Synthesis, transition temperatures, and optical properties of compounds with simple phenyl units linked by double bond, triple bond, ester or propiolate linkages†

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A series of compounds has been prepared with 4-butylsulfanylphenyl and 4-cyano- or 4-isothiocyanato-phenyl units connected by -CH=CH-, -COO-, -C≡C-, or -C≡C-COO- linking groups. The synthesis of the novel compounds is presented and the transition temperatures and optical parameters of the compounds are discussed and compared with those for related biphenyl reference systems. The ester linking group reduces optical and polarisability anisotropy, but the other linking groups give increased optical anisotropy (up to $\Delta n = 0.50$) and polarisability anisotropy [up to $\Delta\alpha = 45.2$ Å^3 (10^{-30} m^3)].

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;[1,2] some examples of our previous work to meet these objectives are given in refs. 3–6. 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 values; in order to maximise the transmission of light, thinner cells are needed and therefore compounds of higher optical anisotropy have to be used. As is always the case with the formulation of liquid crystal mixtures for any application, a compromise has to be reached since no single component will ever meet the extensive list of requirements of physical properties. Specifications of mesophase type, mesophase range, mesophase sequence, melting point, clearing point, viscosity, dielectric, elastic and optical properties *etc.* provide some targets that have to be approached to provide an acceptable formulation in a particular case. Usually, a broadly acceptable composition is formulated from a small number of components and then an attempt is made to optimise the formulation by using additives which enhance a required physical property without diminishing the performance of the basic mixture. High birefringence nematic materials is one example of additives which are particularly valuable and the dilema that has to be faced in designing such materials is that increased molecular polarisability generally leads to increased melting points and reduced miscibility whereas acceptable melting points and mesophase ranges arise from relatively small compounds of only moderate optical anisotropy. The challenge is to design molecules which contain as many advantageous features for enhancing optical anisotropy as possible, whilst still retaining an ability to mix with a host system without altering its other physical properties too seriously.
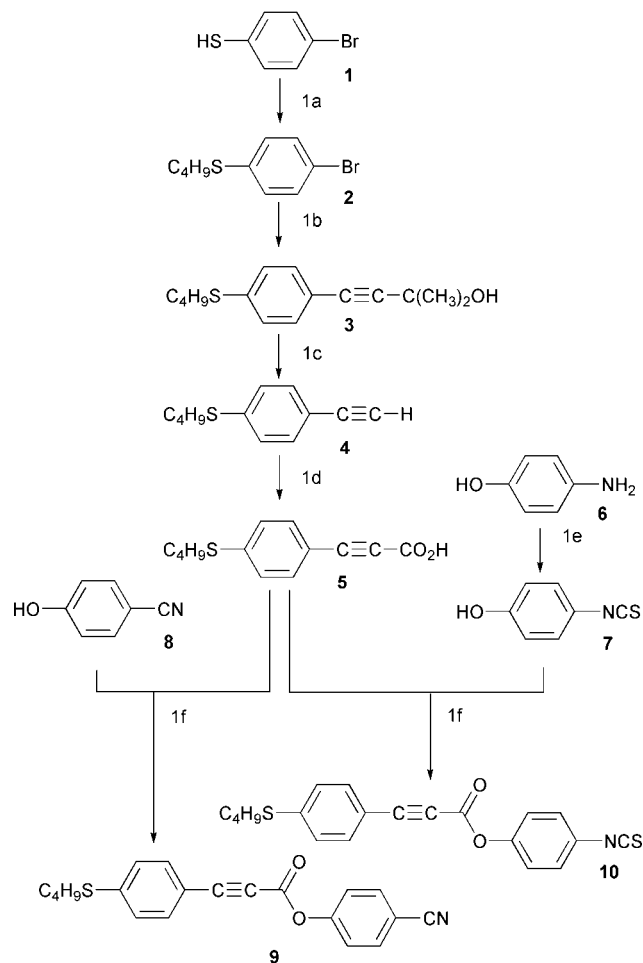
We have undertaken an extensive programme of work to try to assess how those groups and molecular units which are known to confer high optical anisotropy can be combined to give even better additives. Some common groups and rings which have been identified as giving rise to high optical anisotropy are RS-, -CN, -NCS, -C≡C-, >C=C<, -CSO-, -COS-, -CSS-, phenyl, naphthyl, thiophenyl *etc.* as reported in earlier work.[3–6] We have found that the butylsulfanyl unit is a good terminal group in the design of compounds of high optical anisotropies because it is sufficiently long to permit a reasonable mesogenic character, but it is short enough so as not to dilute the polarisability of the core units, and the sulfur atom gives enhanced polarisability compared to the oxygen atom in an alkoxy group. The presence of cyano or isothiocyanato groups also gives rise to good mesogenicity and because of their unsaturated π-system structure they provide an extended region of polarisability in the molecule. In this part of the programme we consider >C=C<, -C≡C- and -COO- linking groups between phenyl rings with -CN, -NCS, C$_4$H$_9$S- or C$_5$H$_{11}$- terminal groups. The fundamental parent core system used is biphenyl (compounds 39[5,6] and 40[3]) and carboxylate ester or ethynyl groups are inserted separately (compounds 41,[4] 42,[4] 14 and 16) and in combination (compounds 9 and 10) between the rings. The compounds 27 and 28 (and their precursors 25 and 26) are included to show the effect of an ethenyl link and the values for 37 (this work, and from ref. 7 for the neat material) and 38[3] are given to show the comparison with the pentyl parent compounds; one example of a pyrimidine compound (32) is reported to show the extent to which heterocyclic nitrogen atoms decrease optical anisotropy in these systems.

Experimental

The synthetic pathways to compounds 9, 10 (Scheme 1), 14, 16 (Scheme 2), 25–28 (Scheme 3) and 32 (Scheme 4) are shown below. Compound 2 was converted into the alkyne 4 (Scheme 1) via compound 3 by using the 2-methylbut-3-yn-2-ol method;[8–10] the alternative preparation of compound 4 (Scheme 2) used the more expensive reagent trimethylsilylacetylene.[11] The lithium salt of 5 was acidified more efficiently with
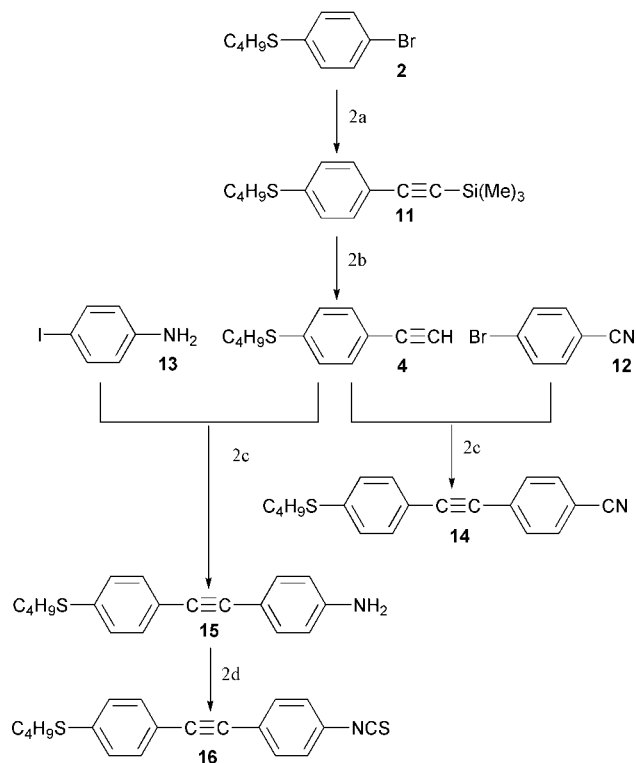
Scheme 1 *Reagents*: 1a, NaOEt, *n*-BuBr, EtOH (80 °C); 1b, HO(Me)$_2$CC≡CH, Pd(PPh$_3$)$_4$, CuI, *i*-Pr$_2$NH; 1c, KOH, toluene; 1d, (i) *n*-BuLi, hexanes, THF, (−10 °C), (ii) CO$_2$(s), Et$_2$O, (iii) glacial AcOH; 1e, CS$_2$, DCC, C$_5$H$_5$N, (−10 °C); 1f, DCC, DMAP, DCM.

