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A new synthesis of alkylsulphanylnaphthalenes and the synthesis and mesomorphic properties of novel naphthylisothiocyanates

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The syntheses and transition temperatures of 2-(4-butylsulphanylphenyl)-6-isothiocyanatonaphthalene and 1-(4-butylsulphanylphenyl)-2-(6-isothiocyanato-2-naphthyl)ethyne are reported and discussed. These are the first examples of mesogenic isothiocyanatonaphthalenes to be reported in the literature. The transition temperatures of these compounds were compared and contrasted with compounds where the naphthalene and benzene rings had been interchanged and the analogous compounds where a cyano group replaced the isothiocyanate. The new compounds had high nematic phase thermal stabilities and relatively low melting points. As part of this work we present a new synthetic method for the synthesis of the key 2-alkylsulphanyl-6-bromonaphthalene building block that is a marked improvement over currently available methodology.

Keywords: alkysulphanyl; isothiocyanate; naphthalene; high polarizability

1. Introduction

A significant number of naphthalene-based materials have been synthesised as highly birefringent materials for electrooptic devices. The majority of naphthalene-based mesogens have the 2,6-disubstitution pattern as this is the most linear substitution pattern for naphthalene. Many of these 2,6-disubstituted mesogens incorporate alkoxy, alkynyl, alkyl and cyano terminal groups to give wide mesophase ranges but often with associated high melting points (*1–7*). 1,5-Disubstituted systems are also known but have received much less attention due to their reduced mesomorphic behaviour (*8–14*).

Some time ago we evaluated the alkylsulphanyl group as a chain that would confer high polarisability (and hence a high birefringence) and wide mesophase ranges whilst at the same time giving melting points that were often significantly lower than their alkoxy and alkynyl naphthalene analogues (*15*). The birefringences and polarisabilities of these materials are among some of the highest values reported in the literature on liquid crystals and hold significant promise for use in electrooptic devices. We previously found that such systems should ideally incorporate a naphthalene ring together with one other ring (e.g. phenyl or thiophene), a short chain (four carbon atoms were determined to be optimum in order to minimise the dilution effect (*16*, *17*)), a polarisable terminal unit (isothiocyanates and nitriles in particular) and possibly with an alkyne linking group. The incorporation of additional rings was often found to be problematic as solubility in commercial nematic hosts decreased dramatically and melting points increased substantially (*6*). It was noted that in such systems the polarisable nitrile group sometimes gives rise to a higher molecular polarisability and birefringence when directly bonded to the naphthalene ring (as opposed to the phenyl ring) (*17*), although this is not observed universally and the values are often close to identical (*6*). The transition temperatures of such analogues, where naphthalene may be present as the left-hand or the right-hand ring, may be nearly identical or significantly different and are not predictable (*5*, *6*).

In this paper we conclude our work on highly birefringent naphthalene-based systems with the synthesis of a new class of naphthylisothiocyanate mesogen **I** and **II** (Figure 1). The transition temperatures of the new mesogens are compared and contrasted with systems where the butylsulphanyl chain is instead directly attached to the naphthalene ring (**III** and **IV**).

Transition temperatures of our new materials are also compared with analogous nitrile-based mesogens and a binaphthylisothiocyanate. In addition, we present a new and improved method of synthesising the key alkyl- and arylsulphanylnaphthalene building blocks (required for the synthesis of **III** and **IV**) from

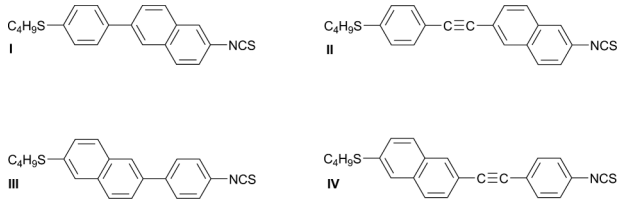

Figure 1. Target naphthylisothiocyanates **I** and **II** and their phenylisothiocyanate analogue **III** and **IV**.

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naphthols. The new method gives high yields of pure products and is a major improvement over currently existing methodology.

2. Synthesis

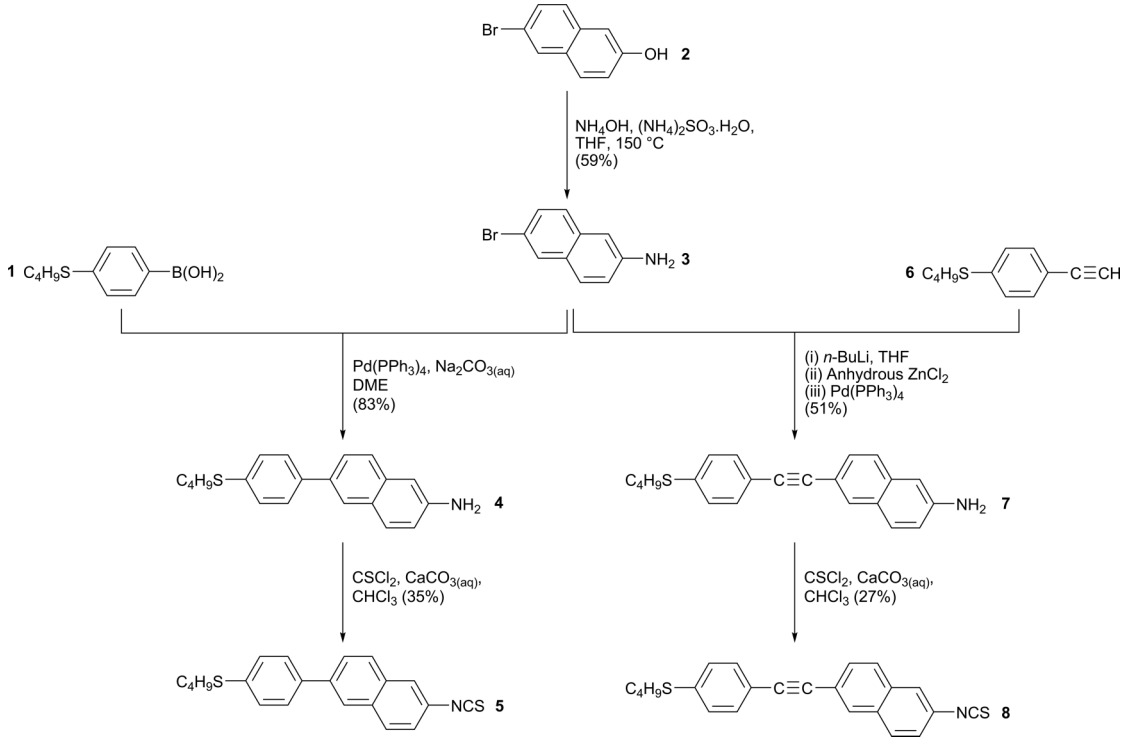
The synthesis of isothiocyanate-based targets **5** and **8** is depicted in Scheme 1.

