrystallisation from petroleum ether gave a white solid that was dried *in vacuo* (P_2O_5). Yield: 2.27 g (44%), m.p. = 34.5–35.5°C. ^{1}H NMR ($CDCl_3$) δ 1.40 (3H, t, $J = 7.2$ Hz), 4.39 (2H, q, $J = 7.1$ Hz), 7.28 (1H, dd, $J = 0.64$ Hz, 5.2 Hz), 7.58 (1H, d, $J = 5.2$ Hz), 7.99 (1H, d, $J = 0.68$ Hz). ^{13}C NMR ($CDCl_3$) δ 14.36, 61.36, 119.73, 125.55, 131.60, 135.21, 138.73, 143.88, 162.65.

5.3 Ethyl 5-bromothieno[3,2-b]thiophene-2-carboxylate (4)

To a stirred, room temperature solution of **3** (4.00 g, 18.8 mmol), chloroform (45 ml), and acetic acid (45 ml) was with added *N*-bromosuccinimide (4.67 g, 26.2 mmol) in one portion. The solution was heated under reflux for 23 h before being allowed to cool to room temperature and was stirred for an additional 24 h. The reaction mixture was diluted with dichloromethane (400 ml), washed with water (3 × 125 ml) and dried ($MgSO_4$). The drying agent was filtered off and the solvent was removed *in vacuo* to give a black solid. The crude product was passed through a silica plug (5% ethyl acetate in petroleum ether) and the combined organic fractions were concentrated *in vacuo* to afford a brown solid. An analytically pure sample (a white solid) was obtained by recrystallisation from a mixture of dichloromethane and petroleum ether. Yield: 4.75g (87%), m.p. = 74.8–76.0°C. ^{1}H NMR ($CDCl_3$) δ 1.39 (3H, t, $J = 7.0$ Hz), 4.38 (2H, q, $J = 7.1$ Hz), 7.29 (1H, d, $J = 0.4$ Hz), 7.88 (1H, d, $J = 0.4$ Hz). ^{13}C NMR ($CDCl_3$) δ 14.35, 61.53, 118.45, 122.49, 124.98, 134.58, 138.91, 142.81, 162.52. Anal. calcd. for $C_9H_7BrO_2S_2$: C, 37.12; H, 2.42. Found C, 37.52; H, 2.45.

5.4 Ethyl 5-(4-hexyloxyphenyl)thieno[3,2-b]thiophene-2-carboxylate (7)

To a stirred solution of 1-bromo-4-hexyloxybenzene (4.321 g, 16.80 mmol) in anhydrous THF (20 ml) at –63°C was added *n*-BuLi (2.5 M solution in hexanes, 6.6 ml, 0.017 mol) over a temperature range from –63°C to –55°C. The reaction mixture was stirred for 10 min at –65°C before a solution of dry zinc chloride (2.348 g, 17.22 mmol) in anhydrous THF (25 ml) was added dropwise over a temperature range from –65°C to –60°C. The resulting solution was stirred for 10 min at –68°C before it was transferred via a cannula (over a period of 5 min) to a room temperature solution of **4** (4.750 g, 16.31 mmol), and $Pd(PPh_3)_4$ (2.069 g, 1.790 mmol) in anhydrous THF (50 ml). The reaction mixture was stirred for an additional 72 h at room temperature (gas chromatography (GC) analysis confirmed completion of the reaction) before being diluted with dichloromethane (500 ml). The solution

was washed successively with water (3 × 150 ml) and brine (150 ml) before being dried ($MgSO_4$). The drying agent was filtered off and the filtrate was concentrated *in vacuo* to give 10.70 g of a yellow solid. The crude product was purified by column chromatography (silica gel/dichloromethane) and recrystallised three times from ethyl acetate to give a white solid that was dried *in vacuo* (P_2O_5). Yield = 3.25 g (51%). Transitions (°C): Cryst 165.1 SmA 209.2 Iso. Liq (Rec. 163.1). ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t, $J = 7.1$ Hz), 1.28–1.42 (4H, m), 1.40 (3H, t, $J = 7.2$ Hz), 1.47 (2H, quint, $J = 7.3$ Hz), 1.80 (2H, quint, $J = 7.1$ Hz), 3.99 (2H, t, $J = 6.6$ Hz), 4.38 (2H, q, $J = 7.1$ Hz), 6.93 (2H, d, $J = 8.8$ Hz), 7.36 (1H, d, $J = 0.4$ Hz), 7.55 (2H, d, $J = 8.8$ Hz), 7.94 (1H, d, $J = 0.4$ Hz). ^{13}C NMR ($CDCl_3$) δ 14.04, 14.40, 22.61, 25.71, 29.19, 31.59, 61.29, 68.21, 114.26, 115.06, 125.79, 126.64, 127.41, 133.67, 137.11, 145.01, 150.88, 159.69, 162.68. Anal. calcd. for $C_{21}H_{24}O_3S_2$: C, 64.92; H, 6.23; S, 16.51. Found C, 64.74; H, 6.28; S, 16.27.

