JOURNAL OF Materials CHEMISTRY

Synthesis, transition temperatures, and optical properties of various 2,6-disubstituted naphthalenes and related 1-benzothiophenes with butylsulfanyl and cyano or isothiocyanato terminal groups

Alexander J. Seed,† Kenneth J. Toyne, John W. Goodby and Michael Hird

Liquid Crystals and Advanced Organic Materials Research Group, The Department of Chemistry, The University, Hull, UK HU6 7RX

Received 12th May 2000, Accepted 21st June 2000
Published on the Web 19th July 2000

Fourteen compounds based on 2,6-disubstituted naphthalenes or related 1-benzothiophene moieties with butylsulfanyl and cyano or isothiocyanato terminal groups have been synthesised. The transition temperatures of the compounds and their refractive indices have been determined and the derived values for the optical anisotropies, polarisabilities and order parameters have been calculated. With one exception (which also shows a smectic A phase), all the compounds with naphthyl and phenyl groups are solely nematogenic; for these compounds the naphthyl unit gives an average increase in T_{N-I} value and melting point of 72 and 20 °C respectively compared to the values for the compounds with a phenyl in place of the naphthyl unit. The incorporation of a 2,5-thiophene unit in place of phenyl lowers T_{N-I} and when it is part of a 1-benzothiophene unit the depression is even greater. The naphthalene compounds increase the values of optical anisotropy by approximately 0.04, compared to the phenyl systems, mainly because they increase the refractive index of the e-ray ($n_{\|}$ values); compound **12** has an exceptionally high optical anisotropy (Δn value) of 0.54.

We are undertaking a major programme which has the objective of gaining a greater understanding of the requirements for designing compounds with very high optical anisotropies.[1–5] Certain core units, terminal groups and linking groups have so far been identified as offering the greatest potential for obtaining such compounds. In general terms, polarisable π-electrons in core units, linking groups, and terminal groups are essential and the extent of saturated, unpolarisable regions in a molecule should be minimised. The limitations in applying these general guidelines to produce specific examples are that frequently the proposed compounds have melting points so high that they are non-mesogenic or they are miscible only to a small extent with nematic host mixtures. As is perennially the case with the design of liquid crystal mixtures, a compromise of the good and bad features of a compound have to be assessed, and compounds which are not optimised in certain properties may still be valuable because of some other advantageous property. For example, in relation to the prospects for the compounds reported here, the likelihood of undesirably high melting points may be compensated by the anticipated high values of optical anisotropy (Δn). The compounds reported here combine several structural units which are recognised as giving high optical anisotropy. The π-electron-rich naphthyl, phenyl and thienyl units, the π-bonded tolane link, and cyano and isothiocyanato terminal groups should give exceptionally high polarisability; the butylsulfanyl group has been used previously as a terminal group which is long enough to offer the prospect of reasonable mesogenicity, but is small enough to limit the dilution effect of the saturated aliphatic chain. Other structural features worth considering are ethenyl links and binaphthyl systems; however, the former are photochemically unstable and the latter have very high melting points [*e.g.*, 6,6′-dipentyl-2,2′-binaphthyl has transition temperatures Cryst 146.5 (E 145.5) SmA 163.5 N 171.5 Iso liq (°C)[6]].

Many applications of liquid crystals require systems of as high a birefringence as possible and in particular compounds of high optical anisotropy are essential for fast third-order non-linear switching using the optical Kerr effect;[7,8] some examples of our previous work to meet these objectives are given in refs. 2–5 and 9. In addition to the specific use of compounds of high optical anisotropy in optical Kerr effect devices, such compounds are useful generally in mixtures designed for twisted nematic and supertwisted nematic displays which require a precise combination of cell thickness and optical anisotropy; in order to maximise the transmission of light, thinner cells are needed and therefore compounds of higher optical anisotropy have to be used.

In this part of the programme we consider the value of the naphthyl unit for promoting high optical anisotropy in compounds where it is connected to a phenyl ring by a single bond, -C≡C-, -COO-, -COS-, or -CSS-; all the compounds have butylsulfanyl and cyano or isothiocyanato terminal groups. The naphthyl compounds are directly related to corresponding phenyl systems presented in a previous publication.[5] A few examples are also presented to show the effect of a thienyl unit in place of phenyl, and a 1-benzothienyl unit in place of naphthyl.

Experimental

^{1}H NMR spectra were obtained using a JEOL GX NM270FT NMR spectrometer with tetramethylsilane as internal standard. IR spectra were recorded using a Perkin-Elmer 783 spectrometer, and mass spectra using a Finnigan-MAT 1020 GC-MS spectrometer. UV spectra were recorded using a Philips PU8720 UV–VIS spectrometer with cyclohexane as solvent (only the major absorption bands are presented).

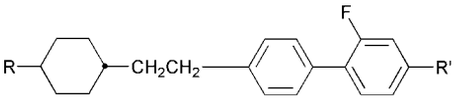
Thin-layer chromatographic analyses were performed using aluminium-backed silica gel plates (Merck 60 F254) and were examined under UV light. Column chromatography was performed under gravity using May and Baker Sorbsil C60 40–60H μm silica gel. The purity of all final products was

†*Present address*: Department of Chemistry, Williams Hall, Kent State University, Kent, Ohio 44242-0001, USA.

determined by HPLC using a Merck–Hitachi HPLC chromatogram incorporating a D6000 interface, a D4000 UV detector and an L6200A intelligent pump in conjunction with a Commodore 286 data station. Gas chromatography was carried out using a Perkin-Elmer 8320 capillary gas chromatograph with a QC2/BP1-1.0 SGE (12 m) capillary column. All final compounds are >99.5% pure by HPLC and gave satisfactory C, H and N analyses.

Melting points of intermediates were determined using a Gallenkamp melting-point apparatus (model MFB 59501CM). Transition temperatures were determined using a Mettler FP52 heating stage and FP5 temperature control unit in conjunction with an Olympus BH-2 polarising microscope, and the transitions were confirmed by using Differential Scanning Calorimetry (Perkin-Elmer DSC7 and IBM data station). Virtual T_{N-I} values were determined from four binary mixtures (from 5–30% m/m) in E7 (Merck Ltd., Poole, Dorset, UK; $T_{N-I}=60\,^{\circ}C$); the values obtained for the mixtures were extrapolated to 100% for the compound being examined using a linear regression computer program to give a straight line of best fit and are accurate to $\pm 5\,^{\circ}C$, assuming ideal mixing behaviour.

The optical anisotropies of the compounds (accurate to 0.01) were measured using an Abbé refractometer (model 60/HR) at 589 nm (D_1 sodium line) in conjunction with a Haake Q silicone oil (Dow-Corning 200/10 CS) bath and Haake F3 temperature control unit.[4] Three mixtures of each compound were made up between 5 and 25% m/m (depending on the solubility of the material) using an I eutectic mixture as the host material. The refractive indices ($n_{\parallel}$ and $n_{\perp}$) of each mixture were measured between 5 and 65 °C at 10 °C intervals and for each measurement a 20 min period was allowed for the temperature of the prisms of the refractometer to stabilise and for the refractive index to become constant. The optical anisotropy (Δn) values (*i.e.* $n_{\parallel}-n_{\perp}$) were plotted against temperature and gave a straight line, which in all cases passed through the individual values. The value for the optical anisotropy at 25 °C for each mixture was taken and extrapolated to 100% of the compound. The values of the optical anisotropies at 25 °C were measured in order to provide a direct indication of the optical properties of the compounds at room temperature. To gain an insight into the value of the different core groups and differing chain lengths, it is necessary to compare compounds at a fixed reduced absolute temperature in order to take into account the variation in T_{N-I} transition temperatures for the different compounds. An arbitrary reduced temperature (T/T_{N-I}) value of 0.7815 was chosen for this purpose (which corresponds to a temperature of 21.6 °C for the I compounds, which have a T_{N-I} transition at 104 °C, and is a reference value used by DERA, Malvern, for many years).



I eutectic host material
R = C_3H_7, R' = C_2H_5 (I32); R = C_3H_7, R' = C_5H_{11} (I35)
R = C_5H_{11}, R' = C_2H_5 (I52) in 1:1:1

The polarisabilities (expressed in units of $10^{-30}\,m^3$) and order parameters were calculated as described in previous papers[4,9] (the error bars are ± 1.14 and ± 0.10, respectively) using a combination of Vuks equation, the Haller plot,[10] the Lorentz–Lorenz equation and the Maier–Saupe expression[11] for the polarisability along the principal molecular axes. The density is assumed to be $1\,g\,cm^{-3}$ and the error in the anisotropy of the molecular polarisability ($\Delta\alpha$) is estimated to be ± 0.34 for the variations in molecular weight.

Preparations

Compound **2** was obtained by the reaction of compound **1** with butane-1-thiol in the presence of trifluoromethanesulfonic acid catalyst.[12,13] The reaction is mechanistically different but superficially similar to the Bucherer reaction, with the nucleophilic thiol attacking the σ-complex formed by protonation of the naphthol. Good yields were obtained but on prolonged reflux (>3.5 h) cleavage of the thioether occurred and 6-bromonaphthalene-2-thiol was formed from compound **2**. Good yields of compound **9** were obtained using the method of Takahashi *et al.*[14] although a cheaper method using 3-methylbut-1-yn-3-ol[15] is also successful. Compound **36** was prepared in excellent yield by a Pomeranz–Fritsch cyclization using polyphosphoric acid,[16] which is known to be a relatively poor proton source but a powerful dehydrating agent; its use helps to avoid the polymerisation and charring observed with sulfuric acid which gave only low yields and tarry by-products. Lithium diisopropylamide cleanly removed the proton α to the sulfur atom in compound **36** without reaction at other acidic sites or rearrangement of the bromo substituent[17–19] and gave a good yield of compound **37**. Product **37** was contaminated with traces of compound **36**, suggesting that iodination or the original metallation was incomplete, but these impurities were easily removed by column chromatography of the product from the subsequent selective coupling reaction. Compound **42** was prepared *via* an analogous route to that used for compound **39**, except that butyllithium could now be used for the metallation of compound **40**. All the other preparations used procedures similar to those already reported; these principally involve low temperature lithiations to give arylboronic acids and palladium-catalysed cross-coupling reactions.