Scheme 2 *Reagents*: 2a, Me$_3$SiC≡CH, Et$_3$N, Pd(PPh$_3$)$_4$, CuI; 2b, KOH, MeOH; 2c, (i) *n*-BuLi, ZnCl$_2$, (ii) Pd(PPh$_3$)$_4$; 2d, CSCl$_2$, CaCO$_3$.

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; $T_{N-I} = 60$ °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 ±5 °C, assuming ideal mixing behaviour.

The optical anisotropies of the compounds (accurate to 0.001) 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.[6] 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 ($= n_\parallel - n_\perp$) were plotted against temperature and gave a straight line, which in all cases passed through the individual values. The value for the optical anisotropies at 25 °C for each mixture was taken and extrapolated to 100% of the compound being examined. 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,

glacial acetic acid than with mineral acid; the preparation of compound **7** employed the method of Jochims[12] and DCC esterification of the phenols[13] gave compounds **9** and **10**. Attempts to couple compound **4** to haloaryl isothiocyanates to give **16** and **32** were unsuccessful (we believe that the palladium or copper catalysts are poisoned by coordination with the sulfur atom in the isothiocyanate), but reactions with haloarylamines (*e.g.* **13** and **30**) were satisfactory. Compounds **25** and **27** were synthesised following the method reported for compounds **26** and **28**.[14]

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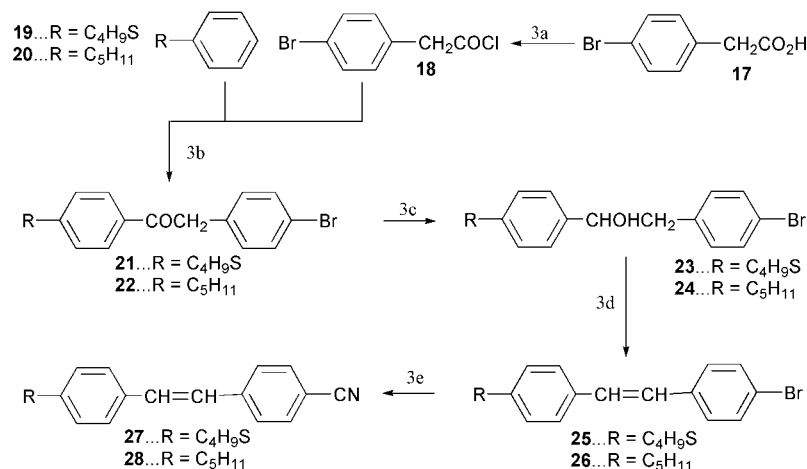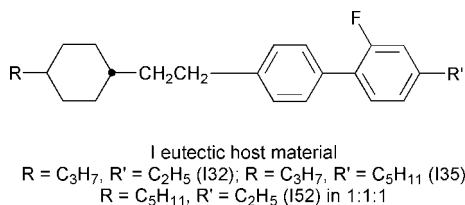
Thin-layer chromatographic analyses were performed using aluminium-backed silica gel plates (Merck 60 F254) and were examined under UV light. Column chromatography was performed under gravity using May and Baker Sorbsil C60 40–60H μm silica gel. The purity of all final products was determined by HPLC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

Scheme 3 *Reagents*: 3a, (COCl)$_2$, DMF; 3b, AlCl$_3$; 3c, LiAlH$_4$; 3d, HCO$_2$H; 3e, CuCN.

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$_3$H$_7$, R' = C$_2$H$_5$ (I32); R = C$_3$H$_7$, R' = C$_5$H$_{11}$ (I35)
R = C$_5$H$_{11}$, R' = C$_2$H$_5$ (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[4,6] (the error bars are ±1.14 and ±0.10, respectively) using a combination of Vuks equation, the Haller plot,[15] the Lorentz–Lorenz equation and the Maier–Saupe expression[16] for the polarisability along the principal molecular axes. The density is assumed to be 1 g cm^{-3} and the error in $\Delta\alpha$ is estimated to be ±0.34 for the variations in molecular weight.

Compounds **2** and **7** were prepared as described in ref. 4, and compounds **33** and **34** as described in ref. 17; compounds **6**, **8**, **12**, **13**, **17**, **20** and **29** were obtained from Aldrich.
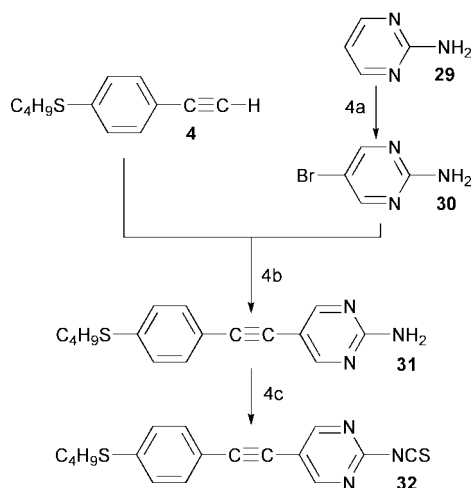
Scheme 4 *Reagents*: 4a, Br$_2$, H$_2$O; 4b, (i) *n*-BuLi, hexanes, ZnCl$_2$, THF, (−10 °C), (ii) Pd(PPh$_3$)$_4$, (reflux); 4c, CSCl$_2$, CaCO$_3$.

1-Butylsulfanyl-4-(3-hydroxy-3-methylbut-1-ynyl)benzene 3

Prepared by a procedure similar to that reported for compound **8** in ref. 18.

Yield 98%. ^{1}H NMR (CDCl$_3$) δ 0.97 (3H, t), 1.44 (2H, sext), 1.62 (6H, s), 1.63 (2H, quint), 2.34 (1H, s), 2.91 (2H, t), 7.19 (2H, d), 7.30 (2H, d). IR (film) ν_{max}/cm^{-1} 820, 910, 960, 1090, 1160, 1270, 1490, 1590, 2220, 2860, 2920, 2940, 3360. MS *m/z* 248 (M$^+$), 233 (C$_{14}$H$_{17}$OS), 177 (C$_{11}$H$_{13}$S), 57 (C$_4$H$_9$), 43 (100%, C$_3$H$_7$).

4-Butylsulfanylphenylethyne 4

Method A. Prepared by a procedure similar to that reported for compound **10** in ref. 18.