Naphthylamine **3** was synthesised from **2** using the Bucherer reaction (*18*). Due to the known toxicity of naphthylamines, the handling of this type of material (compounds **3**, **4**, **7** and **11**) was kept to the bare minimum and spectra, etc., were not recorded unless absolutely essential. Suzuki-Miyaura coupling of **3** with **1** gave **4** and Negishi coupling of **3** with **6** gave **7**. Amines **4** and **7** were reacted with thiophosgene in the presence of calcium carbonate to give isothiocyanates **5** and **8**, respectively (*19*).

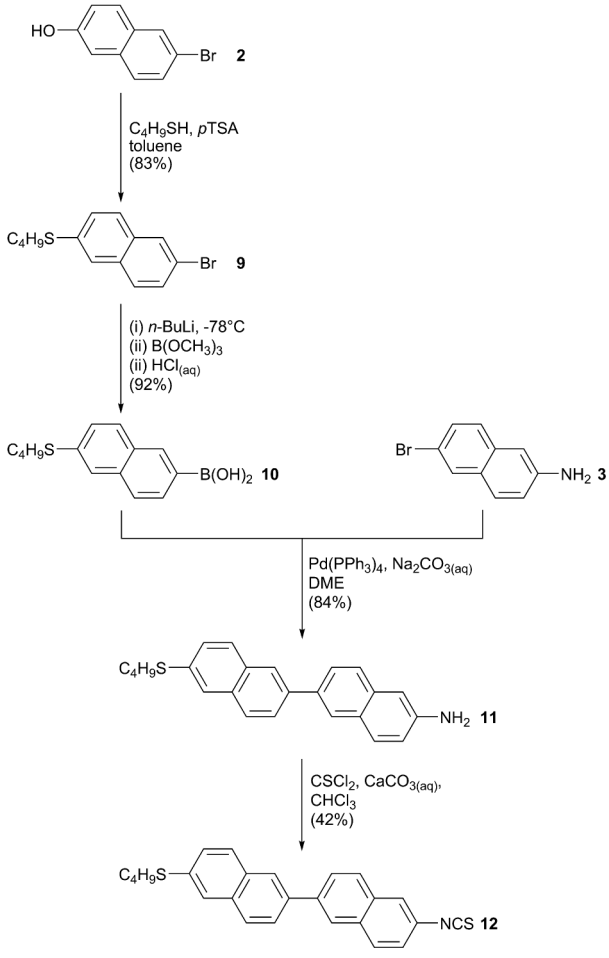
Scheme 2 illustrates the synthesis of binaphthyl **12** via building block **9**; compound **9** has been found to be useful in the synthesis of highly polarisable nematic mesogens.

One of us has previously synthesised materials containing butylsulphanylnaphthalene units (*15*) using the procedure described by Nakazawa *et al.* (*20*). This methodology involves the reaction of 6-bromo-2-naphthol with butanethiol in the presence of trifluoromethanesulphonic acid with benzene as the solvent. The reaction gives a black tarry product that is difficult to purify and yields are modest (the best yield we obtained in six experiments was 61%). In addition, the reaction uses hazardous materials that make it very unattractive on a large scale. A review of the literature revealed that there are relatively few methods available (*20–22*) for the synthesis of such compounds; the method of Furman *et al.* (*22*) appeared to hold the most potential although this procedure gave somewhat variable yields (non-optimised). In this paper we present a new procedure that involves several modifications of Furman's method to give highly pure materials in excellent yields (74–99% for 2-naphthol-based substrates) and on relatively large reaction scales. The scope of the methodology has also been explored and was found to be applicable to the synthesis of a wide range of alkyl and arylsulphanylnaphthalenes (see compounds **9**, **14**-**20**, and **22** in Schemes 2 and 3).

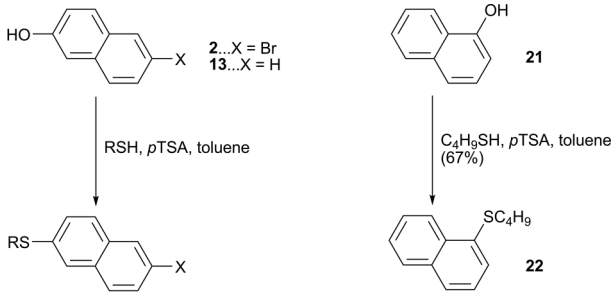
Modifications included carrying out the reaction under dry nitrogen, use of toluene as solvent (Furman's method is solvent-free), and the constant removal of water (Dean-Stark apparatus). In most cases a slight excess of the thiol was used (approximately 5 mol% excess), although in the synthesis of **14** (Scheme 3), the volatility of propanethiol was problematic and a two-fold excess was required to ensure the completion of the reaction. This procedure was



Scheme 1. Synthesis route to naphthylisothiocyanate targets **5** and **8**.



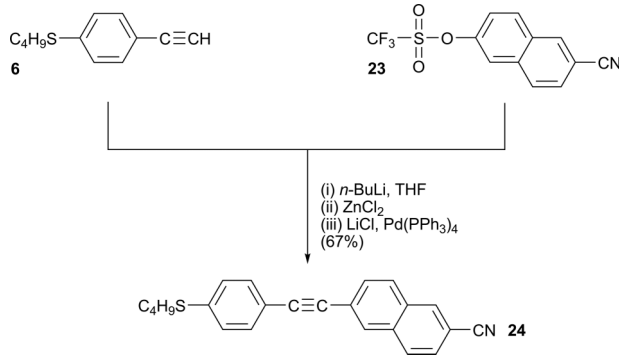
Scheme 2. Synthesis route to naphthylisothiocyanate target **12**.