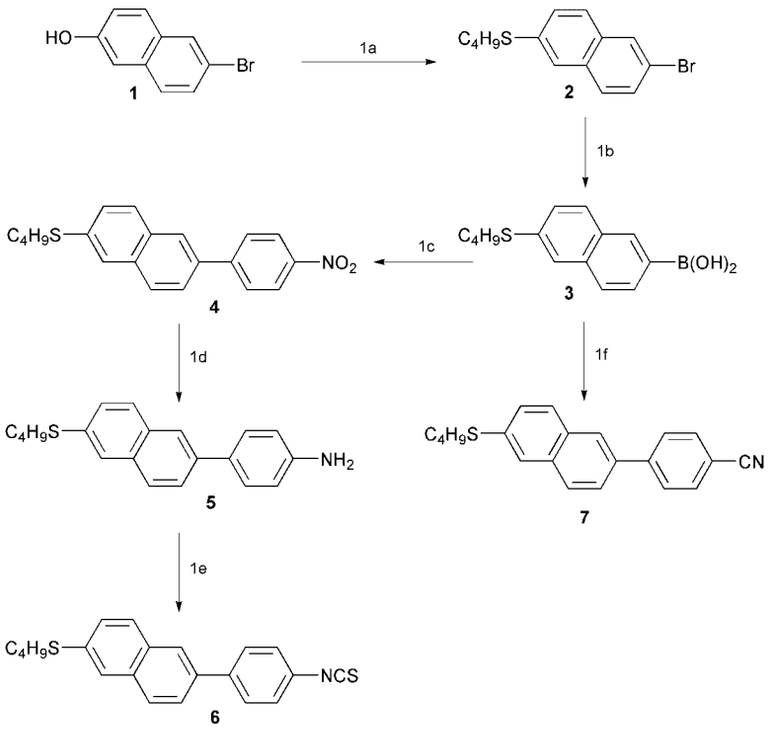
Compounds **1**, **25**, **29** and **34** were obtained from Aldrich. The syntheses of compound **23**[1] and **27**[3] have been described previously. Amine intermediates were not purified so as to avoid unnecessary handling of these potentially carcinogenic materials.

2-Bromo-6-butylsulfanylnaphthalene 2 (Scheme 1)

Trifluoromethanesulfonic acid (25.0 g, 0.176 mol) was added dropwise to a stirred solution of 6-bromo-2-naphthol (**1**) (21.0 g, 0.094 mol) and butane-1-thiol (8.90 g, 0.099 mol) in dry benzene (150 cm^3), under dry nitrogen at room temperature. The reaction mixture was stirred for 3 h at 50 °C (GLC and TLC analyses revealed a complete reaction), poured into ice cold water (400 cm^3), and the product was extracted into ether ($2\times 300\,cm^3$). The combined organic extracts were washed successively with water (400 cm^3), aqueous sodium hydroxide (5%, 250 cm^3) and dried ($MgSO_4$). The solvent was removed *in vacuo* and the product was distilled to give a white solid. Yield 17.0 g (61%), bp 160–162 °C at 0.5 mmHg, mp 39–41 °C. ^1H NMR ($CDCl_3$) δ: 0.95(3H, t), 1.50(2H, sextet), 1.70(2H, quintet), 3.05(2H, t), 7.42(1H, dd), 7.52(1H, dd), 7.63(1H, d), 7.73(2H, dd), 7.93(1H, d). IR (KBr) ν_{max}/cm^{-1} 480, 745, 820, 870, 890, 1380, 1490, 2980. MS *m/z*: 296, 294(M^+), 239, 237, 160, 158(100%).

6-Butylsulfanyl-2-naphthylboronic acid 3

Compound **3** was prepared in a similar way to that described for the preparation of compound **21** in reference 2. Quantities: compound **2** (8.49 g, 0.029 mol), *n*-butyllithium (3.0 cm^3, 10 M in hexane, 0.030 mol), trimethyl borate (5.97 g, 0.057 mol). An off-white solid was obtained which was used in the next step without purification. Yield 7.54 g (100%), mp 110–115 °C. ^1H NMR (DMSO-d_6) δ: 0.94(3H, t), 1.45(2H, sextet), 1.63(2H, quintet), 3.10(2H, t), 7.40(1H, dd), 7.61(1H, dd), 7.76(1H, d), 7.84(2H, dd), 8.15(1H, d), 8.32(2H, s). IR (KBr) ν_{max}/cm^{-1} 690,



Scheme 1 *Reagents*: 1a, n-C_4H_9SH, CF_3SO_3H; 1b, (i) n-C_4H_9Li, $B(OMe)_3$, (ii) HCl; 1c, 4-$BrC_6H_4NO_2$, $Pd(PPh_3)_4$, Na_2CO_3; 1d, 10%Pd-on-C, H_2; 1e, $CSCl_2$, $CaCO_3$; 1f, 4-BrC_6H_4CN, $Pd(PPh_3)_4$, Na_2CO_3.

730, 875, 1030, 1150, 1350, 1380, 1470, 1630, 2890, 2940, 2980, 3150. MS *m/z*: 260(M^+), 237, 117(100%), 90.

4-(6-Butylsulfanyl-2-naphthyl)-1-nitrobenzene 4

Compound **4** was prepared in a similar way to that described for the preparation of compound **8** in reference 2. Quantities: compound **3** (3.34 g, 0.013 mol), 1-bromo-4-nitrobenzene (2.16 g, 0.011 mol), tetrakis(triphenylphosphine)palladium(0) (0.57 g, 0.49 mmol), sodium carbonate (10.0 cm^3, 2.0 M, 0.020 mol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 3 : 1] to give a yellow solid. Yield 2.33 g (63%), mp 93–94 °C. ^1H NMR ($CDCl_3$) δ: 0.96(3H, t), 1.51(2H, sextet), 1.72(2H, quintet), 3.06(2H, t), 7.47(1H, dd), 7.72(1H, dd), 7.75(1H, d), 7.81(2H, d), 7.86(2H, d), 8.04(1H, d), 8.34(2H, d). IR (KBr) ν_{max}/cm^{-1} 785, 830, 1050, 1075, 1330, 1500, 1560, 1570, 2880, 2920. MS *m/z*: 337(M^+), 111, 97, 85, 69(100%).

4-(6-Butylsulfanyl-2-naphthyl)aniline 5

Compound **5** was prepared in a similar way to that described for the preparation of compound **9** in reference 2. Quantities: compound **4** (1.92 g, 5.70 mmol), palladium-on-carbon (10%, 1.48 g). A white solid was obtained which was used in the next step without purification. Yield 1.99 g (quantitative).

4-(6-Butylsulfanyl-2-naphthyl)phenyl isothiocyanate 6

Compound **6** was prepared in a similar way to that described for the preparation of compound **10** in reference 2. Quantities: compound **5** (2.22 g, 7.23 mmol), thiophosgene (0.96 g, 8.35 mmol), calcium carbonate (1.08 g, 0.011 mol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 5 : 1] and was recrystallised (cyclohexane) to give colourless crystals which were dried *in vacuo*. Yield 0.93 g (38%). Transitions (°C) Cryst 98.1 N 125.7 Iso liq. ^1H NMR ($CDCl_3$) δ: 0.95(3H, t), 1.50(2H, sextet), 1.71(2H, quintet), 3.05(2H, t), 7.33(2H, d), 7.44(1H, dd), 7.69(2H, d), 7.72(1H, dd), 7.73(1H, d), 7.80(2H, d), 7.95(1H, d). IR (KBr) ν_{max}/cm^{-1} 810, 840, 925, 1070, 1480, 1590, 1620, 2120, 2290, 3020, 3060. MS *m/z*: 349(M^+, 100%), 293, 234, 202, 189. UV λ_{max} (cyclohexane) 208(39 100 $dm^3\ mol^{-1}\ cm^{-1}$), 246(31 000), 285(28 800), 323(36 200) nm.

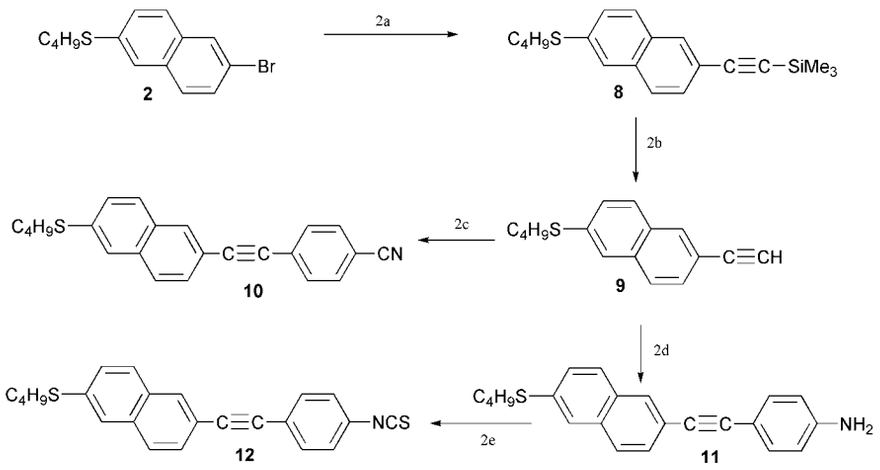
Optical properties and calculated parameters. At $T/T_{N-I} = 0.7815$: $n_{\|} = 2.01$, $n_{\perp} = 1.57$, $\Delta n = 0.44$, $\Delta\alpha = 46.88$, $S = 0.58$.
At 25 °C: $n_{\|} = 2.01$, $n_{\perp} = 1.57$, $\Delta n = 0.44$, $\Delta\alpha = 45.08$, $S = 0.58$.

2-Butylsulfanyl-6-(4-cyanophenyl)naphthalene 7

Compound **7** was prepared in a similar way to that described for the preparation of compound **21** in reference 3. Quantities: compound **3** (1.81 g, 6.96 mmol), 4-bromobenzonitrile (1.15 g, 6.32 mmol), tetrakis(triphenylphosphine)palladium(0) (0.25 g, 0.22 mmol), 2 M sodium carbonate (30 cm^3). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 1 : 1] and was recrystallised (ethanol–ethyl acetate 5 : 1) to give colourless crystals. Yield 1.63 g (81%). Transitions (°C) Cryst 92.0 N 107.0 Iso liq. ^1H NMR ($CDCl_3$) δ: 0.95(3H, t), 1.50(2H, sextet), 1.70(2H, quintet), 3.05(2H, t), 7.46(1H, dd), 7.69(1H, dd), 7.72(1H, d), 7.76(2H, d), 7.82(2H, d), 7.84(2H, d), 7.99(1H, d). IR (KBr) ν_{max}/cm^{-1} 2960, 2940, 2860, 2220, 1610, 1490, 1470, 1185, 1075, 890, 850, 750, 575, 480. MS *m/z*: 317(M^+).

2-Butylsulfanyl-6-trimethylsilylethynylnaphthalene 8 (Scheme 2)

Tetrakis(triphenylphosphine)palladium(0) (0.73 g, 0.63 mmol) and copper(I) iodide (0.12 g, 0.63 mmol) were added all at once to a stirred solution of compound **2** (8.15 g, 0.028 mol) and trimethylsilylacetylene (5.42 g, 0.055 mol) in triethylamine (200 cm^3) at 0 °C under dry nitrogen. The reaction mixture was maintained under these conditions for 1 h and heated under reflux overnight (GLC analysis revealed a complete reaction). The product was extracted into ether (2×200 cm^3); the combined ethereal extracts were washed successively with saturated sodium chloride (250 cm^3), water (500 cm^3) and dried ($MgSO_4$). The solvent was removed *in vacuo* and the product was purified by column chromatography [petroleum fraction (bp 40–60 °C)] to give a pale yellow liquid. Yield 6.26 g (72%);



Scheme 2 *Reagents*: 2a, $Me_3SiC{\equiv}CH$, Et_3N, $Pd(PPh_3)_4$, CuI; 2b, KOH, MeOH; 2c, (i) n-C_4H_9Li, $ZnCl_2$, (ii) 4-BrC_6H_4CN, $Pd(PPh_3)_4$; 2d, (i) n-C_4H_9Li, $ZnCl_2$, (ii) 4-$IC_6H_4NH_2$, $Pd(PPh_3)_4$; 2e, $CSCl_2$, $CaCO_3$.