Yield 78%, bp 120–125 °C at 0.2 mmHg. ^{1}H NMR (CDCl$_3$) δ 0.97 (3H, t), 1.50 (2H, sext), 1.71 (2H, quint), 2.97 (2H, t), 3.13 (1H, s), 7.26 (2H, d), 7.42 (2H, d). IR (film) ν_{max}/cm^{-1} 820, 1090, 1380, 1400, 1460, 1480, 1590, 2100, 2880, 2940, 3300. MS *m/z* 190 (M$^+$), 134 (100%, C$_8$H$_6$S), 89 (C$_7$H$_5$), 74 (C$_6$H$_2$).

Method B. Prepared by a procedure similar to that reported for compound **32** in ref. 17.

Yield 100%.

3-(4-Butylsulfanylphenyl)propiolic acid 5

Prepared by a procedure similar to that reported for compound **12** in ref. 18.

Yield 70%, mp 112–114 °C. ^{1}H NMR (CDCl$_3$) δ 0.59 (3H, t), 1.47 (2H, sext), 1.67 (2H, quint), 2.96 (2H, t), 7.24 (2H, d), 7.50 (2H, d), 10.54 (1H, s). IR (KBr) ν_{max}/cm^{-1} 760, 820, 920, 1010, 1090, 1130, 1210, 1300, 1400, 1490, 1660, 2180, 2220, 2860, 2920, 2960. MS *m/z* 234 (M$^+$), 190 (C$_{12}$H$_{14}$S), 178 (100%, C$_{11}$H$_{14}$S), 89 (C$_7$H$_5$).

4-Cyanophenyl 3-(4-butylsulfanylphenyl)propiolate 9

Prepared by a procedure similar to that reported for compound **7** in ref. 4.

Yield 65%. Transitions (°C) Cryst 78.4 (N 28) Iso liq. ^{1}H NMR (CDCl$_3$) δ 0.59 (3H, t), 1.50 (2H, sext), 1.54 (2H, quint), 2.59 (2H, t), 7.27 (2H, d), 7.34 (2H, d), 7.53 (2H, d), 7.72 (2H, d). IR (KBr) ν_{max}/cm^{-1} 840, 860, 930, 1080, 1140, 1170, 1200, 1290, 1490, 1500, 1580, 1600, 1720, 2200, 2220, 2860, 2920, 2960. λ_{max}/nm (ε/l mol^{-1} cm^{-1}; cyclohexane) 197 (44 260), 230 (13 878), 332 (24 573). MS *m/z* 335 (M$^+$), 291 (C$_{17}$H$_9$NO$_2$S), 217 (100%, C$_{13}$H$_{13}$OS), 165 (C$_{10}$H$_{13}$S). Calc. for C$_{20}$H$_{17}$NO$_2$S: C, 71.62; H, 5.11; N, 4.18. Found: C, 71.56; H, 4.95; N, 4.17%.

Optical properties and calculated parameters. At T/T_{N-I} = 0.7815: $n_\parallel$ = 1.94, $n_\perp$ = 1.57, Δn = 0.37, $\Delta\alpha$ = 27.07, S = 0.79.

At 25 °C: $n_\parallel$ = 1.83, $n_\perp$ = 1.54, Δn = 0.29, $\Delta\alpha$ = 25.32, S = 0.67.

4-Isothiocyanatophenyl 3-(4-butylsulfanylphenyl)propiolate 10

Prepared by a procedure similar to that reported for compound **7** in ref. 4.

Yield 64%. Transitions (°C) Cryst 75.7 (N 34) Iso liq. ^{1}H NMR (CDCl$_3$) δ 0.59 (3H, t), 1.50 (2H, sext), 1.54 (2H, quint), 2.59 (2H, t), 7.04 (2H, d), 7.05 (2H, d), 7.05 (2H, d), 7.51 (2H, d). IR (KBr) v_{max}/cm^{-1} 820, 850, 930, 1080, 1140, 1160, 1190, 1290, 1490, 1580, 1710, 2020, 2200, 2220, 2860, 2920, 2960. λ_{max}/nm (ε/l mol^{-1} cm^{-1}; cyclohexane) 204 (66 570), 222 (38 961), 292 (21 814), 317 (28 421), 329 (33 036). MS m/z 367 (M$^+$), 217 (100%, C$_{13}$H$_{13}$OS), 161 (C$_9$H$_5$OS). Calc. for C$_{20}$H$_{17}$NO$_2$S$_2$: C, 65.36; H, 4.66; N, 3.81. Found: C, 65.90; H, 4.71; N, 3.78%.

Optical properties and calculated parameters. At $T/T_{N-I} = 0.7815$: $n_\parallel = 2.01$, $n_\perp = 1.58$, $\Delta n = 0.43$, $\Delta\alpha = 38.59$, $S = 0.69$.
At 25 °C: $n_\parallel = 1.90$, $n_\perp = 1.56$, $\Delta n = 0.34$, $\Delta\alpha = 36.37$, $S = 0.60$.

1-Butylsulfanyl-4-(trimethylsilylethynyl)benzene 11

Prepared by a procedure similar to that reported for compound **31** in ref. 17.

Yield 69%. ^{1}H NMR (CDCl$_3$) δ 0.17 (9H, s), 0.85 (3H, t), 1.37 (2H, sext), 1.56 (2H, quint), 2.84 (2H, t), 7.13 (2H, d), 7.30 (2H, d). IR (film) v_{max}/cm^{-1} 680, 760, 820, 840, 1010, 1090, 1220, 1250, 1490, 1595, 2160, 2930, 2970. MS m/z 262 (M$^+$), 247 (100%), 190, 115, 73.

1-(4-Butylsulfanylphenyl)-2-(4-cyanophenyl)ethyne 14

Prepared by a procedure similar to that reported for compound **11** in ref. 19.

Yield 31%. Transitions (°C) Cryst 80.3 (N 53.3) Iso liq. ^{1}H NMR (CDCl$_3$) δ 0.94 (3H, t), 1.47 (2H, sext), 1.67 (2H, quint), 2.96 (2H, t), 7.26 (2H, d), 7.43 (2H, d), 7.58 (2H, d), 7.64 (2H, d). IR (KBr) v_{max}/cm^{-1} 825, 840, 1015, 1090, 1400, 1505, 1590, 2220, 2230, 2870, 2940, 2960. UV λ_{max}/nm (ε/l mol^{-1} cm^{-1}; cyclohexane) 208 (16 600), 238 (16 800), 326 (22 900). MS m/z 291 (M$^+$, 100%), 235, 190, 57, 45.

Optical properties and calculated parameters. At $T/T_{N-I} = 0.7815$: $n_\parallel = 1.90$, $n_\perp = 1.56$, $\Delta n = 0.34$, $\Delta\alpha = 27.14$, $S = 0.62$.
At 25 °C: $n_\parallel = 1.83$, $n_\perp = 1.54$, $\Delta n = 0.29$, $\Delta\alpha = 26.10$, $S = 0.56$.

1-(4-Aminophenyl)-2-(4-butylsulfanylphenyl)ethyne 15

Compound **15** was prepared in a similar way to that described for the preparation of compound **14**.
Yield 67%.

1-(4-Butylsulfanylphenyl)-2-(4-isothiocyanatophenyl)ethyne 16

Prepared by a procedure similar to that reported for compound **10** in ref. 3.