14...R = C_3H_7, X = Br (78%)
15...R = C_5H_{11}, X = Br (95%)
16...R = C_9H_{19}, X = Br (99%)
17...R = $CH_2CH_2CH(CH_3)CH_3$, X = Br (74%)
18...R = $CH_2CH(CH_3)CH_2CH_3$, X = Br (79%)
19...R = C_4H_9, X = H (80%)
20...R = *p*-methoxyphenyl, X = Br (95%)

Scheme 3. Novel synthesis of alkylsulphanylnaphthalenes **14**–**20** and **22**.

applied to the synthesis of **9** (Scheme 2) giving an 84% yield of the purified product (23% higher than obtained by the Nakazawa method). The conversion



Scheme 4. Synthesis of cyanonaphthalene target **24**.

of **9** to **10** has been described previously (*15*). Suzuki-Miyaura coupling of **3** and **10** gave amine **11**, which was converted to the isothiocyanate **12** as usual.

Scheme 4 illustrates the coupling of triflate **23** and alkyne **6** to give target **24**.

3. Results and discussion

3.1 Transition temperatures

3.1.1 Mesogenic behaviour of 5, 8, 12 and 24–29

The transition temperatures of **5**, **8**, **12** and **24**–**29** are given in Table 1. The synthesis and transition temperatures of **25**–**29** have been previously reported (*15*). The compounds reported in Table 1 are predominantly nematogenic (all exhibit enantiotropic nematic phases) with binaphthyl **12** also exhibiting an enantiotropic SmB phase that was identified by growth of the typical mosaic texture on cooling from the nematic phase.

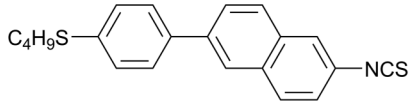
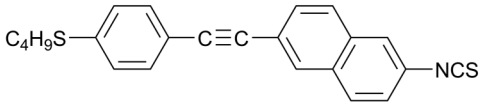
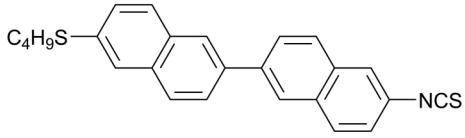
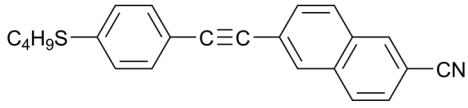
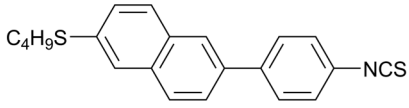
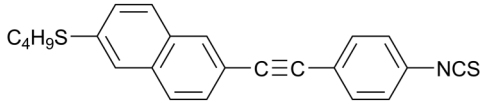
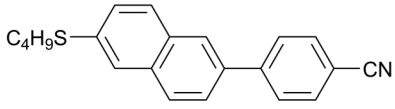
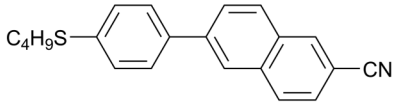
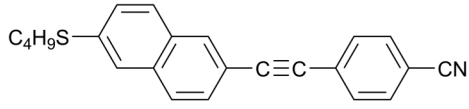
3.1.2 Comparison of the melting points

The replacement of a cyano-terminal group with an isothiocyanate usually results in an increase of the melting point (compare **5** and **28** [increase of 9.2°C], **25** and **27** [increase of 6.1°C], and **26** and **29** [increase of 4.5°C]), although this is not a universal trend (compare **8** and **24** [decrease of 2.4°C]) as has been noted previously (*15*, *23*).

Incorporation of an alkyne linking group between the naphthalene and benzene rings gives a similar result with the alkyne-linked system usually having the lower melting point (compare **5** and **8** [decrease of 2.8°C], **25** and **26** [decrease of 6.6°C] and **27** and **29** [decrease of 5.0°C]), although there is again an exception to the rule (compare **24** and **28** [increase of 8.8°C]).

An examination of the position of the naphthalene ring remains to be discussed. The location of the naphthalene ring as the right-hand or left-hand ring is of particular importance when viewed in relation to

Table 1. Transition temperatures of **5**, **8**, **12** and **24**–**29**.

Compound	Structure	Cryst		SmB		N		Iso Liq.
5		•	102.4	—		•	119.1	•
8		•	99.6	—		•	134.5	•
12		•	158.8	•	164.0	•	195.4	•
24		•	102.0	—		•	143.2	•
25		•	98.1	—		•	125.7	•
26		•	91.5	—		•	136.7	•
27		•	92.0	—		•	107.0	•
28		•	93.2	—		•	114.8	•
29		•	87.0	—		•	131.8	•

the polarisability and birefringence of the system. In previous work one of us (AJS) discovered that when the naphthalene ring was directly bonded to a cyano moiety (right-hand ring), the birefringence and polarisability were greater than when the naphthalene was present as the left-hand ring (compounds **27** and **28**) (*17*). This was attributed to the electron withdrawing nitrile being directly attached to the larger of the two 'electron boxes' (naphthalene having four more π electrons than benzene) and being able to cause a more effective polarisation of the π electrons of the naphthalene ring. In this study when naphthalene is present as the right-hand ring the melting point is seen to be higher than when it is on the left-hand side of the molecule

(compare **5** and **25** [increase of 4.3°C], **8** and **26** [increase of 8.1°C], **24** and **29** [increase of 15.0°C], and **27** and **28** [increase of 1.2°C]). Not surprisingly, when both of the rings are naphthalene the melting point increases significantly (compare **5** and **12** [increase of 56.4°C] and **25** and **12** [increase of 60.7°C]).

3.1.3 Comparison of the clearing points

The replacement of a cyano-terminal group by an isothiocyanate gives a mixture of results. When there is no alkyne linking group the isothiocyanate-based compound always has a higher clearing point than its cyano analogue (compare **5** and **28** [increase of 4.3°C] and **25** and **27** [increase of 18.7°C]) that is most likely a result of the greater polarisabilities and aspect ratios of the isothiocyanates. The presence of the linking group gives a mixture of results and when the naphthalene is the right-hand ring the isothiocyanate has the lower clearing point (compare **8** and **24** [decrease of 8.7°C]), and when it occupies the left-hand ring it has the higher clearing point (compare **26** and **29** [increase of 4.9°C]). This outcome is not clear and may be the result of a subtle interplay of the factors affecting clearing points, i.e. polarisability anisotropy, aspect ratio and antiparallel association (nitriles only).