5.5 5-(4-hexyloxyphenyl)thieno[3,2-b]thiophene-2-carboxylic acid (8)

Compound **7** (2.038 g, 5.245 mmol) was dissolved in THF (100 ml) and stirred and heated to a temperature of 66°C. Aqueous sodium hydroxide (2.1 M, 5.0 ml, 0.011 mol) was added in one portion to the solution and within minutes of the addition a white precipitate started to form. After one day, THF (50 ml) and additional sodium hydroxide (1 eq. in 5 ml of water) were added to the reaction mixture (the reaction was still incomplete). After 4 days the cooled solution was concentrated *in vacuo* and THF (50 ml) and hydrochloric acid (1.0 M, 26 ml, 0.026 mol) were added. The mixture was stirred under reflux for 2 h before being allowed to cool to room temperature and the solvent was then removed *in vacuo*. The resulting white solid was washed with water (100 ml) and dichloromethane (10 ml) before being dried *in vacuo* (P_2O_5, paraffin wax). ^{1}H NMR analysis indicated the presence of a small quantity of an unidentified impurity, although the material was sufficiently pure to be used for the next reaction. When carried out on a 0.5 g scale, washing of the crude product with dichloromethane and water provided an analytically pure sample for liquid crystal and NMR analysis. Yield: 2.3513 g (quant.). Transitions (°C): Cryst 283.0 SmA 297.0 Decomp. ^{1}H NMR (dimethylsulfoxide (DMSO)-d_6) δ 0.89 (3H, t, $J = 7.0$ Hz), 1.24–1.38 (4H, m), 1.42 (2H, quint, $J = 7.2$ Hz), 1.73 (2H, quint, $J = 7.0$ Hz), 4.02 (2H, t, $J = 6.6$ Hz), 7.03 (2H, d, $J = 8.8$ Hz), 7.65 (2H, d, $J = 8.8$ Hz), 7.81 (1H, d, $J = 0.4$ Hz), 8.08 (1H, d, $J = 0.4$ Hz). The carboxylic acid proton was not detected. ^{13}C NMR (DMSO-d_6) δ 14.39, 22.54, 25.63, 29.05, 31.47, 68.12, 115.62, 115.66, 126.46, 126.79, 127.57, 135.03, 137.12, 144.78, 150.12, 159.64, 163.79.

5.6 Heptyl 5-(4-hexyloxyphenyl)thieno[3,2-b]thiophene-2-carboxylate (13)

DCC (0.2914 g, 1.412 mmol), DMAP (0.1464 g, 1.198 mmol), *n*-heptanol (0.164 g, 1.41 mmol) and anhydrous dichloromethane (125 ml) were stirred at room temperature under a nitrogen atmosphere for a few minutes before **8** (0.4629 g, 1.284 mmol) was added in one portion to the solution. The resulting mixture was stirred at room temperature for 5 days (^{1}H NMR analysis showed that the reaction was complete) before the *N*,*N*'-dicyclohexylurea precipitate was filtered off. The filtrate was washed successively with aqueous acetic acid (10%, 100 ml) and brine (100 ml) before being dried ($MgSO_4$). The drying agent was filtered off and the solvent was removed *in vacuo* to give 0.74 g of a pale yellow solid. The crude product was purified by column chromatography twice (silica gel/dichloromethane) and was recrystallised three times from ethyl acetate to afford a white solid. Yield = 0.1132 g (19%). Transitions (°C) Cryst. 140.1 SmA 164.2 Iso. Liq. (Rec. 132.5). ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t, $J = 7.2$ Hz), 0.92 (3H, t, $J = 7.2$ Hz), 1.23–1.53 (14H, m), 1.77 (2H, quint, $J = 6.8$ Hz), 1.80 (2H, quint, $J = 7.0$ Hz), 3.99 (2H, t, $J = 6.6$ Hz), 4.31 (2H, t, $J = 6.6$ Hz), 6.94 (2H, d, $J = 8.8$ Hz), 7.36 (1H, d, $J = 0.4$ Hz), 7.56 (2H, d, $J = 8.4$ Hz), 7.94 (1H, d, $J = 0.4$ Hz). ^{13}C NMR ($CDCl_3$) δ 14.04, 14.09, 22.61, 25.71, 25.95, 28.76, 28.96, 29.19, 31.59, 31.75, 65.46, 68.21, 114.25, 115.05, 125.75, 126.63, 127.41, 133.69, 137.11, 145.01, 150.85, 159.68, 162.76. The missing alkyl signal is due to accidental equivalence. Anal. calcd. for $C_{26}H_{34}O_3S_2$: C, 68.08; H, 7.47. Found C, 67.87; H, 7.20.