^{1}H NMR($CDCl_3$) δ: 0.31(9H, s), 0.95(3H, t), 1.50(2H, sextet), 1.72(2H, quintet), 3.05(2H, t), 7.38(1H, dd), 7.48(1H, dd), 7.64(1H, d), 7.72(2H, d), 7.93(1H, d). IR (KBr) ν_{max}/cm^{-1} 845, 910, 1065, 1190, 1240, 1460, 1480, 1580, 1620, 2140, 2920, 2950. MS *m*/*z*: 312(M^+), 216, 160(100%), 115, 58.

(6-Butylsulfanyl-2-naphthyl)ethyne 9

Potassium hydroxide solution (20.0 cm^3, 1.0 M, 0.020 mol) was added all at once to a stirred solution of compound **8** (6.21 g, 0.020 mol) in methanol (160 cm^3). The mixture was stirred at room temperature for 1 h (GLC analysis confirmed a complete reaction) and the methanol was removed *in vacuo* and water (100 cm^3) added. The product was extracted into dichloromethane (2 × 50 cm^3) and the solvent was removed *in vacuo*. A pale yellow liquid was obtained which was used in the next step without purification. Yield 4.80 g (100%). ^{1}H NMR ($CDCl_3$) δ: 0.94(3H, t), 1.48(2H, sextet), 1.67(2H, quintet), 3.00(2H, t), 3.15(1H, s), 7.40(1H, dd), 7.46(1H, dd), 7.62(1H, d), 7.65(2H, d), 7.93(1H, d). IR (film) ν_{max}/cm^{-1} 810, 865, 890, 1070, 1220, 1270, 1380, 1460, 1485, 1585, 1620, 2200, 2920, 2960, 3300. MS *m*/*z*: 240(M^+), 184, 169(100%), 115, 57.

1-(6-Butylsulfanyl-2-naphthyl)-2-(4-cyanophenyl)ethyne 10

n-Butyllithium (5.8 cm^3, 2.5 M in hexane, 0.015 mol) was added dropwise to a stirred, cooled (0 °C) solution of compound **9** (2.90 g, 0.012 mol) in dry THF (25 cm^3), under dry nitrogen at 0 °C. The reaction mixture was maintained under these conditions for a further 15 min before a solution of anhydrous zinc chloride (1.64 g, 0.012 mol) in dry THF (20 cm^3) was added dropwise at −5 to 0 °C. The mixture was stirred at room temperature for 15 min and a solution of 4-bromobenzonitrile (1.97 g, 0.011 mol) in dry THF (25 cm^3) was added dropwise at 0 °C, followed by the addition of tetrakis(triphenylphosphine)palladium(0) (0.69 g, 0.60 mmol) in one portion. The mixture was heated under reflux overnight (GLC analysis revealed a complete reaction) and quenched with hydrochloric acid (10%, 50 cm^3). The product was extracted into ether (2 × 150 cm^3) and the combined organic extracts were washed with saturated sodium hydrogen carbonate (100 cm^3) and dried ($MgSO_4$). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 1 : 1] and was recrystallised (ethanol) to afford colourless crystals which were dried *in vacuo* (P_2O_5). Yield 2.00 g (53%). Transitions (°C) Cryst 87.0 N 131.8 Iso liq. ^{1}H NMR ($CDCl_3$) δ: 0.96(3H, t), 1.50(2H, sextet), 1.72(2H, quintet), 3.06(2H, t), 7.42(1H, dd), 7.55(1H, dd), 7.62(2H, d), 7.66(1H, d), 7.67(2H, d), 7.72(2H, d), 8.00(1H, d). IR (KBr) ν_{max}/cm^{-1} 815, 830, 880, 1110, 1460, 1500, 1600, 2190, 2220, 2920, 2960. MS *m*/*z*: 341(M^+), 298, 285(100%), 253, 240. UV λ_{max} (cyclohexane) 233(19 900 dm^3 mol^{-1} cm^{-1}), 272(22 100), 341(23 500) nm.

Optical properties and calculated parameters. At T/T_{N-I} = 0.7815: $n_{\parallel}$ = 2.02, $n_{\perp}$ = 1.56, Δn = 0.46, $\Delta\alpha$ = 34.87, S = 0.77.
At 25 °C: $n_{\parallel}$ = 2.02, $n_{\perp}$ = 1.56, Δn = 0.46, $\Delta\alpha$ = 34.88, S = 0.77.

1-(4-Aminophenyl)-2-(6-butylsulfanyl-2-naphthyl)ethyne 11

Compound **11** was prepared in a similar way to that described for the preparation of compound **10** using the quantities stated. Quantities: compound **9** (1.50 g, 6.25 mmol), 4-iodoaniline (1.09 g, 4.98 mmol), *n*-butyllithium (4.4 cm^3, 1.6 M in hexane, 7.04 mmol), anhydrous zinc chloride (1.09 g, 8.01 mmol), tetrakis(triphenylphosphine)palladium(0) (0.29 g, 0.25 mmol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 1 : 1] to afford a black solid. Yield 1.06 g (64%).

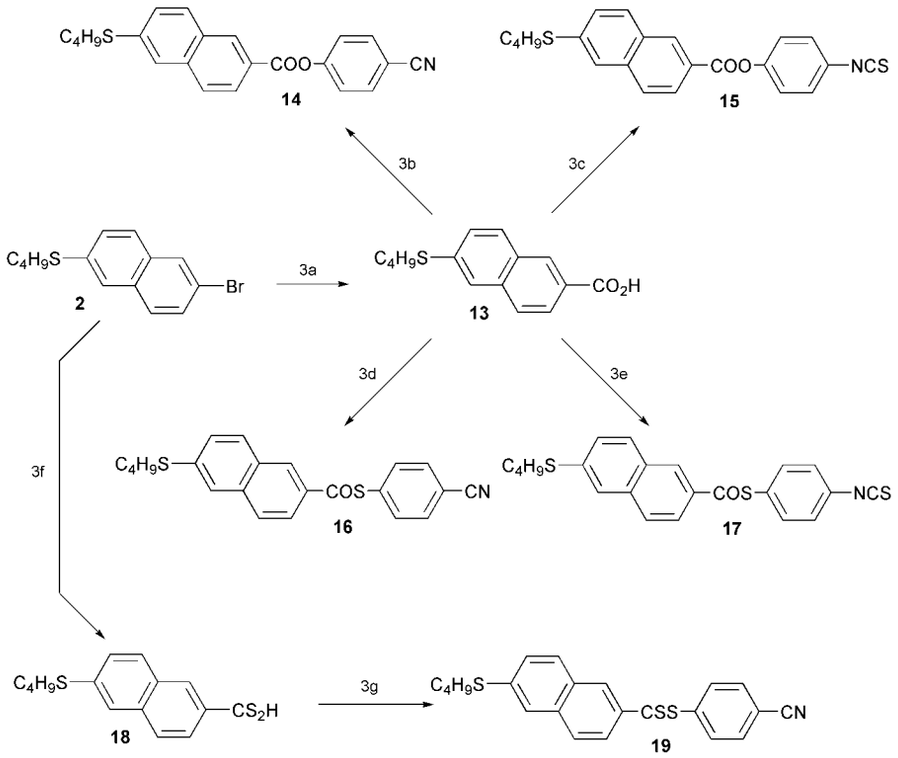
1-(6-Butylsulfanyl-2-naphthyl)-2-(4-isothiocyanatophenyl)-ethyne 12

Compound **12** was prepared in a similar way to that described for the preparation of compound **10** in reference 2. Quantities: compound **11** (0.79 g, 2.39 mmol), thiophosgene (0.33 g, 2.87 mmol), calcium carbonate (0.36 g, 3.60 mmol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 5 : 1] and was recrystallised (ethanol–ethyl acetate 10 : 1) to give white crystals which were dried *in vacuo* (P_2O_5). Yield 0.38 g (42%). Transitions (°C) Cryst 91.5 N 136.7 Iso liq. ^{1}H NMR ($CDCl_3$) δ: 0.96(3H, t), 1.50(2H, sextet), 1.71(2H, quintet), 3.05(2H, t), 7.22(2H, d), 7.42(1H, dd), 7.54(2H, d), 7.55(1H, d), 7.66(1H, d), 7.71(2H, d), 7.98(1H, d). IR (KBr) ν_{max}/cm^{-1} 825, 840, 1050, 1510, 1580, 2060, 2120, 2190, 2930, 2960. MS *m*/*z*: 373(M^+, 100%), 317, 285, 272, 213. UV λ_{max} (cyclohexane) 214(46 140 dm^3 mol^{-1} cm^{-1}), 263(32 340), 302(37 300), 339(52 760) nm.

Optical properties and calculated parameters. At T/T_{N-I} = 0.7815: $n_{\parallel}$ = 2.12, $n_{\perp}$ = 1.58, Δn = 0.54, $\Delta\alpha$ = 53.98, S = 0.63.
At 25 °C: $n_{\parallel}$ = 2.12, $n_{\perp}$ = 1.58, Δn = 0.54, $\Delta\alpha$ = 54.23, S = 0.63.

6-Butylsulfanyl-2-naphthoic acid 13 (Scheme 3)

Compound **13** was prepared in a similar way to that described for the preparation of compound **3** in reference 9. Quantities: compound **2** (5.35 g, 0.018 mol), *n*-butyllithium (7.7 cm^3, 2.5 M in hexane, 0.019 mol). A white solid was obtained. Yield 3.05 g (65%), mp 186–187 °C. ^{1}H NMR ($CDCl_3$, DMSO-d_6) δ:



Scheme 3 *Reagents*: 3a, (i) n-C_4H_9Li, (ii) CO_2, (iii) CH_3CO_2H; 3b, 4-HOC_6H_4CN, DCC, 4-(*N*-pyrrolidino)pyridine; 3c, 4-HOC_6H_4NCS, DCC, 4-(*N*-pyrrolidino)pyridine; 3d, 4-HSC_6H_4CN, DCC, DMAP; 3e, 4-HSC_6H_4NCS, DCC, DMAP; 3f, (i) Mg, CS_2 (ii) HCl; 3g, 4-HSC_6H_4CN, DCC, DMAP.

1.00(3H, t), 1.51(2H, sextet), 1.71(2H, quintet), 3.05(2H, t), 7.42(1H, dd), 7.67(1H, d), 7.76(1H, d), 7.83(1H, d), 8.03 (1H, dd), 8.52(1H, d), the carboxylic acid proton was not detected. IR (KBr) ν_{max}/cm^{-1} 820, 870, 930, 1070, 1140, 1310, 1400, 1430, 1470, 1620, 1680, 2500–2900. MS *m/z*: 260(M^+, 100%). 204, 171, 160, 115.

Compounds **14** and **15** were prepared in a similar way to that described for the preparation of compounds **7** and **8** in reference 9.