The incorporation of an alkyne linkage between ring systems always leads to an increase in the clearing point due to corresponding increases in molecular polarisability and aspect ratio of the molecule (compare **5** and **8** [increase of 15.4°C], **24** and **28** [increase of 28.4°C], **25** and **26** [increase of 11.0°C] and **27** and **29** [increase of 24.8°C]).

The position of the naphthalene ring again leads to mixed results and we will first consider the isothiocyanate-based compounds. When the right-hand ring is naphthalene the clearing point is always found to be lower than when naphthalene is instead present as the left-hand ring (compare **5** and **25** [decrease of 6.6°C] and **8** and **26** [decrease of 2.2°C]). For the cyano-based compounds the trend is just the reverse and when naphthalene occupies the right-hand ring the clearing points are higher than when naphthalene is the left-hand ring (compare **24** and **29** [increase of 11.4°C] and **27** and **28** [increase of 7.8°C]). Again, when both rings are naphthalene the clearing point increases dramatically in accordance with the increase in polarisability and aspect ratio (compare **5** and **12** [increase of 76.3°C] and **12** and **25** [increase of 69.7°C]).

4. Conclusions

We have successfully synthesised the first series of naphthylisothiocyanate-based liquid crystals that display broad enantiotropic nematic phases. The combination of alkylsulphanyl chain, naphthalene ring, alkyne linker and isothiocyanate terminus is expected to confer high birefringence and polarisability that will make these derivatives potentially useful as optical switches, spatial light modulators, etc.

5. Experimental

Confirmation of the structures of intermediates and products was obtained by ^{1}H (Varian INOVA 500 MHz FT nuclear magnetic resonance (NMR) spectrometer with VNMR version 5.3 software) and ^{13}C (125 MHz) NMR spectroscopy in $CDCl_3$. Chemical shifts are reported in ppm downfield from TMS. Combustion analyses were performed by Atlantic Microlab (Norcross, Georgia, USA).

The progress of reactions was monitored using either silica thin layer chromatography (TLC) (aluminium-backed silica gel plates; Sigma-Aldrich, 200 μm layer thickness, 2–25 μm particle size and 60 Å pore size) or gas chromatograpy (GC) (Shimadzu GC-14A gas chromatograph fitted with a 30 m Restek™ RTX-5 capillary column and Shimadzu class VP software).

All chromatographic separations were performed using column chromatography on silica gel (Fisher Davisil® silica gel; 60 Å, 55–75 μm particle size, grade 1740) or alumina (Acros Organics, aluminium oxide-activated basic, 50–200 μm).

Pressure tubes were purchased from Ace Glass Inc. (model # 8648-89 with poly(tetrafluoroethylene) (PTFE) plug) and were pressure rated to 150 psi.

Transition temperatures of the final products were measured using a Mettler FP82HT hot-stage and FP90 control unit in conjunction with a Leica Laborlux 12PolS polarising microscope. All transition temperatures are quoted from microscope measurements and are given upon cooling at a rate of 5°C per minute. The control unit was calibrated with three Merck standards (benzophenone, benzoic acid and caffeine). Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Differential Scanning Calorimeter 2920 at heating and cooling rates of 5°C per minute with indium as internal standard.

The preparations of compounds **1** (*16*), **3** (*24*), **6** (*23*), **10** (*15*) and **23** (*15*) have been described previously. Zinc chloride was dried overnight in an oven at 140°C. Anhydrous tetrahydrofuran (THF) was obtained by distillation from benzophenone ketyl and toluene was dried over sodium metal. All other materials were purchased from Aldrich Chemical Company and Acros Chemical Company and were used without purification.

5.1 Scheme 1

*5.1.1 6-Bromo-2-naphthylamine (**3**)*

A mixture of **2** (10.0 g, 44.8 mmol), ammonium hydroxide (20 ml, 28% in water) saturated with ammonium sulphite monohydrate (7.00 g, 52.2 mmol), and ammonium hydroxide (20 ml, 28% in water), was heated at 150°C for 24 hours in a sealed glass tube. The cooled reaction mixture was poured into dichloromethane (200 ml) and the resulting solution was washed successively with distilled water (2 × 100 ml) and aqueous potassium hydroxide (5% wt/vol, 3 × 100 ml) before being dried ($MgSO_4$). The drying agent was filtered off and the solvent was removed *in vacuo*. The resulting pink/purple solid was then recrystallised three times from ethanol to give a white-pink powder that was dried *in vacuo* (P_2O_5, paraffin wax). Yield 5.87 g, (59%), melting point (mp) 126–127°C (Lit. (*25*) 127–128°C). Analysis calculated for $C_{10}H_8BrN$: C, 54.08; H, 3.63; N 6.31. Found: C, 53.96; H, 3.64; N, 6.19.

*5.1.2 6-(4-Butylsulphanylphenyl)-2-naphthylamine (**4**)*

Aqueous sodium carbonate (7.2 ml, 2M, 0.014 mol), **1** (2.00 g, 9.52 mmol), and tetrakis(triphenylphosphine)-palladium(0) (0.48 g, 0.42 mmol) were added sequentially to a rapidly stirred solution of **3** (1.76 g, 7.93 mmol) in dimethoxyethane (DME), (75 ml) under dry nitrogen. The reaction mixture was heated under reflux overnight and the cooled reaction mixture was extracted with diethyl ether (2 × 200 ml); the combined organic extracts were washed with saturated sodium chloride (3 × 100 ml) before being dried ($MgSO_4$). The drying agent was filtered off and the solvent was removed *in vacuo* before the crude product was purified by column chromatography (silica gel/dichloromethane, petroleum ether 1:1) to afford a white solid. Yield 2.02 g (83%).