5.7 Octyl 5-(4-hexyloxyphenyl)thieno[3,2-b]thiophene-2-carboxylate (14)

Compound **14** was prepared in the same manner as compound **13**, except that *n*-octanol was employed in place of *n*-heptanol and the reaction mixture was stirred for 6 days. Quantities: **8** (0.5336 g, 1.480 mmol), DMAP (0.1603 g, 1.312 mmol), DCC (0.3529 g, 1.710 mmol), *n*-octanol (0.2116 g, 1.625 mmol), dichloromethane (anhydrous, 125 ml). The crude product was purified by column chromatography (silica gel/dichloromethane) and was recrystallised twice from ethyl acetate to afford a white solid that was dried *in vacuo* (P_2O_5, paraffin wax). Yield = 0.0966 g (14%). Transitions (°C) Cryst. 136.3 SmA 160.7 Iso. Liq. (Rec. 129.8). ^{1}H NMR ($CDCl_3$) δ 0.89 (3H, t, $J = 6.8$ Hz), 0.91 (3H, t, $J = 7.2$ Hz), 1.22–1.53 (16H, m), 1.76

(2H, quint, $J = 6.8$ Hz), 1.82 (2H, quint, $J = 6.8$ Hz), 3.99 (2H, t, $J = 6.4$ Hz), 4.31 (2H, t, $J = 6.8$ Hz), 6.93 (2H, d, $J = 8.8$ Hz), 7.36 (1H, s), 7.55 (2H, d, $J = 8.8$ Hz), 7.93 (1H, s). ^{13}C NMR ($CDCl_3$) δ 14.04, 14.11, 22.62, 22.66, 25.72, 26.00, 28.76, 29.20, 29.21, 29.25, 31.59, 31.81, 65.46, 68.21, 114.25, 115.06, 125.74, 126.64, 127.42, 133.71, 137.12, 145.01, 150.86, 159.69, 162.75. Anal. calcd. for $C_{27}H_{36}O_3S_2$: C, 68.60; H, 7.68. Found C, 68.48; H, 7.77.

5.8 Nonyl 5-(4-hexyloxyphenyl)thieno[3,2-b] thiophene-2-carboxylate (15)

Compound **15** was prepared in the same manner as compound **13**, except that *n*-nonanol was employed in place of *n*-heptanol and the reaction mixture was stirred for 7 days. Quantities: **8** (0.4835 g, 1.341 mmol), DMAP (0.1474 g, 1.207 mmol), DCC (0.3079 g, 1.492 mmol), *n*-nonanol (0.2126 g, 1.474 mmol), dichloromethane (anhydrous, 150 ml). The crude product was purified by column chromatography (silica gel/dichloromethane) and was recrystallised twice from ethyl acetate to afford a white solid that was dried *in vacuo* (P_2O_5, paraffin wax). Yield = 0.1305 g (20%). Transitions (°C) Cryst. 133.5 SmA 157.2 Iso. Liq. (Rec. 128.2). ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, $J = 6.8$ Hz), 0.91 (3H, t, $J = 6.8$ Hz), 1.20–1.54 (18H, m), 1.76 (2H, quint, $J = 6.8$ Hz), 1.80 (2H, quint, $J = 6.8$ Hz), 3.99 (2H, t, $J = 6.6$ Hz), 4.31 (2H, t, $J = 6.6$ Hz), 6.93 (2H, d, $J = 8.4$ Hz), 7.35 (1H, s), 7.55 (2H, d, $J = 8.8$ Hz), 7.93 (1H, s). ^{13}C NMR ($CDCl_3$) δ 14.05, 14.12, 22.62, 22.69, 25.72, 26.00, 28.76, 29.20, 29.26, 29.29, 29.51, 31.60, 31.88, 65.46, 68.21, 114.24, 115.06, 125.74, 126.64, 127.41, 133.71, 137.12, 145.01, 150.85, 159.69, 162.74. Anal. calcd. for $C_{28}H_{38}O_3S_2$: C, 69.09; H, 7.87. Found C, 68.94; H, 7.83.