Yield 42%. Transitions (°C) Cryst 84.8 B 85.4 [N 65] Iso liq. ^{1}H NMR (CDCl$_3$) δ 0.94 (3H, t), 1.47 (2H, sext), 1.66 (2H, quint), 2.95 (2H, t), 7.20 (2H, d), 7.25 (2H, d), 7.41 (2H, d), 7.48 (2H, d). IR (KBr) v_{max}/cm^{-1} 820, 840, 1090, 1400, 1500, 1600, 2110, 2190, 2920, 2960. UV λ_{max}/nm (ε/l mol^{-1} cm^{-1}; cyclohexane) 202 (46 000), 219 (30 320), 329 (49 860), 349 (37 780). MS m/z 323 (M$^+$, 100%), 266, 228, 207, 165.

Optical properties and calculated parameters. At $T/T_{N-I} = 0.7815$: $n_\parallel = 2.08$, $n_\perp = 1.58$, $\Delta n = 0.50$, $\Delta\alpha = 45.16$, $S = 0.61$.
At 25 °C: $n_\parallel = 2.05$, $n_\perp = 1.56$, $\Delta n = 0.49$, $\Delta\alpha = 44.18$, $S = 0.61$.

4-Bromophenylacetyl chloride 18

A solution of oxalyl chloride (23.62 g, 0.186 mol) in dry benzene (50 cm^3) was added dropwise to a stirred solution of 4-bromophenylacetic acid (**17**) (20.0 g, 0.093 mol) and dry dimethylformamide (35 drops) in dry benzene (500 cm^3) at room temperature. The mixture was stirred at room temperature overnight and the excess of oxalyl chloride and benzene was removed *in vacuo* to give a red liquid which was used in the

next step without purification. Yield 23.16 g (quantitative). ^{1}H NMR (CDCl$_3$) δ 4.10 (2H, s), 7.15 (2H, d), 7.52 (2H, d). IR (film) v_{max}/cm^{-1} 800, 850, 960, 1010, 1405, 1485, 1795, 2340, 2920. MS m/z 238,236 (M$^+$), 171,169 (100%), 91,89.

Butylsulfanylbenzene 19

Compound **19** was prepared in a similar way to that described for the preparation of compound **2**.

Yield 98%, bp 100–110 °C at 12 mmHg. ^{1}H NMR (CDCl$_3$) δ 0.94 (3H, t), 1.47 (2H, sext), 1.67 (2H, quint), 2.96 (2H, t), 7.36 (2H, dd), 7.47 (1H, tt), 7.61 (2H, dd).

4-Butylsulfanyl-α-(4′-bromophenyl)acetophenone 21

Compound **18** (10.0 g, 0.042 mol) was added dropwise to a stirred, cooled (0 °C) mixture of compound **19** (7.60 g, 0.046 mol) and aluminium chloride (6.10 g, 0.046 mol) at 0 °C. The reaction mixture was maintained under these conditions for 1 h and was heated at 70 to 80 °C for 2 h and added to hydrochloric acid (18%, 50 cm^3). The product was extracted into dichloromethane (2 × 75 cm^3), washed with water (75 cm^3) and dried (MgSO$_4$). The solvent was removed *in vacuo* and the crude product was recrystallised from ethanol to afford colourless needles which were dried *in vacuo* (P$_2$O$_5$). Yield 9.74 g (64%), mp 136–137 °C. ^{1}H NMR (CDCl$_3$) δ 0.95 (3H, t), 1.50 (2H, sext), 1.69 (2H, quint), 3.00 (2H, t), 4.18 (2H, s), 7.14 (2H, d), 7.26 (2H, d), 7.45 (2H, d), 7.89 (2H, d). IR (KBr) v_{max}/cm^{-1} 805, 815, 995, 1010, 1090, 1200, 1210, 1330, 1585, 1740, 2920, 2960. MS m/z 364,362 (M$^+$), 193 (100%), 137, 109.

4-Pentyl-α-(4′-bromophenyl)acetophenone 22

Compound **22** was prepared in a similar way to that described for the preparation of compound **21**.

Yield 65%, mp 125–126 °C. ^{1}H NMR (CDCl$_3$) δ 0.90 (3H, t), 1.34 (4H, m), 1.63 (2H, quint), 2.64 (2H, t), 4.23 (2H, s), 7.13 (2H, d), 7.30 (2H, d), 7.44 (2H, d), 7.91 (2H, d). IR (KBr) v_{max}/cm^{-1} 805, 1220, 1330, 1410, 1485, 1605, 1675, 2860, 2930, 2950. MS m/z 346,344 (M$^+$), 175,177 (100%), 120,118.

2-(4-Bromophenyl)-1-(4-butylsulfanylphenyl)ethanol 23

A solution of compound **21** (6.0 g, 0.017 mol) in dry THF (75 cm^3) was added dropwise to a stirred mixture of lithium aluminium hydride (0.54 g, 0.014 mol) in dry THF (100 cm^3) under dry nitrogen at room temperature. The reaction mixture was stirred at 55 °C for 3 h and the excess of the reducing agent was destroyed by the careful addition of water (18 cm^3) followed by concentrated hydrochloric acid (11 cm^3). The product was extracted into ether (2 × 200 cm^3), washed with water (400 cm^3) and dried (MgSO$_4$). The solvent was removed *in vacuo* to afford a white solid which was used in the next step without purification. Yield 6.70 g (quantitative), mp 58–59 °C. ^{1}H NMR (CDCl$_3$) δ 0.92 (3H, t), 1.46 (2H, sext), 1.62 (2H, quint), 1.98 (1H, s), 2.92 (2H, t), 2.93 (2H, d), 4.81 (1H, t), 7.02 (2H, d), 7.23 (2H, d), 7.28 (2H, d), 7.40 (2H, d). IR (KBr) v_{max}/cm^{-1} 800, 830, 1010, 1050, 1070, 1400, 1480, 2920, 2950, 3100–3600. MS m/z 366,364 (M$^+$), 195,193 (100%), 139.

2-(4-Bromophenyl)-1-(4-pentylphenyl)ethanol 24

Compound **24** was prepared in a similar way to that described for the preparation of compound **23**.

Yield quantitative, mp 59–60 °C. ^{1}H NMR (CDCl$_3$) δ 0.91 (3H, t), 1.35 (4H, m), 1.63 (2H, quint), 1.94 (1H, s), 2.61 (2H, t), 2.97 (2H, d), 4.84 (1H, t), 7.06 (2H, d), 7.16 (2H, d), 7.25 (2H, d), 7.41 (2H, d). IR (KBr) v_{max}/cm^{-1} 815, 1010, 1070, 1400, 1485, 1510, 2920, 2950, 3120–3600. MS m/z 348, 346 (M$^+$), 177, 175 (100%), 91.

(E)-4-Bromo-4′-butylsulfanylstilbene 25

A solution of compound 23 (6.48 g, 0.018 mol) in formic acid (98%, 100 cm^3) was heated under reflux with stirring for 5 h (GLC and TLC analysis revealed a complete reaction). The cooled reaction mixture was added to water (200 cm^3) and the product was filtered off and washed well with water. The product was recrystallised from ethanol–ethyl acctate 1:1 to afford colourless crystals which were dried *in vacuo* (P$_2$O$_5$). Yield 4.02 g (64%). Transitions (°C) Cryst 149.5 [N 134] Iso liq. ^{1}H NMR (CDCl$_3$) δ 0.93 (3H, t), 1.46 (2H, sext), 1.65 (2H, quint), 2.94 (2H, t), 6.98 (1H, d), 7.06 (1H, d), 7.29 (2H, d), 7.36 (2H, d), 7.41 (2H, d), 7.47 (2H, d). IR (KBr) v_{max}/cm^{-1} 525, 820, 970, l005, 1070, 1405, 1490, 1590, 2920, 2960. λ_{max}/nm (ε/l mol^{-1} cm^{-1}; cyclohexane) 206 (19 930), 235 (11 760), 338 (36 400). MS *m/z* 348,346 (M$^+$,100%), 292,290, 177.