4-Cyanophenyl 6-butylsulfanyl-2-naphthoate 14

Quantities: compound **13** (2.60 g, 0.010 mol), *N,N′*-dicyclohexylcarbodiimide (2.47 g, 0.012 mol), 4-hydroxybenzonitrile (1.19 g, 0.01 mol), 4-(*N*-pyrrolidino)pyridine (0.49 g, 3.27 mmol). The product was purified by column chromatography (dichloromethane) and was recrystallised (ethanol–ethyl acetate 5 : 1) to give colourless crystals which were dried *in vacuo* (P_2O_5). Yield 2.56 g (71%). Transitions (°C) Cryst 108.2 N 118.7 Iso liq. ^1H NMR ($CDCl_3$) δ: 0.98(3H, t), 1.53(2H, sextet), 1.75(2H, quintet), 3.09(2H, t), 7.41(2H, d), 7.47(1H, dd), 7.69(1H, d), 7.77(2H, d), 7.82(1H, d), 7.87(1H, d), 8.14(1H, dd), 8.69(1H, d). IR (KBr) ν_{max}/cm^{-1} 810, 870, 910, 1060, 1140, 1170, 1220, 1280, 1400, 1465, 1500, 1600, 1620, 1740, 2240, 2930, 2960. MS *m/z*: 361(M^+), 243(100%), 186, 159, 115. UV λ_{max} (cyclohexane) 228(37 900 $dm^3\ mol^{-1}\ cm^{-1}$), 271(28 300), 326(20 000) nm.

Optical properties and calculated parameters. At $T/T_{N-I} = 0.7815$: $n_{\|} = 1.85$, $n\perp = 1.55$, $\Delta n = 0.30$, $\Delta\alpha = 26.68$, $S = 0.69$.
At 25 °C: $n_{\|} = 1.85$, $n_{\perp} = 1.55$, $\Delta n = 0.30$, $\Delta\alpha = 26.70$, $S = 0.70$.

4-Isothiocyanatophenyl 6-butylsulfanyl-2-naphthoate 15

Quantities: compound **13** (0.35 g, 1.35 mmol), 4-isothiocyanatophenol[9] (0.17 g, 1.13 mmol), *N,N′*-dicyclohexylcarbodiimide 0.27 g, 1.25 mmol), 4-(*N*-pyrrolidino)pyridine (0.06 g, 0.40 mmol). The product was purified by column chromatography (dichloromethane) and was recrystallised (cyclohexane) to give white crystals which were dried *in vacuo* ($CaCl_2$). Yield 0.28 g (65%). Transitions (°C) Cryst 86.7 N 119.3 Iso liq. ^1H NMR ($CDCl_3$) δ: 0.98(3H, t), 1.52(2H, sextet), 1.74(2H, quintet), 3.09(2H, t), 7.24(2H, d), 7.30(2H, d), 7.50(1H, dd), 7.70(1H, d), 7.82(1H, d), 7.84(1H, d), 8.15(1H, dd), 8.70(1H, d). IR (KBr) ν_{max}/cm^{-1} 735, 805, 865, 900, 1070, 1180, 1215, 1270, 1385, 1505, 1625, 1745, 2020, 2920, 2960. MS *m/z*: 393(M^+), 243(100%), 159, 122, 115. UV λ_{max} (cyclohexane) 233(43 400 $dm^3\ mol^{-1}\ cm^{-1}$), 275(42 700), 342(23 700) nm.

Optical properties and calculated parameters. At $T/T_{N-I} = 0.7815$: $n_{\|} = 1.92$, $n_{\perp} = 1.57$, $\Delta n = 0.35$, $\Delta\alpha = 32.99$, $S = 0.71$.
At 25 °C: $n_{\|} = 1.91$, $n_{\perp} = 1.57$, $\Delta n = 0.35$, $\Delta\alpha = 32.93$, $S = 0.71$.

Compounds **16** and **17** were prepared in a similar way to that described for the preparation of compounds **13** and **14** in reference 9.

S-(4-Cyanophenyl) 6-butylsulfanylthio-2-naphthoate 16

Quantities: compound **13** (0.40 g, 1.54 mmol), 4-cyanothiophenol[9] (0.17 g, 1.26 mmol), 4-(*N,N*-dimethylamino)pyridine (0.07 g, 0.56 mmol), *N,N′*-dicyclohexylcarbodiimide (0.31 g, 1.44 mmol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 1 : 1] and was recrystallised (ethanol–ethyl acetate 20 : 1) to give colourless crystals which were dried *in vacuo* (P_2O_5). Yield 0.23 g (47%). Transitions (°C) Cryst 115.0 N 160.7 Iso liq. ^1H NMR ($CDCl_3$) δ: 0.98(3H, t), 1.53(2H, sextet), 1.74(2H, quintet), 3.09(2H, t), 7.47(1H, dd), 7.67(1H, d), 7.69(2H, d), 7.76(2H, d), 7.80(1H, d), 7.87(1H, d), 7.98(1H, dd), 8.52(1H, d). IR (KBr) ν_{max}/cm^{-1} 830, 850, 1070, 1130, 1205, 1255, 1460, 1610, 1660, 2240, 2930, 2960. MS *m/z*: 377(M^+), 243, 193(100%), 137, 109. UV λ_{max} (cyclohexane), 197(29 280 $dm^3\ mol^{-1}\ cm^{-1}$) 244(36 840), 281(30 700), 341(24 970) nm.

Optical properties and calculated parameters. At $T/T_{N-I} = 0.7815$: $n_{\|} = 1.89$, $n_{\perp} = 1.56$, $\Delta n = 0.33$, $\Delta\alpha = 33.77$, $S = 0.64$.
At 25 °C: $n_{\|} = 1.91$, $n_{\perp} = 1.57$, $\Delta n = 0.34$, $\Delta\alpha = 34.43$, $S = 0.64$.

S-(4-Isothiocyanatophenyl) 6-butylsulfanylthio-2-naphthoate 17

Quantities: compound **13** (0.64 g, 2.26 mmol), 4-isothiocyanatothiophenol[9] (0.33 g, 1.98 mmol), 4-(*N*,*N*-dimethylamino)pyridine (0.10 g, 0.8 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.50 g, 2.31 mmol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 5 : 1] and was recrystallised (ethyl acetate) to give white crystals which were dried *in vacuo* (P_2O_5). Yield 0.60 g (73%). Transitions (°C) Cryst 90.7 SmA 94.3 N 136.1 Iso liq. ^{1}H NMR ($CDCl_3$) δ: 0.97(3H, t), 1.53(2H, sextet), 1.74(2H, quintet), 3.08(2H, t), 7.32(2H, d), 7.47(1H, dd), 7.54(2H, d), 7.67(1H, d), 7.79(1H, d), 7.87(1H, d), 7.98(1H, dd), 8.51(1H, d). IR (KBr) ν_{max}/cm^{-1} 850, 1125, 1210, 1400, 1480, 1615, 1670, 2050, 2080, 2920, 2940, 2960. MS *m*/*z*: 409(M^+), 243(100%), 215, 159, 115. UV λ_{max} (cyclohexane), 235(40 640 dm^3 mol^{-1} cm^{-1}), 281(38 180), 337(27 090) nm.

Optical properties and calculated parameters. At T/T_{N-I} = 0.7815: $n_{\parallel}$ = 1.95, $n_{\perp}$ = 1.58, Δn = 0.38, $\Delta\alpha$ = 39.86, S = 0.66.
At 25 °C: $n_{\parallel}$ = 1.97, $n_{\perp}$ = 1.58, Δn = 0.39, $\Delta\alpha$ = 40.28, S = 0.68.

6-Butylsulfanyldithio-2-naphthoic acid 18

Compound **18** was prepared in a similar way to that described for the preparation of compound **15** in reference 9 except that the formation of the Grignard reagent required heating under reflux for 4 h. Quantities: compound **2** (3.71 g, 0.013 mol), magnesium turnings (0.94 g, 0.039 mol), carbon disulfide (1.09 g, 0.014 mol).

A purple solid was obtained. Yield 0.73 g (19%), mp 46–47 °C. ^{1}H NMR ($CDCl_3$) δ: 0.97(3H, t), 1.53(2H, sextet), 1.73(2H, quintet), 3.11(2H, t), 7.43(1H, dd), 7.65(1H, d), 7.69(1H, d), 7.86(1H, d), 8.15(1H, dd), 8.55(1H, d). The thioacid proton was not detected. IR (KBr) ν_{max}/cm^{-1} 825, 870, 1090, 1180, 1460, 1610, 2460, 2870, 2920, 2950. MS *m*/*z*: 292(M^+), 259, 232, 203, 176(100%).

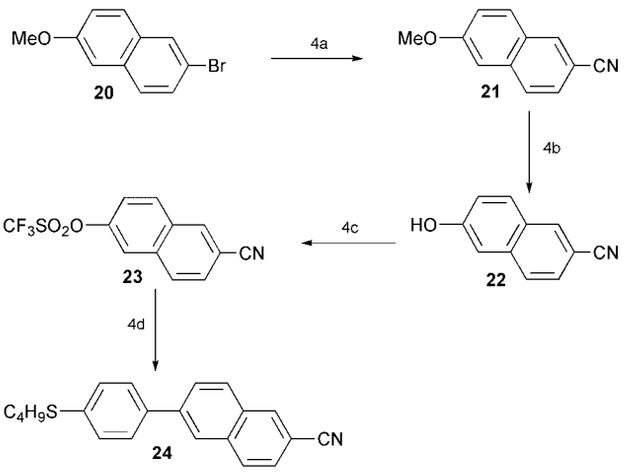
4-Cyanophenyl 6-butylsulfanyldithio-2-naphthoate 19

Compound **19** was prepared in a similar way to that described for the preparation of compound **18** in reference 9. Quantities: compound **18** (0.28 g, 0.96 mmol), 4-cyanothiophenol[9] (0.10 g, 0.74 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.24 g, 1.11 mmol), 4-(*N*,*N*-dimethylamino)pyridine (0.05 g, 0.4 mmol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 1 : 1] and was recrystallised [petroleum fraction (bp 40–60 °C)–ethyl acetate 1 : 1] to give red crystals which were dried *in vacuo* (P_2O_5). Yield 0.05 g (17%). Transitions (°C) Cryst 154.0 N 169.4 Iso liq. ^{1}H NMR ($CDCl_3$) δ: 0.97(3H, t), 1.52(2H, sextet), 1.74(2H, quintet), 3.09(2H, t), 7.45(1H, dd), 7.64(2H, d), 7.65(1H, d), 7.73(1H, d), 7.80(2H, d), 7.88(1H, d), 8.16(1H, dd), 8.62(1H, d). IR (film) ν_{max}/cm^{-1} 830, 890, 1060, 1180, 1210, 1455, 1485, 1610, 2240, 2920, 2950, 2960. MS *m*/*z*: 393(M^+), 259(100%), 203, 171, 158. UV λ_{max} (cyclohexane), 201(38 190 dm^3 mol^{-1} cm^{-1}), 242(36 730), 388(21 420) nm.

Optical properties and calculated parameters. At T/T_{N-I} = 0.7815: $n_{\parallel}$ = 2.10, $n_{\perp}$ = 1.70, Δn = 0.41, $\Delta\alpha$ = 66.85, S = 0.39.
At 25 °C: $n_{\parallel}$ = 2.18, $n_{\perp}$ = 1.59, Δn = 0.59, $\Delta\alpha$ = 67.28, S = 0.59.