5.9 Decyl 5-(4-hexyloxyphenyl)thieno[3,2-b] thiophene-2-carboxylate (16)

Compound **16** was prepared in the same manner as compound **13**, except that *n*-decanol was employed in place of *n*-heptanol and the reaction mixture was stirred for 3 days. Quantities: **8** (0.400 g, 1.11 mmol), DCC (0.235 g, 1.14 mmol), DMAP (0.127 g, 1.04 mmol), *n*-decanol (0.23 ml, $d = 0.829$ g/ml, 1.2 mmol) and anhydrous dichloromethane (150 ml). The crude product (0.28 g) was purified by column chromatography (silica gel/dichloromethane) and was recrystallised twice from ethyl acetate to afford a white solid that was dried *in vacuo* (P_2O_5). Yield: 0.112 g (20%). Transitions (°C): Cryst 131.1 SmA 154.2 Iso Liq. (Rec. 127.8). ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, $J = 6.7$ Hz), 0.92 (3H, t, $J = 7.0$ Hz), 1.20–1.52 (20H, m), 1.76 (2H, quint, $J = 6.8$ Hz), 1.80 (2H, quint, $J = 6.8$ Hz), 4.00 (2H, t, $J = 6.6$ Hz), 4.31 (2H, t, $J = 6.6$ Hz), 6.94 (2H, d, $J = 8.8$ Hz), 7.36 (1H, s), 7.56 (2H, d, $J = 8.8$ Hz), 7.94 (1H, s). ^{13}C NMR ($CDCl_3$) δ 14.05, 14.13, 22.62, 22.70, 25.72, 25.99, 28.74, 29.19, 29.28, 29.32, 29.55, 31.59, 31.91, 65.47, 68.21, 114.25, 115.05, 125.75, 126.63, 127.42, 133.69, 137.11, 145.01, 150.85, 159.68, 162.77. The missing alkyl signal is due to accidental equivalence. Anal. calcd. for $C_{29}H_{40}O_3S_2$: C, 69.56; H, 8.05. Found C, 69.03; H, 8.01.

Acknowledgements

Financial support from Kent State University is gratefully acknowledged. We would like to thank Dr. Mahinda Gangoda for assistance in obtaining some of the NMR spectra and Dr. Robert J. Twieg for use of his DSC instrument.

References

[1] Contoret, A.E.A.; Farrar, S.R.; Jackson, P.O.; Khan, S.M.; May, L.; O'Neill, M.; Nicholls, J.E.; Kelly, S.M.; Richards, G.J. *Adv. Mater.* **2000**, *12*, 971–974.
[2] Noh, Y.-Y.; Kim, D.-Y.; Misaki, M.; Yase, K. *Thin Solid Films* **2008**, *516*, 7505–7510.
[3] Seed, A. *Chem. Soc. Rev.* **2007**, *36*, 2046–2069.
[4] Chang, Y.-C.; Chen, Y.-D.; Chen, C.-H.; Wen, Y.-S.; Lin, J.T.; Chen, H.-Y.; Kuo, M.-Y.; Chao, I. *J. Org. Chem.* **2008**, *73*, 4608–4614.
[5] Curtis, M.D., Cao, J.; Kampf, J.W. *J. Am. Chem. Soc.* **2004**, *126*, 4318–4328.
[6] Liu, P.; Wu, Y.; Pan, H.; Li, Y.; Gardner, S.; Ong, B.S.; Zhu, S. *Chem. Mater.* **2009**, *21*, 2727–2732.
[7] San Miguel, L.; Matzger, A.J. *J. Org. Chem.* **2008**, *73*, 7882–7888.
[8] Biniek, L.; Chochos, C.L.; Leclerc, N.; Hadziioannou, G.; Kallitsis, J.K.; Bechara, R.; Lévêque, P.; Heiser, T. *J. Mater. Chem.* **2009**, *19*, 4946–4951.
[9] Ahmed, M.O.; Wang, C.; Keg, P.; Pisula, W.; Lam, Y.-M.; Ong, B.S.; Ng, S.-C.; Chen, Z.-K.; Mhaisalkar, S.G. *J. Mater. Chem.* **2009**, *19*, 3449–3456.
[10] Kim, K.H.; Chi, Z.; Cho, M.J.; Jin, J.-I.; Cho, M.Y.; Kim, S.J.; Joo, J.-S.; Choi, D.H. *Chem. Mater.* **2007**, *19*, 4925–4932.
[11] Lee, J.-Y.; Shin, W.-S.; Haw, J.-R.; Moon, D.-K. *J. Mater. Chem.* **2009**, *19*, 4938–4945.
[12] San Miguel, L.; Porter, W.W.; Matzger, A.J. *Org. Lett.* **2007**, *9*, 1005–1008.
[13] Chang, Y.C.; Chen, Y.D.; Chen, C.H.; Wen, Y.S.; Lin, J.T.; Chen, H.Y.; Kuo, M.Y.; Chao, I. *J. Org. Chem.* **2008**, *73*, 4608–4614.
[14] DeLongchamp, D.M.; Kline, R.J.; Jung, Y.; Lin, E.K.; Fischer, D.A.; Gundlach, D.J.; Cotts, S.K.; Moad, A.J.; Richter, L.J.; Toney, M.F.; Heeney, M.; McCulloch, I. *Macromolecules* **2008**, *41*, 5709–5715.
[15] Blenkle, M.; Boldt, P.; Bräuchle, C.; Grahn, W.; Ledoux, I.; Nerenz, H.; Stadler, S.; Wichern, J.; Zyss, J. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1377–1384.
[16] DeLongchamp, D.M.; Kline, R.J.; Jung, Y.; Germack, D.S.; Lin, E.K.; Moad, A.J.; Richter, L.J.;