Optical properties and calculated parameters. At $T/T_{N\text{-}I} =$ 0.7815: $n_\parallel = 1.87$, $n_\perp = 1.53$, $\Delta n = 0.34$, $\Delta\alpha = 36.27$, $S = 0.58$.
At 25 °C: $n_\parallel = 1.93$, $n_\perp = 1.54$, $\Delta n = 0.40$, $\Delta\alpha = 35.85$, $S = 0.66$.

(E)-4-Bromo-4′-pentylstilbene 26

Compound 26 was prepared in a similar way to that described for the preparation of compound 25.

Yield 68%. Transitions (°C) Cryst 149.2 B 151.1 [N 110] Iso liq. ^{1}H NMR (CDCl$_3$) δ 0.89 (3H, t), 1.32 (4H, m), 1.62 (2H, quint), 2.61 (2H, t), 6.98 (1H, d), 7.08 (1H, d), 7.17 (2H, d), 7.36 (2H, d), 7.42 (2H, d), 7.47 (2H, d). IR (KBr) v_{max}/cm^{-1} 530, 820, 970, 1070, 1505, 1630, 1740, 2850, 2920. λ_{max}/nm (ε/l mol^{-1} cm^{-1}; cyclohexane) 207 (19 180), 232 (14 685), 306 (34 040), 320 (34 310). MS *m/z* 330,328 (M$^+$,100%), 272,270, 191,189.

Optical properties and calculated parameters. At $T/T_{N\text{-}I} =$ 0.7815: $n_\parallel = 1.83$, $n_\perp = 1.53$, $\Delta n = 0.30$, $\Delta\alpha = 25.90$, $S = 0.68$.
At 25 °C: $n_\parallel = 1.82$, $n_\perp = 1.53$, $\Delta n = 0.29$, $\Delta\alpha = 24.75$, $S = 0.67$.

(E)-4-Butylsulfanyl-4′-cyanostilbene 27

Prepared by a procedure similar to that reported for compound 19 in ref. 19.

Yield 36%. Transitions (°C) Cryst 96.7 (N 90.7) Iso liq. ^{1}H NMR (CDCl$_3$) δ 0.94 (3H, t), 1.47 (2H, sext), 1.67 (2H, quint), 2.96 (2H, t), 7.04 (1H, d), 7.17 (1H, d), 7.30 (2H, d), 7.44 (2H, d), 7.56 (2H, d), 7.63 (2H, d). IR (KBr) v_{max}/cm^{-1} 825, 970, 1090, 1485, 1635, 1650, 2220, 2330, 2920, 2960. λ_{max}/nm (ε/l mol^{-1} cm^{-1}; cyclohexane) 206 (21 660), 243 (11 120), 346 (35 280). MS *m/z* 293 (M$^+$,100%), 237, 204, 190, 116.

Optical properties and calculated parameters. At $T/T_{N\text{-}I} =$ 0.7815: $n_\parallel = 2.00$, $n_\perp = 1.56$, $\Delta n = 0.44$, $\Delta\alpha = 35.72$, $S = 0.64$.
At 25 °C: $n_\parallel = 1.97$, $n_\perp = 1.55$, $\Delta n = 0.42$, $\Delta\alpha = 33.53$, $S = 0.64$.

(E)-4-Cyano-4′-pentylstilbene 28

Compound 28 was prepared in a similar way to that described for the preparation of compound 27.

Yield 93%. Transitions (°C) Cryst 57.1 N 102.8 Iso liq (lit.[20] Cryst 55.1 N 101.0 Iso liq). ^{1}H NMR (CDCl$_3$) δ 0.90 (3H, t), 1.32 (4H, m), 1.62 (2H, quint), 2.62 (2H, t), 7.04 (1H, d), 7.20 (2H, d), 7.21 (1H, d), 7.56 (2H, d), 7.63 (2H, d), 7.45 (2H, d). IR (KBr) v_{max}/cm^{-1} 830, 970, 1070, 1410, 1505, 1595, 2220, 2860, 2920. λ_{max}/nm (ε/l mol^{-1} cm^{-1}; cyclohexane) 208 (13 910), 236 (13 550), 292 (15 550). MS *m/z* 275 (M$^+$), 218 (100%), 203, 189, 91.

Optical properties and calculated parameters. At $T/T_{N\text{-}I} = 0.7815$: $n_\parallel = 1.93$, $n_\perp = 1.54$, $\Delta n = 0.39$, $\Delta\alpha = 24.02$, $S = 0.79$.
At 25 °C: $n_\parallel = 1.87$, $n_\perp = 1.52$, $\Delta n = 0.35$, $\Delta\alpha = 22.13$, $S = 0.75$.

2-Amino-5-bromopyrimidine 30

Bromine (18.6 g, 0.116 mol) was added dropwise to a stirred, cooled solution of compound 29 (10.0 g, 0.105 mol) in water (100 cm^3) at room temperature. The mixture was stirred at room temperature for 2 h; the resulting precipitate was filtered off and recrystallised (ethanol) to give yellow/grey plates that were dried *in vacuo* (P$_2$O$_5$). Yield 7.6 g (42%), mp 246–248 °C (lit.[21] 242–244 °C). ^{1}H NMR (DMSO-d_6) δ 7.55 (2H, s), 8.60 (2H, s). IR (KBr) v_{max}/cm^{-1} 680, 880, 1360, 1685, 3100. MS *m/z* 175,173 (M$^+$), 94 (100%, C$_4$H$_4$N$_3$).

1-(2-Aminopyrimidin-5-yl)-2-(4-butylsulfanylphenyl)ethyne 31

Compound 31 was prepared in a similar way to that described for the preparation of compound 14.
Yield 59%.

1-(4-Butylsulfanylphenyl)-2-(2-isothiocyanatopyrimidin-5-yl)ethyne 32

Prepared by a procedure similar to that reported for compound 10 in ref. 3.

Yield 43%. Transitions (°C) Cryst 107.3 [N 3] Iso liq. ^{1}H NMR (CDCl$_3$) δ 0.95 (3H, t), 1.48 (2H, sext), 1.68 (2H, quint), 2.98 (2H, t), 7.28 (2H, d), 7.45 (2H, d), 8.74 (2H, s). IR (KBr) v_{max}/cm^{-1} 760, 810, 1090, 1170, 1400, 1480, 1540, 1580, 2200, 2920, 2960. λ_{max}/nm (ε/l mol^{-1} cm^{-1}; cyclohexane) 194 (32 597), 270 (19 757), 327 (29 635), 349 (26 728). MS *m/z* 325 (M$^+$,100%), 268 (C$_{13}$H$_6$N$_3$S$_2$), 236 (C$_{13}$H$_6$N$_3$S), 57 (C$_4$H$_9$). Calc. for C$_{17}$H$_{15}$N$_3$S$_2$: C, 62.74; H, 4.65; N, 12.91. Found: C, 62.68; H, 4.67; N, 12.86%.