2-(4-Butylsulfanylphenyl)-6-cyanonaphthalene 24 (Scheme 4)

Compound **24** was prepared in a similar way to that described for the preparation of compound **29** in reference 1. Quantities: 4-butylsulfanylphenylboronic acid[2] (6.91 g, 0.033 mol), compound **23**[1] (3.42 g, 0.011 mol) tetrakis(triphenylphosphine)palladium(0) (0.70 g, 0.61 mmol), sodium carbonate (11.3 cm^3, 2.0 M, 0.23 mol), lithium chloride (1.44 g, 0.034 mol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 1 : 1] and was recrystallised (ethanol) to give white crystals which were dried *in vacuo* (P_2O_5). Yield 3.00 g (86%). Transitions (°C) Cryst 93.2 N 114.8 Iso liq. ^{1}H NMR ($CDCl_3$) δ: 0.96(3H, t), 1.50(2H, sextet), 1.70(2H, quintet), 3.00(2H, t), 7.46(2H, d), 7.63(2H, dd), 7.64(2H, d), 7.84(1H, dd), 7.96(1H, d), 8.05(1H, s), 8.24(1H, d). IR (KBr) ν_{max}/cm^{-1} 805, 895, 1095, 1395, 1460, 1485, 1590, 1620, 2220, 2860, 2920, 2950. MS *m*/*z*: 317(M^+), 261(100%), 227, 94, 59. UV λ_{max} (cyclohexane) 223(32 890 dm^3 mol^{-1} cm^{-1}), 239(51 570), 325(28 760) nm.



Scheme 4 *Reagents*: 4a, CuCN; 4b, BBr_3; 4c, $(CF_3SO_2)_2O$; 4d, 4-$C_4H_9SC_6H_4B(OH)_2$, $Pd(PPh_3)_4$, Na_2CO_3.

Optical properties and calculated parameters. At T/T_{N-I} = 0.7815: $n_{\parallel}$ = 1.92, $n_{\perp}$ = 1.56, Δn = 0.36, $\Delta\alpha$ = 33.07, S = 0.62.
At 25 °C: $n_{\parallel}$ = 1.92, $n_{\perp}$ = 1.56, Δn = 0.36, $\Delta\alpha$ = 31.80, S = 0.61.

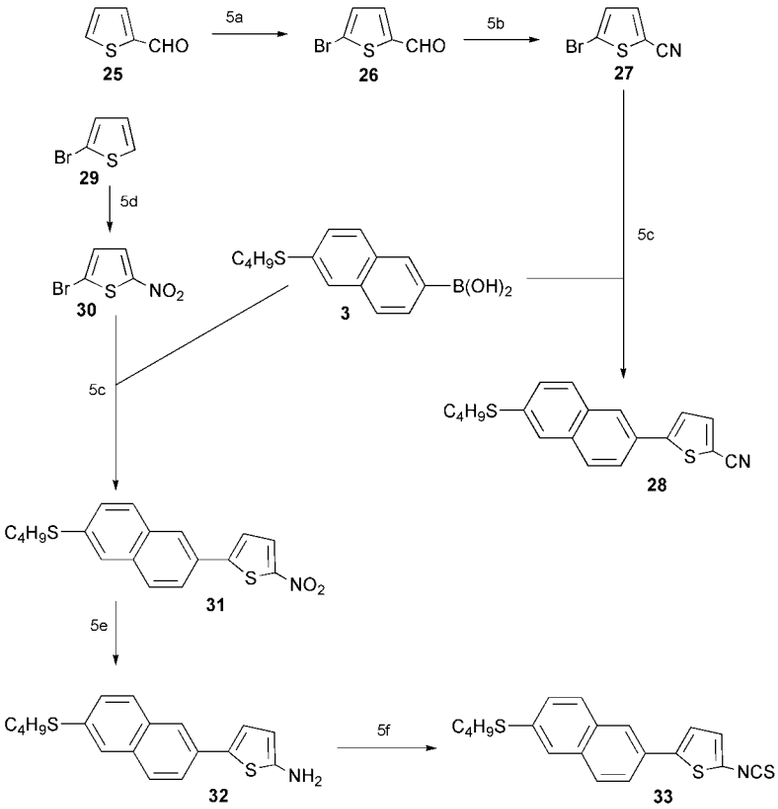
2-(6-Butylsulfanyl-2-naphthyl)-5-cyanothiophene 28 (Scheme 5)

Compound **28** was prepared in a similar way to that described for the preparation of compound **8** in reference 2. Quantities: compound **3** (0.44 g, 1.69 mmol), 2-bromo-5-cyanothiophene (**27**)[3] (0.27 g, 1.44 mmol), tetrakis(triphenylphosphine)palladium(0) (0.08 g, 0.069 mmol), sodium carbonate (1.5 cm^3, 2.0 M, 3.00 mmol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 1 : 5] and was recrystallised (ethanol) to give a pale green solid which was dried *in vacuo* (P_2O_5). Yield 0.10 g (22%). Transitions (°C) Cryst 93.6 (N 73.2) Iso liq. ^{1}H NMR ($CDCl_3$) δ: 0.96(3H, t), 1.51(2H, sextet), 1.71(2H, quintet), 3.06(2H, t), 7.38(1H, d), 7.45(1H, dd), 7.63(1H, d), 7.65(1H, dd), 7.68(1H, d), 7.78(2H, dd), 8.00(1H, d). IR (KBr) ν_{max}/cm^{-1} 805, 810, 860, 1065, 1165, 1220, 1370, 1440, 1455, 1570, 1585, 1620, 2210, 2920, 2960, 3090. MS *m*/*z*: 323(M^+, 100%), 267, no other peaks present. UV λ_{max} (cyclohexane) 226(32 060 dm^3 mol^{-1} cm^{-1}), 245(22 120), 263(22 610), 284(21 740), 347(27 100) nm.

Optical properties and calculated parameters. At T/T_{N-I} = 0.7815: $n_{\parallel}$ = 1.97, $n_{\perp}$ = 1.58, Δn = 0.38, $\Delta\alpha$ = 33.46, S = 0.63.
At 25 °C: $n_{\parallel}$ = 1.94, $n_{\perp}$ = 1.57, Δn = 0.37, $\Delta\alpha$ = 32.93, S = 0.61.

2-Bromo-5-nitrothiophene 30

A solution of nitric acid (24.0 g, 0.381 mol, 1.42 sp gr) in acetic anhydride (50 cm^3) at 0 °C was added dropwise to a cooled (0 °C), rapidly stirred solution of 2-bromothiophene (24.8 g, 0.152 mol) in acetic anhydride (50 cm^3). At the end of the addition, the stirring was continued for 0.5 h and the nitration mixture was refrigerated overnight (GLC and TLC analysis revealed a complete reaction). The mixture was poured into ice–water (400 cm^3) and the precipitate was filtered off, dissolved in ether (2 × 200 cm^3), and washed with water until



Scheme 5 *Reagents*: 5a, Br_2; 5b, $EtNO_2$, pyridine hydrobromide; 5c, $Pd(PPh_3)_4$, Na_2CO_3; 5d, HNO_3, $(CH_3CO)_2O$; 5e, 10% Pd-on-carbon, H_2; 5f, $CSCl_2$, $CaCO_3$.

free of acid. The solvent was removed *in vacuo* and the product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 5 : 1] and was recrystallised (ethanol–1,2-dimethoxyethane 10 : 1) to give yellow crystals which were dried *in vacuo* (P_2O_5). Yield 20.9 g (66%), mp 44–46 °C (lit.[20] 45–46 °C). ^{1}H NMR ($CDCl_3$) δ: 7.10(1H, d), 7.70(1H,d). IR (KBr) ν_{max}/cm^{-1} 730, 815, 1340, 1400, 1510, 1530, 3110. MS *m*/*z*: 209, 207(M^+), 151, 149(100%), 81.

2-(6-Butylsulfanyl-2-naphthyl)-5-nitrothiophene 31

Compound **31** was prepared in a similar way to that described for the preparation of compound **4**. Quantities: compound **3** (4.0 g, 0.015 mol), compound **30** (2.92 g, 0.014 mol), tetrakis-(triphenylphosphine)palladium(0) (0.80 g, 0.69 mmol), sodium carbonate (14.0 cm^3, 2.0 M, 0.028 mol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 5 : 1] to afford an orange solid. Yield 3.41 g (71%), mp 81–82 °C. ^{1}H NMR ($CDCl_3$) δ: 1.00(3H, t), 1.56(2H, sextet), 1.74(2H, quintet), 3.06(2H, t), 7.35(1H, d), 7.45(1H, dd), 7.69(1H, dd), 7.77(1H, d), 7.81(2H, d), 7.95(1H, d), 8.05(1H, d). IR (KBr) ν_{max}/cm^{-1} 740, 820, 830, 870, 1050, 1075, 1345, 1435, 1480, 1500, 1600, 2940, 2980. MS *m*/*z*: 343(M^+), 342(100%), 287, 197, 152.

2-Amino-5-(6-butylsulfanyl-2-naphthyl)thiophene 32

Compound **32** was prepared in a similar way to that described for the preparation of compound **5**. Quantities: compound **31** (2.62 g, 7.64 mmol), palladium-on-carbon (10%, 2.22 g). A black solid was obtained which was used in the next step without purification. Yield 2.39 g (95%).

2-(6-Butylsulfanyl-2-naphthyl)-5-isothiocyanatothiophene 33

Compound **33** was prepared in a similar way to that described for the preparation of compound **6**. Quantities: compound **32** (2.30 g, 7.35 mmol), thiophosgene (0.97 g, 8.43 mmol), calcium carbonate (1.17 g, 0.012 mol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 5 : 1] and was recrystallised (hexane) to give a pale green solid which was dried *in vacuo* ($CaCl_2$). Yield 0.57 g (23%). Transitions (°C) Cryst 100.5 B 104.5 [N 47] Iso liq. ^{1}H NMR ($CDCl_3$) δ: 0.97(3H, t), 1.54(2H, sextet), 1.71(2H, quintet), 3.05(2H, t), 6.88(1H, d), 7.13(1H, d), 7.42(1H, dd), 7.63(1H, dd), 7.65(1H, d), 7.74(2H, d), 7.89(1H, d). IR (KBr) ν_{max}/cm^{-1} 470, 790, 815, 860, 875, 1140, 1440, 1460, 1490, 1585, 2050, 2920, 2950. MS *m*/*z*: 355(M^+, 100%), 297, 189, 82, 69. UV λ_{max} (cyclohexane) 204(31 850 dm^3 mol^{-1} cm^{-1}), 253(21 800), 358(28 900) nm.