*5.1.3 2-(4-Butylsulphanylphenyl)-6-isothiocyanatonaphthalene (**5**)*

A solution of compound **4**, (2.00 g, 6.51 mmol) in chloroform (50 ml) was added dropwise at 0–5°C to a stirred mixture of thiophosgene (0.86 g, 7.5 mmol), chloroform (50 ml), calcium carbonate (0.97 g, 9.7 mmol) and water (40 ml) at 5°C. Once the addition was complete the solution was allowed to warm to room temperature and was stirred for 10 minutes before being heated at 35°C for 1 hour. The reaction mixture was poured into water (100 ml) and the organic layer was washed with hydrochloric acid (1%, 100 ml) before being dried ($MgSO_4$). The drying agent was filtered off and the solvent was removed *in vacuo* before the crude product was purified twice by column chromatography (silica gel/hexane, followed by silica ge /hexane: ethyl acetate, 9:1). The product was crystallised twice from hexane: ethyl acetate (9:1) to give a white solid which was dried *in vacuo* (P_2O_5, paraffin wax). Yield 0.79 g (35%). Transitions (°C) Cryst. 102.4 N 119.1 Iso Liq. (rec. 100.8). ^{1}H NMR ($CDCl_3$) δ 0.96 (3H, t, J = 7.4 Hz), 1.50 (2H, sext, J = 7.2 Hz), 1.70 (2H, quint, J = 7.4 Hz), 3.00 (2H, t, J = 7.4 Hz), 7.35 (1H, dd, J = 2.2, 9.0 Hz), 7.43 (2H, d, J = 8.4 Hz), 7.63 (2H, d, J = 8.8 Hz), 7.71 (1H, d, J = 1.6 Hz), 7.78 (1H, dd, J = 1.8, 8.6 Hz), 7.86 (2H, app. t, J = 8.0 Hz), 8.00 (1H, app. s). ^{13}C NMR ($CDCl_3$) δ 13.67, 22.02, 31.21, 33.11, 123.74, 124.22, 125.30, 126.72, 127.66(2C), 128.08, 128.48, 129.01(2C), 129.91, 132.18, 132.42, 135.63, 137.07, 137.65, 138.87. Analysis calculated for $C_{21}H_{19}NS_2$: C, 72.16; H, 5.48; N 4.01. Found: C, 71.98; H, 5.50; N, 3.90.

*5.1.4 1-(6-Amino-2-naphthyl)-2-(4-butylsulphanyl) ethyne (**7**)*

n-Butyllithium (5.7 ml, 2.5 M in hexanes, 0.014 mol) was added dropwise to a stirred, cooled (–7°C) solution of **6** (2.46 g, 12.9 mmol) in anhydrous THF (100 ml), under dry nitrogen, at –3°C to –7°C (a colour change from yellow to deep red was noted). The reaction conditions were maintained for a further 40 minutes before a solution of dry zinc chloride (1.96 g, 14.4 mmol) in anhydrous THF (50 ml) was added dropwise at –3°C to +3°C. Once the addition was complete the reaction mixture was allowed to warm to room temperature and was stirred for an additional 30 minutes before being cooled to 0°C. Compound **3** (2.57 g, 11.6 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.94 g, 0.81 mmol) were added all at once and the reaction mixture was heated under a gentle reflux overnight (gas liquid chromatography (GLC) analysis revealed a complete reaction). The cooled mixture was poured into water (200 ml) and extracted with dichloromethane (2 × 200 ml); the combined organic extracts were washed with saturated sodium hydrogen carbonate (200 ml) and dried (MgSO4). The drying agent was filtered off and the solvent was removed *in vacuo* before the crude product was purified by column chromatography (silica gel/petroleum fraction (boiling point (bp) 40–60°C), dichloromethane, 1:1) to afford a yellow solid. Yield 1.96 g (51%).

*5.1.5 1-(4-Butylsulphanylphenyl)-2-(6-isothiocyanato-2-naphthyl)ethyne (**8**)*

The experimental procedure was as described for the preparation of **5** using the quantities stated: compound **7** (1.96 g, 5.91 mmol), thiophosgene (0.82 g, 7.1 mmol), and calcium carbonate (0.89 g, 8.9 mmol).

The crude product was purified by column chromatography (silica gel/petroleum fraction, bp 40–60°C, dichloromethane, 5:1) and was recrystallised from hexane: ethyl acetate, 35:13 to afford white crystals which were dried *in vacuo* (P_2O_5, paraffin wax). Yield 0.60 g (27%). Transitions (°C) Cryst 99.6 N 134.5 Iso Liq. (rec. 94.1). ^{1}H NMR ($CDCl_3$) δ 0.96 (3H, t, J = 7.3 Hz), 1.49 (2H, sext, J = 7.4 Hz), 1.68 (2H, quint, J = 7.5 Hz), 2.98 (2H, t, J = 7.4 Hz), 7.29 (2H, d, J = 8.5 Hz), 7.34 (1H, dd, J = 1.9, 8.4 Hz), 7.47 (2H, d, J = 8.5 Hz), 7.61 (1H, dd, J = 1.5, 8.4 Hz), 7.67 (1H, d, J = 2.2 Hz), 7.75 (1H, d, J = 8.7 Hz), 7.80 (1H, d, J = 8.7 Hz), 8.01 (1H, app. s). ^{13}C NMR ($CDCl_3$) δ 13.65, 22.01, 31.02, 32.57, 89.50, 90.65, 119.67, 121.69, 123.82, 124.49, 127.56, 127.70(2C), 129.21, 129.53, 129.83, 131.09, 131.48, 131.96(2C), 132.64, 136.09, 138.63. Analysis calculated for $C_{23}H_{19}NS_2$: C, 73.95; H, 5.13; N 3.75. Found: C, 74.18; H, 4.99; N, 3.82.