Optical properties and calculated parameters. At $T/T_{N\text{-}I} = 0.7815$: $n_\parallel = 1.90$, $n_\perp = 1.62$, $\Delta n = 0.28$, $\Delta\alpha = 13.01$, $S = 0.59$.
At 25 °C: $n_\parallel = 1.76$, $n_\perp = 1.53$, $\Delta n = 0.23$, $\Delta\alpha = 11.35$, $S = 0.97$.

3-(4-Butoxyphenyl)propiolic acid 35

Prepared by a procedure similar to that reported for compound 5.

Yield 70%, mp 130–131 °C. ^{1}H NMR (CDCl$_3$) δ 0.98 (3H, t), 1.42–1.57 (2H, m), 1.72–1.84 (2H, m), 4.00 (2H, t), 6.89 (2H, d), 7.55 (2H, d), the acid proton was not detected. IR (KBr) v_{max}/cm^{-1} 830, 1170, 1210, 1255, 1600, 1675, 2195, 2400–3400. MS *m/z* 218 (M$^+$), 162, 134, 118, 58 (100%).

4-Cyanophenyl 3-(4-butoxyphenyl)propiolate 36

Compound 36 was prepared in a similar way to that described for the preparation of compound 9.

Yield 38%. Transitions (°C) Cryst 80.4 (N 69.6) Iso liq. ^{1}H NMR (CDCl$_3$) δ 0.99 (3H, t), 1.42–1.58 (2H, m), 1.73–1.85 (2H, m), 4.01 (2H, t), 6.91 (2H, d), 7.34 (2H, d), 7.58 (2H, d), 7.73 (2H, d). IR (KBr) v_{max}/cm^{-1} 830, 1140, 1210, 1260, 1510, 1607, 1722, 2203 cm^{-1}. MS *m/z* 319 (M$^+$), 201 (100%), 145, 58.

Results and discussion

Transition temperatures

The transition temperatures of the new compounds and related compounds are given in Table 1. Only two of the compounds in Table 1 (compounds 28 and 37) show enantiotropic nematic phases and, of the others, seven show monotropic phases and six of the values are from virtual determinations (see Experimental section). Compounds 37–40 are the parent compounds which provide the reference values on which to judge the effect of using various linking units. For the compounds with C$_4$H$_9$S- and -NCS terminal groups relative to the parent biphenyl compound 40 ($T_{N\text{-}I}$ 44 °C), the -COO- (compound 42) and -C≡C- (compound 16) linking groups give

Table 1 Transition temperatures (°C) of compounds with 4-butylsulfanylphenyl and 4-cyano- or 4-isothiocyanato-phenyl units connected by various linking groups, and related reference compounds[a]

Compound	Structure	Cryst	E	B	N	Iso liq
9	C$_4$H$_9$S–C$_6$H$_4$–C≡C–COO–C$_6$H$_4$–CN	• 78.4	—	—	(• 28)	•
10	C$_4$H$_9$S–C$_6$H$_4$–C≡C–COO–C$_6$H$_4$–NCS	• 75.7	—	—	(• 34)	•
14	C$_4$H$_9$S–C$_6$H$_4$–C≡C–C$_6$H$_4$–CN	• 80.3	—	—	(• 53.3)	•
16	C$_4$H$_9$S–C$_6$H$_4$–C≡C–C$_6$H$_4$–NCS	• 84.8	—	• 85.4	[• 65]	•
25	C$_4$H$_9$S–C$_6$H$_4$–CH=CH–C$_6$H$_4$–Br	• 149.5	—	—	[• 134]	•
26	C$_5$H$_{11}$–C$_6$H$_4$–CH=CH–C$_6$H$_4$–Br	• 149.2	—	• 151.1	[• 110]	•
27	C$_4$H$_9$S–C$_6$H$_4$–CH=CH–C$_6$H$_4$–CN	• 96.7	—	—	(• 90.7)	•
28	C$_5$H$_{11}$–C$_6$H$_4$–CH=CH–C$_6$H$_4$–CN	• 57.1	—	—	• 102.8	•
32	C$_4$H$_9$S–C$_6$H$_4$–C≡C–(pyrimidine)–NCS	• 107.3	—	—	[• 3]	•
37[24]	C$_5$H$_{11}$–C$_6$H$_4$–C$_6$H$_4$–CN	• 24.0	—	—	• 35.3	•
38[3]	C$_5$H$_{11}$–C$_6$H$_4$–C$_6$H$_4$–NCS	• 53.5	• 74.5	—	[• 43]	•
39[5,6]	C$_4$H$_9$S–C$_6$H$_4$–C$_6$H$_4$–CN	• 64.8	—	—	(• 35.5)	•
40[3]	C$_4$H$_9$S–C$_6$H$_4$–C$_6$H$_4$–NCS	• 78.4	—	• 78.6	[• 44]	•
41[4]	C$_4$H$_9$S–C$_6$H$_4$–COO–C$_6$H$_4$–CN	• 82.2	—	—	(• 56.3)	•
42[4]	C$_4$H$_9$S–C$_6$H$_4$–COO–C$_6$H$_4$–NCS	• 75.2	—	—	(• 54.1)	•

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

higher T_{N-I} values (54.1 and 65 °C respectively), but the combined -C≡C-COO- link (compound **10**) gives a lower value (34 °C). The parallel result is seen for the C$_4$H$_9$S- and -CN compounds, where the parent biphenyl (**39**) value of 35.5 °C is increased to 56.3 and 53.3 °C by the -COO- (**41**) and -C≡C- (**14**) links respectively, but the -C≡C-COO- link (**9**) causes a lower value of 28 °C. The -CH=CH- link is clearly the most effective unit with respect to mesogenicity and raises T_{N-I} values to 90.7 (**27**) from 35.5 °C (**39**) and to 102.8 (**28**) from 35.3 °C (**37**).

One would expect that the presence of the ethynyl and ester linking groups together would give a longer and more polarisable region in the molecule, and that this should lead to enhanced T_{N-I} values compared to those for the compounds with either unit used separately or for the compounds with a single bond as the link. It is therefore surprising to find that the propiolates **9** and **10** have lower T_{N-I} values than the

compounds which have the two linking groups present independently (*i.e.* the benzoates **41** and **42**, and tolanes **14** and **16** respectively) and the values are even lower than for the parent compounds without any linking group (**39** and **40** respectively). However, a butylsulfanyl terminal group is not commonly used in the design of nematic materials and examples for this terminal unit and other linking groups are not easy to find. In order to check the ranking of various linking groups in their ability to promote nematogenicity in more usual systems, we therefore prepared the butoxy compound **36**; the route used is shown in Scheme 5 and the method of preparation illustrates an additional way of obtaining ethynyl compounds to those shown in Schemes 1 and 2. The preparation of compound **36** completes a more extensive range of linking groups and the T_{N-I} values for this series of 4-butoxyphenyl/4-cyanophenyl compounds are given

in Table 2. The value for compound **43** provides the reference point and all the single linking units of ethenyl (**44**), ethynyl (**45**) and carbonyloxy (**46**) give increases in T_{N-I} values of 64.5, 35.5 and 11.6 °C respectively. With two ethenyl (**47**) or two ethynyl (**48**) groups the T_{N-I} values are significantly enhanced from the values for compounds with only one unit present; in fact the presence of the second ethynyl group gives a bigger increase (82.9 °C) than when the first unit is introduced (35.5 °C), but the second ethenyl group gives a smaller increase (46 °C) than for the first double bond (64.5 °C). Comparing the values for the compound with the ethenylcarboxy unit (**49**) and compound **44** shows that adding the carboxy group to the double bond gives a further small increase of 4.5 °C, but for the comparison of the ethynylcarboxy compound (**36**) and compound **45** there is a decrease in T_{N-I} value of 41.4 °C. The clear conclusions to be drawn from these comparisons are that the carbonyloxy linking group is inferior to the ethenyl and ethynyl groups in promoting mesogenicity and the combination of ethynyl and carbonyloxy units is inferior to either group used separately and inferior to the parent system without any linking group; these observations confirm the comments made above for the butylsulfanyl compounds in Table 1.