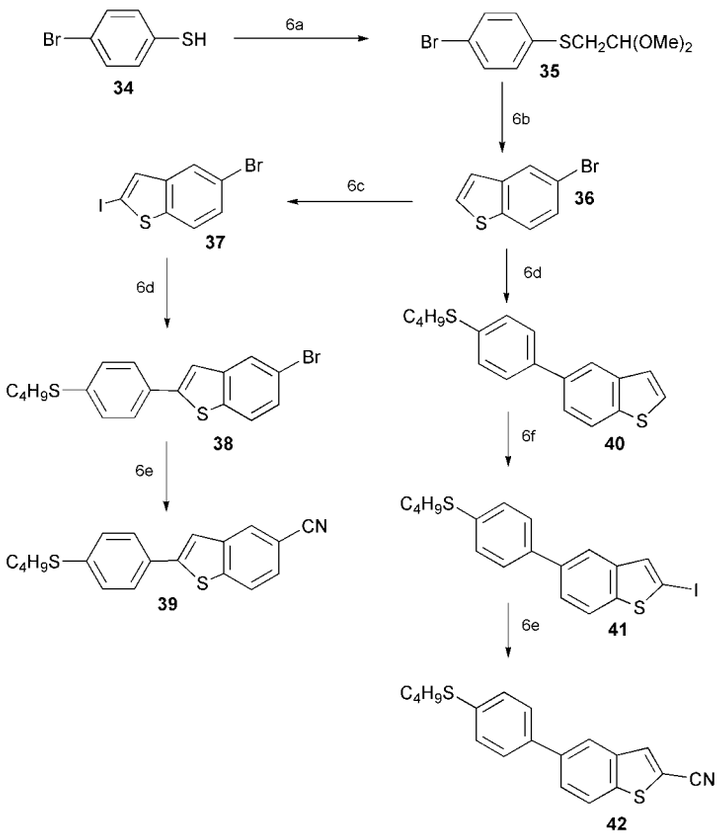
Optical properties and calculated parameters. At $T/T_{N-I} = 0.7815$: $n_{\parallel} = 2.03$, $n_{\perp} = 1.61$, $\Delta n = 0.43$, $\Delta\alpha = 40.95$, $S = 0.63$.
At 25 °C: $n_{\parallel} = 2.01$, $n_{\perp} = 1.59$, $\Delta n = 0.42$, $\Delta\alpha = 39.98$, $S = 0.64$.

1-Bromo-4-(2,2-dimethoxyethylsulfanyl)benzene 35 (Scheme 6)

Compound **35** was prepared in a similar way to that described for the preparation of compound **2** in reference 9. Quantities: compound **34** (30.0 g, 0.159 mol) ethanolic sodium ethoxide (4.01 g of sodium in 150 cm^3 of super-dry ethanol), bromoacetaldehyde dimethyl acetal (53.6 g, 0.317 mol). A colourless liquid was obtained. Yield 35.6 g (81%), bp 132–136 at 2 mmHg. ^{1}H NMR ($CDCl_3$) δ: 3.09(2H, d), 3.36(6H, s), 4.51(1H, t), 7.25(2H, d), 7.41(2H, d). IR (film) ν_{max}/cm^{-1} 810, 1010, 1060, 1090, 1120, 1385, 1470, 2840, 2940, 2990. MS *m*/*z*: 278, 276(M^+), 166, 108, 75(100%), 47.

5-Bromo-1-benzothiophene 36

Compound **35** (24.4 g, 0.088 mol) was added dropwise to a stirred mixture of dry chlorobenzene (650 cm^3) and polyphosphoric acid (25.0 g), under reflux, under dry nitrogen over 1 h. The reaction mixture was maintained under these conditions overnight, cooled and the layers were separated. Water (200 cm^3) was added to the aqueous layer which was



Scheme 6 *Reagents*: 6a, $BrCH_2CH(OMe)_2$, NaOEt; 6b, polyphosphoric acid; 6c, (i) $LiN(iPr)_2$, (ii) I_2; 6d, 4-$C_4H_9SC_6H_4B(OH)_2$, $Pd(PPh_3)_4$, Na_2CO_3; 6e, CuCN; 6f, (i) n-C_4H_9Li, (ii) I_2.

subsequently washed with dichloromethane ($2 \times 200\ cm^3$) before the organic washings and the chlorobenzene solutions were dried ($MgSO_4$). The solvent was removed *in vacuo* and the product was purified by column chromatography [petroleum fraction (bp 40–60 °C)] and was recrystallised [petroleum fraction (bp 40–40 °C)] to give white crystals which were dried *in vacuo* ($CaCl_2$). Yield 16.9 g (90%), mp 42–44 °C. ^1H NMR ($CDCl_3$) δ: 7.27(1H, dd), 7.44(1H, dd), 7.48(1H, d), 7.74(1H, dd), 7.96(1H, d). IR (KBr) ν_{max}/cm^{-1} 695, 805, 895, 1060, 1400, 1570. MS *m/z*: 214, 212(M^+, 100%), 149, 133, 89.

5-Bromo-2-iodo-1-benzothiophene 37

A solution of compound **36** (7.0 g, 0.033 mol) in dry THF (50 cm^3) was added dropwise to a stirred, cooled (−10 °C) solution of LDA (0.036 mol) in dry THF (150 cm^3) under dry nitrogen at −10 °C. The reaction mixture was maintained under these conditions for a further 30 min before the temperature was lowered to −78 °C. Iodine (8.32 g, 0.033 mol) in dry THF (20 cm^3) was added dropwise at −78 °C and the reaction mixture was maintained at this temperature for 30 min before being allowed to warm to room temperature. The mixture was poured into an excess of saturated sodium thiosulfate and the two layers were separated. The aqueous layer was washed with ether ($2 \times 100\ cm^3$) and the combined organic washings were dried ($MgSO_4$). The solvent was removed *in vacuo* and the product was purified by column chromatography [petroleum fraction (bp 40–60 °C)] to give a pink semi-solid. Yield 8.92 g (80%). ^1H NMR ($CDCl_3$) δ: 7.45(1H, d), 7.61(1H, d), 7.69(1H, d), 7.87(1H, dd). IR (film) ν_{max}/cm^{-1} 680, 750, 795, 810, 870, 920, 1060, 1150, 1190, 1245, 1270, 1400, 1420, 1575, 2920, 2960, 3100. MS *m/z*: 340, 338(M^+, 100%), 213, 211, 132.

5-Bromo-2-(4-butylsulfanylphenyl)-1-benzothiophene 38

Compound **38** was prepared in a similar way to that described for the preparation of compound **8** in reference 2. Quantities: 4-butylsulfanylphenylboronic acid[2] (2.11 g, 0.01 mol), compound **37** (3.08 g, 9.09 mmol), tetrakis(triphenylphosphine)-palladium(0) (0.53 g, 0.46 mmol), sodium carbonate (9.1 cm^3, 2.0 M, 0.018 mol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–diethyl ether 10 : 1] to give a yellow semi-solid. Yield 2.77 g (82%). ^1H NMR ($CDCl_3$) δ: 0.93(3H, t), 1.49(2H, sextet), 1.69(2H, quintet), 2.96(2H, t), 7.23–8.20(8H, m). IR (film) ν_{max}/cm^{-1} 680, 750, 810, 1060, 1090, 1190, 1400, 1435, 1480, 1580, 1595, 2870, 2890, 2920, 2950. MS *m/z*: 378, 376(M^+), 186, 184(100%), 152, 150.

2-(4-Butylsulfanylphenyl)-5-cyano-1-benzothiophene 39

Compound **39** was prepared in a similar way to that described for the preparation of compound **14** in reference 3 but using *N*-methylpyrrolidin-2-one as the solvent. Quantities: compound **38** (0.50 g, 1.33 mmol), copper(I) cyanide (0.71 g, 7.98 mmol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 1 : 1] and was recrystallised twice (ethanol) to give white crystals which were dried *in vacuo* (P_2O_5). Yield 0.49 g (87%). Transitions (°C) Cryst 104.5 [N −97] Iso liq. ^1H NMR ($CDCl_3$) δ: 0.97(3H, t), 1.51(2H, sextet), 1.71(2H, quintet), 3.00(2H, t), 7.45(4H, d), 7.53(1H, d), 7.60(1H, dd), 8.00(1H, d), 8.20(1H, d). IR (KBr) ν_{max}/cm^{-1} 800, 820, 905, 1050, 1090, 1315, 1425, 1590, 2220, 2920, 2950, 3100. MS *m/z*: 323(M^+, 100%), 267, 233, 190, 159. UV λ_{max} (cyclohexane) 205(29 910 $dm^3\ mol^{-1}\ cm^{-1}$), 232(37 980), 277(18 450) nm.

Optical properties and calculated parameters. At $T/T_{N-I} = 0.7815$: $n_{\|} = 1.92$, $n_{\perp} = 1.66$, $\Delta n = 0.26$, $\Delta\alpha = 23.17$, $S = 0.61$.

At 25 °C: $n_{\|}=1.72$, $n_{\perp}=1.62$, $\Delta n=0.11$, $\Delta\alpha=20.78$, $S=0.28$.

5-(4-Butylsulfanylphenyl)-1-benzothiophene 40

Compound **40** was prepared in a similar way to that described for the preparation of compound **8** in reference 2. Quantities: 4-butylsulfanylphenylboronic acid[2] (1.94 g, 9.24 mmol), compound **36** (1.65 g, 7.75 mmol), tetrakis(triphenylphosphine)-palladium(0) (0.45 g, 0.39 mmol), sodium carbonate (7.7 cm^3, 2.0 M, 0.015 mol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–diethyl ether 10 : 1] to give a white solid. Yield 2.70 g (quantitative), mp 85–86 °C. ^{1}H NMR ($CDCl_3$) δ: 0.91(3H, t), 1.41(2H, sextet), 1.60(2H, quintet), 2.91(2H, t), 7.33(2H, d), 7.41–7.50(2H, m), 7.51(3H, m), 7.86(1H, d), 7.93(1H, d). IR (KBr) ν_{max}/cm^{-1} 705, 810, 905, 1055, 1095, 1430, 1470, 1590, 2870, 2920, 2950. MS *m*/*z*: 298(M^+), 242(100%), 186, 152, 166.

5-(4-Butylsulfanylphenyl)-2-iodo-1-benzothiophene 41

Compound **41** was prepared in a similar way to that described for the preparation of compound **37** except that *n*-butyllithium was used instead of LDA. Quantities: compound **40** (1.85 g, 6.21 mmol), *n*-butyllithium (2.7 cm^3, 2.5 M in hexane, 6.75 mmol), iodine (2.0 g, 7.87 mmol). A white solid was obtained which was used in the next step without purification. Yield 3.27 g. Purity (GLC) 95%. ^{1}H NMR ($CDCl_3$) δ: 0.95(3H, t), 1.48 (2H, sextet), 1.68(2H, quintet), 2.98(2H, t), 7.40–7.60(2H, m), 7.40(2H, d), 7.55(2H, d), 7.81(1H, d), 7.89(1H, d). IR (KBr) ν_{max}/cm^{-1} 810, 885, 920, 1095, 1430, 1470, 1510, 2920, 2950. MS *m*/*z*: 424(M^+, 100%), 368, 240, 208, 163.