5.2 Scheme 2

5.2.1 2-Bromo-6-butylsulphanylnaphthalene (**9**)

A mixture of **2** (19.0 g, 85.2 mmol), butanethiol (8.00 g, 88.7 mmol), *p*-toluenesulphonic acid (5.40 g, 31.4 mmol), and dry toluene (250 ml), under dry argon, was heated under reflux for 48 hours (GC analysis confirmed a complete reaction) with constant removal of water (Dean-Stark trap). The cooled reaction mixture was washed successively with water (250 ml), aqueous sodium hydroxide (5% wt/vol, 2 × 200 ml), and water (250 ml) before being dried ($MgSO_4$). The drying agent was filtered off and the solvent was removed *in vacuo* before the crude product was recrystallised from ethanol to afford a white solid which was dried *in vacuo* (P_2O_5, paraffin wax). Yield 21.0 g (83%), mp 47.5–48.4°C (Lit. 39–41°C). ^{1}H NMR ($CDCl_3$) δ 1.06 (3H, t, J = 7.5 Hz), 1.50 (2H, sext, J = 7.3 Hz), 1.63 (2H, quint, J = 7.1 Hz), 3.00 (2H, t, J = 7.2 Hz), 7.42 (1H, dd, J = 2.4, 8.3 Hz), 7.52 (1H, dd, J = 2.3, 8.7 Hz), 7.59 (1H, d, J = 8.7 Hz), 7.63 (1H, d, J = 8.7 Hz), 7.66 (1H, app. s), 7.93 (1H, d, J = 1.6 Hz). ^{13}C NMR ($CDCl_3$) δ 13.68, 22.03, 31.09, 32.91, 119.16, 125.65, 127.30, 127.99, 128.57, 129.77, 129.85, 132.23, 132.55, 135.62. Analysis calculated for $C_{14}H_{15}BrS$: C, 56.95; H, 5.12. Found: C, 56.93; H, 5.13.

5.2.2 6-(6-Butylsulphanylnaphth-2-yl)-2-naphthylamine (**11**)

The preparation of **11** was as described for the preparation of compound **4** using the quantities stated: tetrakis (triphenylphosphine)palladium (0) (0.40 g, 0.35 mmol), **10** (1.67 g, 6.42 mmol), **3** (1.30 g, 5.85 mmol), aqueous sodium carbonate (2.0 M, 6.5 ml, 13 mmol). A brown solid was obtained which was used in the next step without purification. Yield 1.75 g (84%).

5.2.3 6-(6-Butylsulphanylnaphth-2-yl)-2-isothiocyanatonaphthalene (**12**)

The preparation of **12** was as described for the preparation of compound **5** using the quantities stated: **11** (1.70 g, 4.76 mmol), thiophosgene (0.640 g, 5.57 mmol) and calcium carbonate (0.720 g, 7.19 mmol). The crude product was recrystallised from petroleum ether to afford a yellow-white solid. Yield 0.80 g (42%). Transitions (°C) Cryst 158.8 SmB 164.0 N 195.4 Iso Liq. ^{1}H NMR ($CDCl_3$) δ 0.98 (3H, t, J = 7.3 Hz), 1.53 (2H, sext, J = 6.8 Hz), 1.73 (2H, quint, J = 7.3 Hz), 3.08 (2H, t, J = 7.3 Hz), 7.38 (1H, dd, J = 1.9, 6.8 Hz), 7.48 (1H, dd, J = 1.9, 6.8 Hz), 7.76 (2H, d, J = 10.0 Hz), 7.81–7.94 (6H, m), 8.13 (2H, d, J = 13.2 Hz). ^{13}C NMR ($CDCl_3$) δ 13.92, 22.28, 31.39, 33.28, 123.99, 124.48, 125.68, 125.84, 126.04, 126.08, 126.27, 127.05, 127.69, 127.75, 128.15, 128.60, 129.98, 131.81, 132.22, 132.48, 133.17, 135.40, 137.28, 139.25, 170.60. Analysis calculated for $C_{25}H_{21}NS_2$: C, 75.15; H, 5.30. Found: C, 75.48; H, 5.44.

5.3 Scheme 3

5.3.1 2-Bromo-6-propylsulphanylnaphthalene (**14**)

The preparation of **14** was as described for the preparation of compound **9** using the quantities stated: **2** (5.00 g, 22.4 mmol), propanethiol (3.50 g, 46.0 mmol), *p*-toluenesulphonic acid (3.00 g, 17.4 mmol) and dry toluene (250 ml). The crude product was recrystallised from ethanol to afford a white solid which was dried *in vacuo* (P_2O_5, paraffin wax). Yield 4.90 g (78%), mp 43.1–43.7°C. ^{1}H NMR ($CDCl_3$) δ 1.06 (3H, t, J = 7.5 Hz), 1.72 (2H, sext, J = 7.3 Hz), 2.99 (2H, t, J = 7.1 Hz), 7.42 (1H, dd, J = 2.4, 8.3 Hz), 7.52 (1H, dd, J = 2.3, 8.7 Hz), 7.59 (1H, d, J = 8.7 Hz), 7.63 (1H, d, J = 8.7 Hz), 7.66 (1H, app. s), 7.93 (1H, d, J = 1.6 Hz). ^{13}C NMR ($CDCl_3$) δ 13.39, 22.31, 35.14, 119.06, 125.68, 127.18, 127.95, 128.44, 129.63, 129.72, 132.10, 132.44, 135.37. Analysis calculated for $C_{13}H_{13}BrS$: C, 55.52; H, 4.66. Found: C, 55.41; H, 4.55.

5.3.2 2-Bromo-6-pentylsuphanylnaphthalene (**15**)

The preparation of **15** was as described for the preparation of compound **9** using the quantities stated: **2** (10.0 g, 44.8 mmol), pentanethiol (4.80 g, 46.1 mmol), *p*-toluenesulphonic acid (3.00 g, 17.4 mmol) and dry

toluene (250 ml). The crude product was recrystallised from ethanol to afford a white solid which was dried *in vacuo* (P_2O_5, paraffin wax). Yield 13.1 g (95%), mp 43.2–43.7°C. ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t, J = 7.1 Hz), 1.35 (2H, sext, J = 7.2 Hz), 1.44 (2H, quint, J = 7.1 Hz), 1.70 (2H, quint, J = 7.3 Hz), 3.01 (2H, t, J = 7.5 Hz), 7.42 (1H, dd, J = 1.5, 8.7 Hz), 7.52 (1H, dd, J = 2.3, 8.7 Hz), 7.59 (1H, d, J = 8.7 Hz), 7.63 (1H, d, J = 8.7 Hz), 7.66 (1H, app. s), 7.93 (1H, d, J = 1.6 Hz). ^{13}C NMR ($CDCl_3$) δ 14.51, 22.82, 29.27, 31.63, 33.78, 119.72, 126.22, 127.85, 128.55, 129.12, 130.42(2C), 132.80, 133.11, 136.18. Analysis calculated for $C_{15}H_{17}BrS$: C, 58.25; H, 5.54. Found: C, 58.33; H, 5.63.