At first sight it appears strange that propiolate systems have lower clearing points than the parent systems with a single-bond linkage. This reduced level of mesophase stability can be attributed to the fact that there is not a free flow of electrons through the alkynic unit, as might be expected, and it can be justified in the following way. In aryl systems, the most efficient simple linking group for promoting mesogenicity is the -CH=CH- unit, with the -C≡C- and -CO₂- units having similar but inferior efficiencies (see the transition temperatures for compounds **44**, **45**, **46** and **27**, **14**, **41**). This efficiency order can be rationalised on the following basis: (a) the -CH=CH- unit is composed of p-orbitals on sp²-hybridised carbon atoms, which are similar in size and nature to the neighbouring carbon atoms in the aryl rings, and so allow good conjugation and polarisability, (b) the -C≡C- unit is composed of smaller p-orbitals on sp-hybridised carbon atoms which retain the electron density more effectively and reduce the extent of conjugation and polarisability, (c) the -CO₂- unit allows efficient delocalisation in the aryl-carbonyl and the oxygen-aryl regions but also has an opposing effect from the phenol oxygen into the carbonyl group. For the -CH=CH-CO₂- linkage, the high efficiency of the -CH=CH- unit is only improved slightly by the low efficiency of the ester group which is still linked to sp²-hybridised carbon atoms (compounds **49** and **44**). This situation contrasts with that for -C≡C-CO₂- in which the ester group is now acting on a triple bond composed of sp-hybridised carbon atoms; the more compact orbitals of the triple bond resist electron withdrawal by the carbonyl group which therefore remains distinctly localised as C(δ+)–
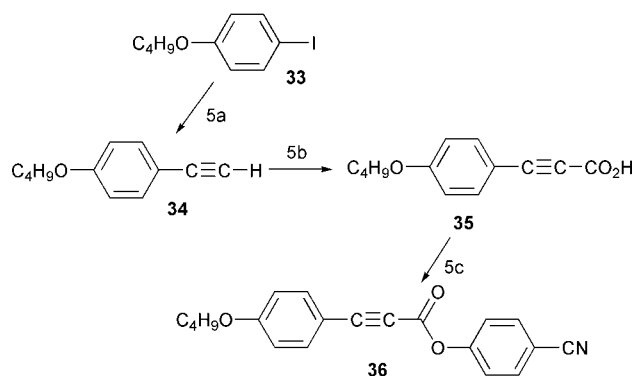
Scheme 5 *Reagents*: 5a, (i) HC≡CLi·H₂NCH₂CH₂NH₂, ZnCl₂, THF, (ii) compound **33**, Pd(PPh₃)₄, THF; 5b, (i) *n*-BuLi, hexanes, THF, (−10 °C), (ii) CO₂(s), Et₂O; (iii) glacial AcOH; 5c, DCC, DMAP, DCM, 4-hydroxybenzonitrile (**8**).

Table 2 Values of T_{N-I} for compounds with various linking groups (X) in the following structure[a]

Compound	Linking group X	T_{N-I} values/°C
43[25]	Single bond	(75.5)
44[26]	*trans* -CH=CH-	140
45[27]	-C≡C-	111
46[28]	-CO₂-	87.1
47[29]	*trans,trans* -CH=CH-CH=CH-	186
48[30]	-C≡C-C≡C-	193.9
49[31]	*trans* -CH=CH-CO₂-	144.5
36	-C≡C-CO₂-	(69.6)

[a]( ) denotes a monotropic transition.

O(δ−). The consequences are that this situation would encourage a greater back-flow of electron density from the phenol oxygen atom (diminishing its delocalisation into the aryl ring) and would give a hard-core dipole in the ester group leading to greater lateral repulsion; both of these effects diminish the efficiency of the propiolate linking group.

The comparison of pentyl and butylsulfanyl groups reveals erratic differences in T_{N-I} values depending on the nature of the rest of the molecule. For the simple cyano and isothiocyanato biphenyls (compare compounds **37**, **38** with **39**, **40** respectively), the pentyl and butylsulfanyl groups give very similar T_{N-I} values which suggests that the effect of the increased polarisability of the butylsulfanyl group may be fortuitously balanced by its increase in size. However, the pentyl compound gives higher T_{N-I} values than butylsulfanyl for the ethenyl linked cyano compounds (**28** and **27**) and lower values for the ethenyl linked bromo compounds (**26** and **25**). Two other notable points on the values of T_{N-I} are that those of the terminal bromo compounds (**25** and **26**) are higher than those of the terminal cyano counterparts (**27** and **28** respectively), and the pyrimidine compound **32** has a much lower T_{N-I} value than the phenyl analogue **16**.

With few exceptions, any modification to molecular structure by introducing a linking group leads to a higher melting point than that of the parent compound. For example, for the C₅H₁₁-/-CN terminal groups, the melting point of the parent compound (**37**) increases from 24.0 to 57.1 °C (**28**), for the C₄H₉S-/-CN terminal groups the increases are from 64.8 (compound **39**) to 78.4 (**9**), 80.3 (**14**), 82.2 (**41**), and 96.7 °C (**27**), and for the C₄H₉S-/-NCS terminal groups the changes are relatively small, from 78.4 (compound **40**) to 84.8 (**16**), 75.2 (**42**) and 75.7 °C (**10**). A plausible contributory factor to the changes in melting points is that the parent biphenyl systems are significantly non-planar because of inter-annular twisting, but the twisting is diminished by the presence of linking groups which allow a greater planarity, better packing and a consequential higher melting point. The overall result of melting point and clearing point changes is that all the compounds with linking groups suffer from relatively high melting points without offering the benefits of particularly good nematogenicity.