5-(4-Butylsulfanylphenyl)-2-cyano-1-benzothiophene 42

Compound **42** was prepared in a similar way to that described for the preparation of compound **39** using the quantities stated. Quantities: compound **41** (1.47 g, 3.47 mmol), copper(I) cyanide (0.37 g, 4.16 mmol). The product was purified by column chromatography [petroleum fraction (bp 40–60 °C)–dichloromethane 1 : 1] and was recrystallised (ethanol) to give pale yellow crystals which were dried *in vacuo* (P_2O_5). Yield 0.24 g (25%). Transitions (°C) Cryst 77.7 [N 23] Iso liq. ^{1}H NMR ($CDCl_3$) δ: 0.95(3H, t), 1.49(2H, sextet), 1.69(2H, quintet), 2.99(2H, t), 7.42(2H, d), 7.55(2H, d), 7.75(1H, dd), 7.92(2H, 2 × d), 8.05(1H, d). IR (KBr) ν_{max}/cm^{-1} 800, 895, 1095, 1175, 1430, 1490, 1590, 2230, 2920, 2960, 3080. MS *m*/*z*: 323(M^+), 267(100%), 233, 94, 59. UV λ_{max} (cyclohexane) 196(34 390 $dm^3\ mol^{-1}\ cm^{-1}$), 205(30 530), 252(33 440), 290(46 900) nm.

Optical properties and calculated parameters. At $T/T_{N-I}=0.7815$: $n_{\|}=1.90$, $n_{\perp}=1.59$, $\Delta n=0.32$, $\Delta\alpha=28.08$, $S=0.62$.

At 25 °C: $n_{\|}=1.85$, $n_{\perp}=1.57$, $\Delta n=0.29$, $\Delta\alpha=27.08$, $S=0.58$.

Results and discussion

Transition temperatures

The transition temperatures for the new compounds are given in Table 1; our previous work[1] with naphthalene systems used pentyl, butoxy and cyano terminal groups and a single bond or an ethynyl link between the naphthyl and phenyl rings, and some of those results are given in Table 2 for comparison with the current work.

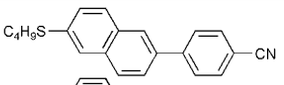
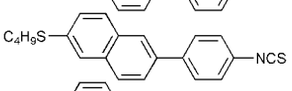
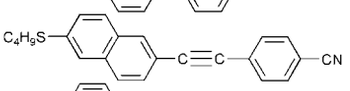
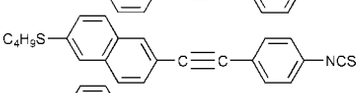
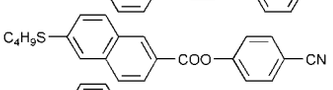
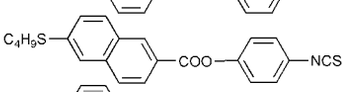
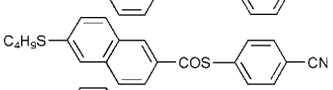
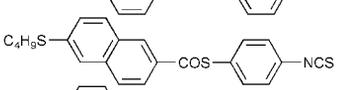
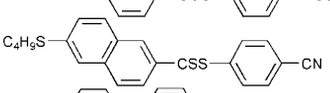
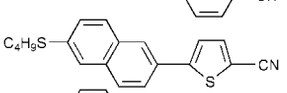
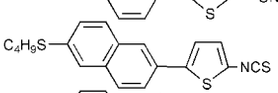
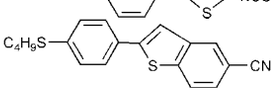
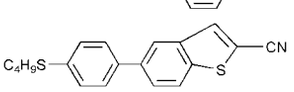
All the compounds in Table 1 are predominantly nematogenic; the compounds with naphthyl and phenyl rings present give solely an enantiotropic nematic phase except for compound **17** which also gives a smectic A phase. The clearing points for the naphthyl/phenyl systems range from 107.0 °C, for compound **7** with directly linked rings, to 169.4 °C for compound **19** with a dithio ester linking group. The melting points for these compounds are relatively high and are in the range 86.7 to 154.0 °C. The clearing temperatures for compounds **43**, **45** and **24** [alkyl (130.0 °C), alkoxy (167.5 °C) and alkylsulfanyl (114.8 °C) respectively] show that the incorporation of the large sulfur atom has a pronounced effect on mesophase stability, to the extent that the butylsulfanyl compound gives a clearing point more than 50 °C lower than for the alkoxy compound and, surprisingly, even lower than that for the alkyl compound. Most of the compounds shown in Table 1 have the butylsulfanyl group in the naphthalene unit and the cyano or thiocyanato terminal group in a phenyl ring. The reversed arrangement (*e.g.*, compound **24** in Table 1) has been examined for other terminal groups in previous work[1] and in some cases this type of structure gives lower melting points and higher clearing points, as is the case for compounds **43** and **45** in comparison with compounds **44** and **46** respectively. However, this relationship is not universal [compounds **47** and **24** have higher melting points than **48** and **7** respectively] and in order to minimise the number of compounds considered, the current work deals mainly with the type of compound having the butylsulfanyl substituent in the naphthalene unit. The evidence from previous work has been that this type of structure and the reversed arrangement give almost identical values of optical anisotropies (see Table 2).

The presence of linking groups between phenyl/phenyl and naphthyl/phenyl systems which have butylsulfanyl and cyano or isothiocyanato terminal groups gives compounds which do not show consistent changes in T_{N-I} values (see Table 3) and the values illustrate how difficult it is to predict whether a structural change in one type of system will have a similar effect in another. The presence of the -C≡C- or -COS- links always gives higher T_{N-I} values than for the parent compounds. However, the -COO- link can give compounds with lower T_{N-I} values than the parent system (see column D) and the -CSS- link, surprisingly, varies from being the worst (column B) to the best linkage (column C).

Compounds **28**, **33**, **39** and **42** were prepared to compare thienyl and phenyl systems and 1-benzothienyl and naphthyl systems and to give a comparison with earlier work on phenylthiophenes.[3] Modifying the naphthalene unit to give a 1-benzothiophene has a huge effect on the T_{N-I} values, with depressions of 211.8 °C for compound **39** and 91.8 °C for compound **42** in comparison with the value for compound **24**. The magnitude of the depression is large but the relative order of nematogenicity of the compounds is understandable on the basis of the core of compound **42** being more linear (with the deformation from linearity occurring at the end of the core) than compound **39**, where the bend in the structure occurs almost at the centre of the molecular core. Compounds **28** and **33** in comparison with compounds **7** and **6** show the result of converting a phenyl ring into a thiophene unit; for the cyano compounds and isothiocyanato compounds the depressions in T_{N-I} values are 33.8 °C and 78.7 °C respectively, and the former value is similar to that reported for the corresponding change in biphenyl compounds.[3]

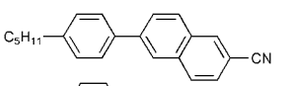
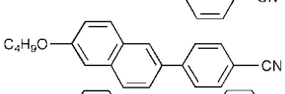
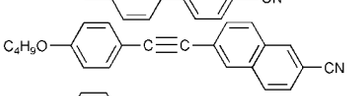
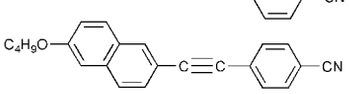
The effect on melting points and T_{N-I} values caused by replacing a benzene unit by a naphthalene unit can now be determined for many of the compounds in Table 1, by comparison with values reported previously;[5,9] for compounds **7**, **6**, **10**, **12**, **14** and **15** the values for the corresponding phenyl compounds are from reference 5, and for compounds **16**, **17** and **19** from reference 9. For compounds **7**, **6**, **10**, **12**, **14**, **15**, **16**, **17** and **19**, the melting points are always higher by 27.2, 19.7, 6.7, 6.7, 26.0, 11.5, 22.4, 14.8 and 42.9 °C respectively, giving an average increase of approximately 20 °C; the T_{N-I} values are also always higher by 71.5, 81.7, 78.5, 71.7, 62.4, 65.2, 66.1, 54.8 and 98.5 °C respectively, corresponding to an average increase of approximately 72 °C. In general, the melting point increases are not too severe and in the specific case of

Table 1 Transition temperatures (°C) of compounds based on various naphthyl, phenyl, thienyl and 1-benzothienyl core systems with butylsulfanyl and cyano or isothiocyanato terminal groups

Compound	Structure	Cryst		B		SmA		N[a]		Iso liq
7		•	92.0	—	—	—	—	•	107.0	•
6		•	98.1	—	—	—	—	•	125.7	•
10		•	87.0	—	—	—	—	•	131.8	•
12		•	91.5	—	—	—	—	•	136.7	•
14		•	108.2	—	—	—	—	•	118.7	•
15		•	86.7	—	—	—	—	•	119.3	•
16		•	115.0	—	—	—	—	•	160.7	•
17		•	90.7	—	—	•	94.3	•	136.1	•
19		•	154.0	—	—	—	—	•	169.4	•
24		•	93.2	—	—	—	—	•	114.8	•
28		•	93.6	—	—	—	—	(•	73.2)	•
33		•	100.5	•	104.5	—	—	[•	47]	•
39		•	104.5	—	—	—	—	[•	−97]	•
42		•	77.5	—	—	—	—	[•	23]	•

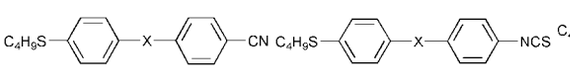
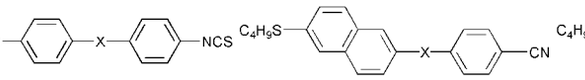
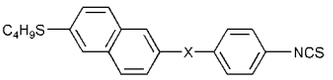
[a]( ) denotes a monotropic transition. [ ] denotes a virtual transition determined from mixtures in E7 (see text).

Table 2 Transition temperatures (°C) and optical anisotropies (Δn) at a reduced temperature of $T/T_{N-I}=0.7815$, for compounds related to those in Table 1[a]

Compound	Structure	Cryst		N		Iso liq	Δn
43		•	68.0	•	130.0	•	0.30
44		•	84.0	•	126.5	•	0.30
45		•	98.5	•	167.5	•	0.33
46		•	125.0	•	159.0	•	0.33
47		•	120.5	•	186.0	•	0.41
48		•	111.5	•	186.0	•	0.42

[a]Values from reference 1.

Table 3 Values of T_{N-I} (°C) for related phenyl/phenyl and naphthyl/phenyl compounds

Link (X)	 A	 B	C	 D
Single bond	(35.5)[5]	[44][5]	107.0[21]	125.7
-C≡C-	(53.3)[5]	[65][5]	131.8	136.7
-COO-	(56.3)[5]	(54.1)	118.7	119.3
-COS-	94.6[9]	81.3[9]	160.7	136.1
-CSS-	(70.9)[9]	(34.4)[9]	169.4	

[a]( ) and [ ] indicate monotropic and virtual transitions, respectively.

compound **12**, which is useful because of its particularly high optical anisotropy (see below), the melting point increase is only 6.7 °C.

Refractive indices, optical anisotropies, polarisabilities and order parameters

The optical properties and related parameters for the novel compounds are given in Table 4. For a fair comparison of structural changes on the optical properties, the values at a constant reduced temperature should be used (in this case $T/T_{N-I}=0.7815$ is the value chosen; see Experimental section), but the values at 25 °C are also reported because in practical terms it is important to have the information for a temperature at which the materials may be used; unless otherwise stated, the discussion below concentrates on the reduced temperature values.