*5.3.3 2-Bromo-6-nonylsulphanylnaphthalene (**16**)*

The preparation of **16** was as described for the preparation of compound **9** (except that the reaction mixture was heated under reflux for 24 hours) using the quantities stated: **2** (10.0 g, 44.8 mmol), nonanethiol (7.50 g, 46.8 mmol), *p*-toluenesulphonic acid (3.00 g, 17.4 mmol) and dry toluene (250 ml). The crude product was recrystallised from ethanol to afford a white solid which was dried *in vacuo* (P_2O_5, paraffin wax). Yield 16.2 g (99%), mp 51.1–52.0°C. ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, J = 7.1 Hz), 1.27 (10H, m), 1.46 (2H, quint, J = 7.1 Hz), 1.69 (2H, quint, J = 7.1 Hz), 3.01 (2H, t, J = 7.1 Hz), 7.42 (1H, dd, J = 1.6, 8.7 Hz), 7.52 (1H, dd, J = 1.3, 8.8 Hz), 7.59 (1H, d, J = 8.7 Hz), 7.64 (1H, d, J = 8.7 Hz), 7.65 (1H, app. s), 7.93 (1H, d, J = 1.6 Hz). ^{13}C NMR ($CDCl_3$) δ 13.99, 22.55, 28.77, 28.89, 29.06, 29.13, 29.34, 31.75, 33.12, 119.02, 125.54, 127.16, 127.87, 128.43, 129.63, 129.72, 132.10, 132.43, 135.30. Analysis calculated for $C_{19}H_{25}BrS$: C, 62.46; H, 6.90. Found: C, 62.60; H, 6.94.

*5.3.4 2-Bromo-6-(3-methyl- butylsulphanyl) naphthalene (**17**)*

The preparation of **17** was as described for the preparation of compound **9** (except that the reaction mixture was heated under reflux for 17 hours) using the quantities stated: **2** (10.0 g, 44.8 mmol), 3-methylbutanethiol (4.84 g, 46.4 mmol), *p*-toluenesulphonic acid (3.00 g, 17.4 mmol) and dry toluene (250 ml). The crude product was recrystallised from ethanol to afford a white solid which was dried *in vacuo* (P_2O_5, paraffin wax). Yield 10.3 g (74%), mp 33.8–34.5°C. ^{1}H NMR ($CDCl_3$) δ 0.94 (6H, d, J = 6.5 Hz), 1.59 (2H, q, J = 6.8 Hz), 1.76 (1H, nonet, J = 6.5 Hz), 3.02 (2H, t, J = 7.4 Hz), 7.41 (1H, dd, J = 1.4, 8.3 Hz), 7.52 (1H, dd, J = 1.4, 8.9 Hz), 7.60 (1H, d, J = 8.9 Hz), 7.64 (1H, d, J = 8.9 Hz), 7.65 (1H, app. s), 7.93 (1H, d, J = 1.4 Hz). ^{13}C NMR ($CDCl_3$) δ 22.17, 27.41, 31.12, 37.78, 119.03, 125.47, 127.17, 127.81, 128.43, 129.64, 129.73, 132.10, 132.43, 135.47. Analysis calculated for $C_{15}H_{17}BrS$: C, 58.25; H, 5.54. Found: C, 58.19; H, 5.53.

*5.3.5 2-Bromo-6-(2-methyl-butylsulphanyl) naphthalene (**18**)*

The preparation of **18** was as described for the preparation of compound **9** (except that the reaction mixture was heated under reflux for 17 hours) using the quantities stated: **2** (10.0 g, 44.8 mmol), 2-methylbutanethiol (4.80 g, 46.1 mmol), *p*-toluenesulphonic acid (3.00 g, 17.4 mmol) and dry toluene (250 ml). A brown liquid was obtained which was filtered through a basic alumina column (ethyl acetate was used as eluent) to give a colourless oil. Yield 10.9 g (79%). ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t, J = 7.6 Hz), 1.03 (3H, d, J = 6.8 Hz), 1.24–1.41 (1H, m), 1.51–1.67 (1H, m), 1.68–1.82 (1H, m), 2.85 (1H, dd, J = 7.7, 12.0 Hz), 3.05 (1H, dd, J = 6.0, 12.0 Hz), 7.42 (1H, dd, J = 2.0, 8.5 Hz), 7.52 (1H, dd, J = 1.8, 8.8 Hz), 7.58 (1H, d, J = 9.0 Hz) 7.62 (1H, d, J = 9.0 Hz), 7.65 (1H, d, J = 2.9 Hz), 7.92 (1H, d, J = 2.9 Hz). ^{13}C NMR ($CDCl_3$) δ 11.21, 18.93, 28.77, 34.39, 40.17, 118.98, 125.36, 127.14, 127.88, 128.42, 129.63, 129.71, 132.11, 132.38 135.98. Analysis calculated for $C_{15}H_{17}BrS$: C, 58.25; H, 5.54. Found: C, 58.40; H, 5.78.

*5.3.6 2-Butylsulphanylnaphthalene (**19**)*

The preparation of **19** was as described for the preparation of compound **9** (except that the reaction mixture was heated under reflux for 25 hours) using the quantities stated: **13** (10.0 g, 69.4 mmol), butanethiol (6.50 g, 72.1 mmol), *p*-toluenesulphonic acid (3.00 g, 17.4 mmol) and dry toluene (250 ml). A brown liquid was obtained which was filtered through a basic alumina column (ethyl acetate was used as eluent) to give a colourless oil. Yield 12.0 g (80%). ^{1}H NMR ($CDCl_3$) δ 1.00 (3H, t, J = 7.0 Hz), 1.54 (2H, sext, J = 7.4 Hz), 1.74 (2H, quint, J = 7.4 Hz), 3.07 (2H, t, J = 7.4 Hz), 7.44–7.54 (3H, m), 7.77 (1H, d, J = 2.5 Hz), 7.79 (2H, app. s), 7.82 (1H, d, J = 7.9 Hz). ^{13}C NMR ($CDCl_3$) δ 14.33, 22.67, 31.83, 33.78, 126.08, 126.88, 127.12, 127.62, 127.83, 128.35, 128.92, 132.26, 134.48, 135.33. Analysis calculated for $C_{14}H_{16}S$: C, 77.72; H, 7.45. Found: C, 77.96; H, 7.55.