Toney, M.F.; Heeney, M.; McCulloch, L. *ACS Nano.* **2009**, *3*, 780–787.
[17] Kline, R.J.; DeLongchamp, D.M.; Fischer, D.A.; Lin, E.K.; Heeney, M.; McCulloch, I.; Toney, M.F. *Appl. Phys. Lett.* **2007**, *90*, 062117–062117-3.
[18] Lucas, L.A.; DeLongchamp, D.M.; Vogel, B.M.; Lin, E.K.; Fasolka, M.J.; Fischer, D.A.; McCulloch, I.; Heeney, M.; Jabbour, G.E. *Appl. Phys. Lett.* **2007**, *90*, 012112–012112-3.
[19] McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; Macdonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M.L.; Kline, R.J.; McGehee, M.D.; Toney, M.F. *Nature Materials* **2006**, *5*, 328–333.
[20] Umeda, T.; Kumaki, D.; Tokito, S. *J. Appl. Phys.* **2009**, *105*, 024516–024516-5.
[21] Tso, H.-H.; Wang, J.-S.; Wu, C.-Y.; Lin, H.-C. *New J. Chem.* **1998**, *22*, 771–773.
[22] Fuller, L.S.; Iddon, B.; Smith, K.A. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3465–3470.
[23] Prugh, J.D.; Hartman, G.D.; Mallorga, P.J.; McKeever, B.M.; Michelson, S.R.; Murcko, M.A.; Schwam, H.; Smith, R.L.; Sondey, J.M.; Springer, J.P.; Sugrue, M.F. *J. Med. Chem.* **1991**, *34*, 1805–1818.
[24] Rutherford, D.R.; Stille, J.K.; Elliott, C.M.; Reichert, V.R. *Macromolecules* **1992**, *25*, 2294–2306.
[25] Prim, D.; Kirsch, G. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2603–2606.
[26] Litvinov, V.P. The chemistry of thienothiophenes, In *Advances in Heterocyclic Chemistry*; Katritzky, A.R., Ed.; Amsterdam: Academic Press, 2006; pp. 125–203.
[27] Bugge, A. *Chem. Scr.* **1972**, *2*, 137–142.
[28] Bugge, A. *Acta Chem. Scand.* **1971**, *25*, 27–34.
[29] Lawesson, S.-O. *Ark. Kemi* **1957**, *11*, 373–386.
[30] Goldfarb, J.L.; Volkenštein, J.B.; Belenkij, L.I. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 519–529.
[31] Seed, A.J.; Cross, G.J.; Toyne, K.J.; Goodby, J.W. *Liq. Cryst.* **2003**, *30*, 1089–1107.
[32] Bugge, A. *Acta Chem. Scand.* **1969**, *23*, 2704–2710.
[33] Negishi, E.-I. *Acc. Chem. Res.* **1982**, *15*, 340–348.
[34] Tranchier, J.-P.; Chavignon, R.; Prim, D.; Auffrant, A.; Plyta, Z.F.; Rose-Munch, F.; Rose, E. *Tetrahedron Lett.* **2000**, *41*, 3607–3610.
[35] Hassner, A.; Alexanian, V. *Tetrahedron Lett.* **1978**, 4475–4478.
[36] Gipson, R.M. The synthesis of novel thieno[3,2-*b*]thiophene-2-carboxylate liquid crystals, *Senior honors thesis*, Kent State University, May 2009.
[37] Goodby, J.W.; Gray, G.W. *J. Phys. (Paris)* **1976**, *37*, 17–26.
[38] Gray, G.W.; Hird, M.; Lacey, D.; Toyne, K.J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 2041–2053.