Excluding the thiophene-based systems from the initial discussion, all the naphthalene-containing compounds have very high optical anisotropies, ranging from 0.30–0.54. Most of the values given in Table 4 for naphthalene compounds can be compared to values for compounds in which the naphthalene unit has replaced a phenyl ring[5,9] and these relationships are more clearly shown by grouping the values together in Table 5. In these comparisons, the naphthalene compound always has a higher optical anisotropy than the phenyl compound, and the

Table 4 Refractive indices of compounds shown in Table 1 at a reduced temperature (RedT) of $T/T_{N-I}=0.7815$ (first line) and at 25 °C (second line)

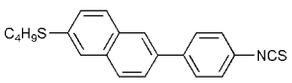
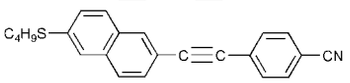
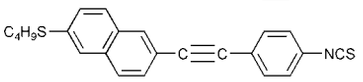
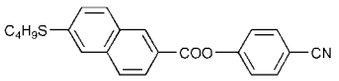
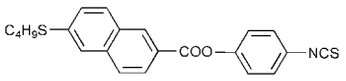
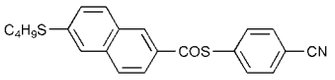
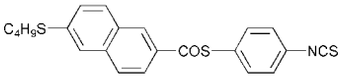
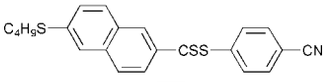
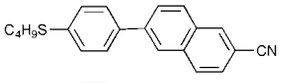
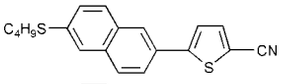
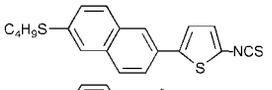
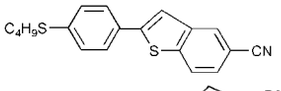
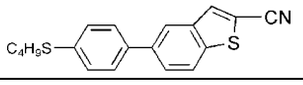
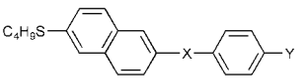
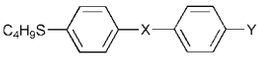
Compound	Structure		$n_{\parallel}$	$n_{\perp}$	Δn	$\Delta\alpha/10^{-30}$ m^3	S
6		RedT	2.01	1.57	0.44	46.88	0.58
		25 °C	2.01	1.57	0.44	45.08	0.58
10		RedT	2.02	1.56	0.46	34.87	0.77
		25 °C	2.02	1.56	0.46	34.88	0.77
12		RedT	2.12	1.58	0.54	53.98	0.63
		25 °C	2.12	1.58	0.54	54.23	0.63
14		RedT	1.85	1.55	0.30	26.68	0.69
		25 °C	1.85	1.55	0.30	26.70	0.70
15		RedT	1.92	1.57	0.35	32.99	0.71
		25 °C	1.91	1.57	0.35	32.93	0.71
16		RedT	1.89	1.56	0.33	33.77	0.64
		25 °C	1.91	1.57	0.34	34.43	0.64
17		RedT	1.95	1.58	0.38	39.86	0.66
		25 °C	1.97	1.58	0.39	40.28	0.68
19		RedT	2.10	1.70	0.41	66.85	0.39
		25 °C	2.18	1.59	0.59	67.28	0.59
24		RedT	1.92	1.56	0.36	33.07	0.62
		25 °C	1.92	1.56	0.36	31.80	0.61
28		RedT	1.97	1.58	0.38	33.46	0.63
		25 °C	1.94	1.57	0.37	32.93	0.61
33		RedT	2.03	1.61	0.43	40.95	0.63
		25 °C	2.01	1.59	0.42	39.98	0.64
39		RedT	1.92	1.66	0.26	23.17	0.61
		25 °C	1.72	1.62	0.11	20.78	0.28
42		RedT	1.90	1.59	0.32	28.08	0.62
		25 °C	1.85	1.57	0.29	27.08	0.58

Table 5 Refractive indices and optical anisotropies of compounds with naphthyl/phenyl and phenyl/phenyl rings at a reduced temperature of $T/T_{N-I}=0.7815$





Linkage (X)	Terminal Group (Y)	Cpd	$n_{\parallel}$	$n_{\perp}$	Δn	Cpd[a]	$n_{\parallel}$	$n_{\perp}$	Δn
—	NCS	**6**	2.01	1.57	0.44	**49**	1.96	1.56	0.40
-C≡C-	CN	**10**	2.02	1.56	0.46	**50**	1.90	1.56	0.34
-C≡C-	NCS	**12**	2.12	1.58	0.54	**51**	2.08	1.58	0.50
-COO-	CN	**14**	1.85	1.55	0.30	**52**	1.80	1.54	0.26
-COO-	NCS	**15**	1.92	1.57	0.35	**53**	1.87	1.55	0.32
-COS-	CN	**16**	1.89	1.56	0.33	**54**	1.86	1.56	0.30
-COS-	NCS	**17**	1.95	1.58	0.38	**55**	1.94	1.57	0.37
-CSS-	CN	**19**	2.10	1.70	0.41	**56**	1.96	1.56	0.40

[a]Compounds **49**–**53** (from ref. 5); compounds **54**–**56** (from ref. 9).

Δn value is on average 0.04 greater than for the phenyl systems. The increase is almost entirely attributable to the differences in the $n_{\parallel}$ values (which are on average 0.06 greater for the naphthyl compounds) whereas the $n_{\perp}$ values are very similar for phenyl and naphthyl compounds. There is some marginal evidence for a slightly higher value of $n_{\perp}$ for the naphthyl compounds but the similarity of values reflects the fact that the nature of the breadth of each molecule is largely the same, being that defined by the breadth of the aromatic π-system. The $n_{\parallel}$ values, as expected, are more affected by the structural change which increases the length of the polarisable core unit. We have previously studied the thiophene unit as a replacement for one or both of the phenyl rings in 4-butylsulfanyl-4′-cyanobiphenyl[3] and compound **28** ($\Delta n=0.38$) compared with 2-(4-butylsulfanylphenyl)-5-cyanothiophene ($\Delta n=0.34$) again shows a typical increase of approximately 0.04 for naphthyl replacing a phenyl unit.

Two other observations confirm the situation revealed in previous work: (a) the terminal isothiocyanato compounds always have greater values of Δn than the terminal cyano compounds (compare compounds **12**, **15**, **17** and **33** with **10**, **14**, **16** and **28** respectively), and (b) the decreasing order of Δn for the various linking units is -C≡C- > single bond > -COS- > -COO-.[2,4,5,9] Although the ester units would be expected to extend the length of the polarisable core, they clearly limit the polarisability, probably because the phenol oxygen or sulfur of the ester group breaks the π-electron character of the rest of the core; biphenyls and phenyl benzoates have been compared previously[5,9] and the ester linking group lowers the optical anisotropy in these systems also. However, the ethynyl group is able to enhance the interaction of the two aromatic units to which it is connected because of its double π-character and also because twisting or rotation of either aromatic unit about the linking group still maintains conjugation between the rings. The current work has three examples of thioesters and the order of Δn values for the cyano compounds **14** (-COO- link, $\Delta n=0.30$), **16** (-COS-, 0.33) and **19** (-CSS-, 0.41) is exactly parallel to the results for phenyl benzoates and thiobenzoates;[9] compounds **17** and **15** show the same relationship for the isothiocyanato terminal group.

Compound **12** has the best set of structural features for enhancing optical anisotropy and it has the highest Δn value (0.54) for the compounds reported; its relatively low melting point and acceptably high clearing point, in comparison to other compounds in Table 1, support its usefulness as a high birefringence additive. In the previous work[5] with phenyl systems, the same molecular units gave the highest Δn value of 0.50 for that set of compounds (see compound **51** in Table 5).

The values of order parameters (S) of the phenyl/naphthyl systems are mainly in the 0.60–0.70 range both at the reduced temperature and at 25 °C, which principally reflects the fundamentally similar shape of all the compounds and the reasonably similar clearing points. The exceptionally low S value for compound **39** at 25 °C is attributable to its very low virtual T_{N-I} value of −97 °C.

Acknowledgements

The work reported here was supported by the Defence Evaluation Research Agency (Malvern) and is published by permission of the Director, HMSO. We thank Mrs B. Worthington, Dr D. F. Ewing, Mr R. Knight and Mr A. D. Roberts for spectroscopic measurements.

References

1 M. Hird, K. J. Toyne, G. W. Gray, S. E. Day and D. G. McDonnell, *Liq. Cryst.*, 1993, **15**, 123.
2 M. Hird, A. J. Seed, K. J. Toyne, J. W. Goodby, G. W. Gray and D. G. McDonnell, *J. Mater. Chem.*, 1993, **3**, 851.
3 A. J. Seed, K. J. Toyne and J. W. Goodby, *J. Mater. Chem.*, 1995, **5**, 653.
4 A. J. Seed, K. J. Toyne and J. W. Goodby, *J. Mater. Chem.*, 1995, **5**, 2201.
5 G. J. Cross, A. J. Seed, K. J. Toyne, J. W. Goodby, M. Hird and M. C. Artal, *J. Mater. Chem.*, 2000, **10**, 1555.
6 U. H. Lauk, P. Skrabal and H. Zollinger, *Helv. Chim. Acta*, 1985, **68**, 1406.
7 L. Domash, P. Levin, J. Ahn, J. Kumar and S. Tripathy in *All-optical switching using optical fibres and nonlinear organic liquids*, ed. R. M. Metzger, P. Day and G. C. Papavassiliou, Plenum Press, New York, 1991.
8 P. N. Pasad in *Lower-dimensional Systems and Molecular Electronics*, ed. R. M. Metzger, P. Day, and G. C. Papavassiliou, Plenum Press, New York, 1991, p. 563.
9 A. J. Seed, K. J. Toyne, J. W. Goodby and D. G. McDonnell, *J. Mater. Chem.*, 1995, **5**, 1.
10 I. Haller, *Prog. Solid-State Chem.*, 1975, **10**, 103.
11 W. Maier and A. Saupe, *Z. Naturforsch.*, 1959, **14a**, 882.
12 T. Nakazawa, N. Hirose and K. Itabashi, *Synthesis*, 1989, 955.
13 F. M. Furman, J. H. Thelin, D. W. Hein and W. B. Hardy, *J. Am. Chem. Soc.*, 1960, **82**, 1450.
14 S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, 1980, 627.
15 A. Carpita, A. Lessi and R. Rossi, *Synthesis*, 1984, 571.
16 M. J. Bevis, E. J. Forbes and B. C. Uff, *Tetrahedron*, 1969, **25**, 1585.
17 C. van Pham, R. S. Macomber, H. B. Mark and H. Zimmer, *J. Org. Chem.*, 1984, **49**, 5250.
18 F. Sauter, H. Froehlich and W. Kalt, *Synthesis*, 1989, 771.
19 D. W. Hawkins, B. Iddon, D. S. Longthorne and P. J. Rosyk, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2735.
20 V. S. Babasinian, *J. Am. Chem. Soc.*, 1935, **57**, 1763.
21 M. Hird, personal communication..