*5.3.7 2-Bromo-6-(4-methoxy- phenylsulphanyl) naphthalene (**20**)*

The preparation of **20** was as described for the preparation of compound **9** (except that the reaction mixture was heated under reflux for 36 hours) using

the quantities stated: **2** (10.0 g, 44.8 mmol), 4-methoxythiophenol (6.50 g, 46.4 mmol), *p*-toluenesulphonic acid (3.00 g, 17.4 mmol) and dry toluene (250 ml). The product was recrystallised from ethanol to give a white solid which was dried *in vacuo* (P_2O_5, paraffin wax). Yield 14.7 g (95%), mp 100.7–102.4°C. ^{1}H NMR ($CDCl_3$) δ 3.84 (3H, s), 6.93 (2H, d, J = 8.5 Hz), 7.29 (1H, dd, J = 1.8, 8.8 Hz), 7.46 (2H, d, J = 9.0 Hz), 7.49–7.53 (3H, m), 7.60 (1H, d, J = 8.7 Hz), 7.91 (1H, app. s). ^{13}C NMR ($CDCl_3$) δ 55.39, 115.16(2C), 119.30, 123.54, 125.58, 127.31, 127.53, 128.71, 129.73, 129.86, 132.18, 132.67, 135.70(2C), 137.13, 160.11. Analysis calculated for $C_{17}H_{13}BrOS$: C, 59.14; H, 3.80. Found: C, 59.38; H, 3.80.

*5.3.8 1-Butylsulphanylnaphthalene (**22**)*

The preparation of **22** was as described for the preparation of compound **9** (except that the reaction mixture was heated under reflux for 25 hours) using the quantities stated: **21** (10.0 g, 69.4 mmol), butanethiol (6.80 g, 75.4 mmol), *p*-toluenesulphonic acid (3.00 g, 17.4 mmol) and dry toluene (250 ml). The crude product was filtered through a basic alumina column (ethyl acetate was used as eluent) to give a colourless oil. Yield 10.0 g (67%). ^{1}H NMR ($CDCl_3$) δ 0.96 (3H, t, J = 7.3 Hz), 1.52 (2H, sext, J = 7.5 Hz), 1.70 (2H, quint, J = 7.5 Hz), 3.03 (2H, t, J = 7.5 Hz), 7.44 (1H, app. t, J = 7.8 Hz), 7.52–7.61 (3H, m), 7.74 (1H, d, J = 11.0 Hz), 7.87 (1H, d, J = 10.0 Hz), 8.46 (1H, d, J = 12.0 Hz). ^{13}C NMR ($CDCl_3$) δ 14.31, 22.67, 31.87, 34.50, 125.65, 126.17, 126.77, 126.85, 127.42, 128.00, 129.15, 133.50, 134.51, 134.88. Analysis calculated for $C_{14}H_{16}S$: C, 77.72; H, 7.45. Found: C, 77.89; H, 7.60.

5.4 Scheme 4

*5.4.1 1-(4-Butylsulphanylphenyl)-2-(6-cyano-2-naphthyl)ethyne (**24**)*

n-Butyllithium (4.2 ml, 1.92 M in hexanes, 8.1 mmol) was added dropwise at 0°C to a stirred, cooled (0°C) solution of **6** (1.40 g, 7.36 mmol) in anhydrous THF (40 ml) under dry nitrogen. The reaction conditions were maintained for a further 15 minutes before dry zinc chloride (1.11 g, 8.14 mol) was added slowly at 0°C and the reaction mixture was allowed to warm to room temperature (20 minutes). A solution of **23** (1.7767 g, 5.8980 mmol) in anhydrous THF (30 ml) was added dropwise at 0°C followed by lithium chloride (0.64 g, 15 mmol in one portion) and tetrakis(triphenylphosphine)palladium(0) (0.43 g, 0.37 mmol in one portion). The mixture was allowed to warm to room temperature and was stirred for a further 42 hours. The mixture was stirred for 10 minutes with hydrochloric acid (25 ml, 3M) before being extracted with diethyl ether (2 × 30 ml). The combined organic extracts were washed with saturated sodium bicarbonate solution, brine, and dried ($MgSO_4$). The drying agent was filtered off and the solvent was removed *in vacuo* before the crude product was purified by column chromatography (silica gel/petroleum ether: dichloromethane, 1:1] and recrystallised from ethanol to afford white-yellow crystals which were dried *in vacuo* (P_2O_5, paraffin wax). Yield 1.36 g (67%). Transitions (°C) Cryst. 102.0 N 143.2 Iso Liq. (rec. 79.9). ^{1}H NMR ($CDCl_3$) δ 0.94 (3H, t, J = 7.3 Hz), 1.47 (2H, sext, J = 7.4 Hz), 1.67 (2H, quint, J = 7.4 Hz), 2.96 (2H, t, J = 7.4 Hz), 7.28 (2H, d, J = 8.4 Hz), 7.47 (2H, d, J = 8.4 Hz), 7.61 (1H, dd, J = 1.6, 8.4 Hz), 7.67 (1H, dd, J = 1.6, 8.5 Hz), 7.85 (2H, app. t, J = 8.8 Hz), 8.04 (1H, app. s), 8.19 (1H, app. s). ^{13}C NMR ($CDCl_3$) δ 13.65, 22.01, 30.99, 32.46, 89.10, 91.87, 109.87, 119.06, 119.26, 124.18, 127.12, 127.56(2C), 128.45, 128.92, 130.19, 131.04, 131.45, 132.02(2C), 133.84, 134.31, 139.13. Analysis calculated for $C_{23}H_{19}NS$: C, 80.90; H, 5.61; N, 4.10. Found: C, 81.03; H, 5.53; N, 4.10.

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