Refractive indices, optical anisotropies, polarisabilities and order parameters

The optical properties and related parameters for the novel compounds and known reference compounds are given in Table 3. 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

Table 3 Refractive indices, optical anisotropies, molecular polarisabilities and order parameters for compounds with 4-butylsulfanylphenyl and 4-cyano- or 4-isothiocyanato-phenyl units connected by various linking groups, and related reference compounds, at a reduced temperature (RedT) of $T/T_{N\text{-}I} = 0.7815$ (first line) and at 25 °C (second line)

Compound	Structure		$n_{\parallel}$	$n_{\perp}$	Δn	$\Delta\alpha/10^{-30}\,\mathrm{m^3}$	S
9	C_4H_9S–⬡–C≡C–CO–O–⬡–CN	RedT	1.94	1.57	0.37	27.07	0.79
		25 °C	1.83	1.54	0.29	25.32	0.67
10	C_4H_9S–⬡–C≡C–CO–O–⬡–NCS	RedT	2.01	1.58	0.43	38.59	0.69
		25 °C	1.90	1.56	0.34	36.37	0.60
14	C_4H_9S–⬡–C≡C–⬡–CN	RedT	1.90	1.56	0.34	27.14	0.62
		25 °C	1.83	1.54	0.29	26.10	0.56
16	C_4H_9S–⬡–C≡C–⬡–NCS	RedT	2.08	1.58	0.50	45.16	0.61
		25 °C	2.05	1.56	0.49	44.18	0.61
25	C_4H_9S–⬡–CH=CH–⬡–Br	RedT	1.87	1.53	0.34	36.27	0.58
		25 °C	1.93	1.54	0.40	35.85	0.66
26	C_5H_{11}–⬡–CH=CH–⬡–Br	RedT	1.83	1.53	0.30	25.90	0.68
		25 °C	1.82	1.53	0.29	24.75	0.67
27	C_4H_9S–⬡–CH=CH–⬡–CN	RedT	2.00	1.56	0.44	35.72	0.64
		25 °C	1.97	1.55	0.42	33.53	0.64
28	C_5H_{11}–⬡–CH=CH–⬡–CN	RedT	1.93	1.54	0.39	24.02	0.79
		25 °C	1.87	1.52	0.35	22.13	0.75
32	C_4H_9S–⬡–C≡C–(pyrimidine)–NCS	RedT	1.90	1.62	0.28	13.01	0.59
		25 °C	1.76	1.53	0.23	11.35	0.57
37[24]	C_5H_{11}–⬡–⬡–CN	RedT	1.77	1.52	0.25	15.37	0.71
		25 °C	1.74	1.50	0.24	14.52	0.67
		25 °C[7,a]	1.72	1.53	0.19	23.30	0.55
38[3]	C_5H_{11}–⬡–⬡–NCS	RedT	1.96	1.56	0.41	29.06	0.68
		25 °C	1.86	1.53	0.33	27.29	0.57
39[5,6]	C_4H_9S–⬡–⬡–CN	RedT	1.86	1.56	0.30	20.83	0.67
		25 °C	1.83	1.55	0.28	19.50	0.63
40[3]	C_4H_9S–⬡–⬡–NCS	RedT	1.96	1.56	0.40	32.06	0.63
		25 °C	1.91	1.56	0.36	30.23	0.59
41[4]	C_4H_9S–⬡–CO–O–⬡–CN	RedT	1.80	1.54	0.26	20.05	0.69
		25 °C	1.77	1.52	0.25	19.58	0.68
42[4]	C_4H_9S–⬡–CO–O–⬡–NCS	RedT	1.87	1.55	0.32	28.39	0.67
		25 °C	1.84	1.54	0.30	27.08	0.63

[a] Neat material.

information for a temperature at which the materials may be used; unless otherwise stated, the discussion below concentrates on the reduced temperature values.

The molecular short axes for all the compounds presented have similar dimensions and a general analysis of the results in Table 3 shows that for all the benzene-based systems with a butylsulfanyl terminal group, as a consequence of this similar breadth, the values of $n_{\perp}$ are substantially constant (1.53–1.58). However, there is a much greater variation in the $n_{\parallel}$ values, which range from 1.80–2.08 in response to alterations to the nature of the π-system along the molecular axis, and the changes in $n_{\parallel}$ values are therefore the major factor in determining Δn values; a plot of Δn values against $n_{\parallel}$ shows a close correlation between the two and the only point clearly off the line is for the pyrimidine compound 32 (see Fig. 1). There is also a close relationship between the anisotropy of molecular polarisability ($\Delta\alpha$) and $n_{\parallel}$, but in this case compounds 32 (heterocyclic) and 25 (terminal bromo) lie off the correlation

line. One possible effect of heterocyclic nitrogen atom substitution is neatly illustrated by comparison of the refractive indices for compounds 16 and 32. It appears that the lone pairs of electrons on the nitrogen atoms of 32 give a significant increase in $n_{\perp}$ but greatly reduce $n_{\parallel}$ probably because the more electronegative nitrogen atoms reduce the polarisability of the molecule by localizing the electron density, and the value of 13.01 is by far the lowest value for $\Delta\alpha$ given in Table 3. Heterocyclic nitrogen centres at the 2-position in a biphenyl, as in 2-phenylpyridine or 2-phenylpyrimidine systems, increase Δn values[22] and it may be that this type of nitrogen substitution leads to less interannular twisting and so allows the existence of a more planar core unit,[23] with consequentially increased polarisability. The type of nitrogen substitution in compound 32 does not affect the planarity of the core in this way and the factors referred to above dominate in this situation.

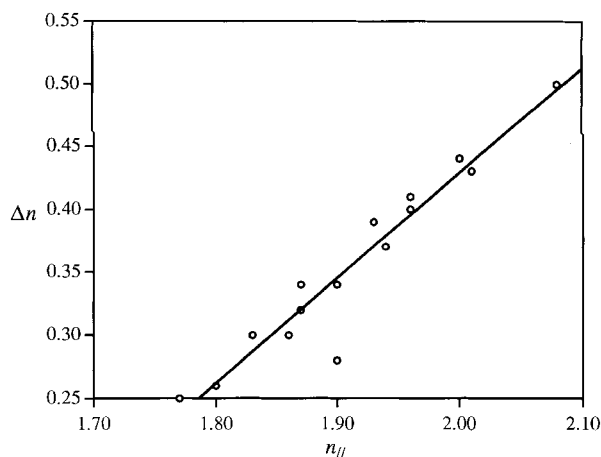Using 39 as the reference point for terminal cyano compounds, the incorporation of a linking unit between the

Fig. 1 A plot of Δn values against $n_{\parallel}$ values (at $T/T_{N-I} = 0.7815$) for the compounds listed in Table 2.

phenyl rings affects the optical anisotropies in the following way; the reference value of 0.30 for compound **39** falls for the ester link (0.26 for **41**), increases slightly for the triple bond (0.34 for **14**) and increases further for the propiolate linking group (0.37 for **9**). None of these changes are large but the highest value of all arises for the compound with an ethenyl link (**27**) which gives a Δn value of 0.44. A similar, but not identical, sequence of changes occurs for the terminal isothiocyanato compounds; in this case the reference parent compound is **40** ($\Delta n = 0.40$) and the ester link gives a reduction to 0.32 (**42**), the triple bond gives the greatest increase to 0.50 (**16**) and the propiolate link gives a more modest increase to 0.43 (**10**). The ethenyl compound (**27**) has a higher polarisability and higher birefringence than the ethynyl compound (**14**), probably because the sp-hybridised carbon atoms of the alkyne more effectively localise the π-electrons in the linking group than do the sp^2-hybridised carbon atoms of the alkene.

The values given in Table 3 for compound **37** from measurements on the neat material at 25 °C[7] differ slightly from the values we report which are obtained by extrapolation from mixtures in a nematic host. The major differences are seen for the $\Delta\alpha$ and S values and it seems likely that extrapolation of measurements from an 'ordering' nematic host lead to higher values of order parameters than those from the neat material although the values of S obtained in this work are internally consistent.

This systematic study of the effect of various common linking groups on mesogenicity and optical parameters allows some general observations to be made, as follows:

(a) modest increases in T_{N-I} values are achieved by introducing -COO- or -C≡C- linking groups, but the -C≡C-COO- unit gives a reduction in T_{N-I};

(b) any of the three linking groups between phenyl rings generally increases melting point;

(c) the values of $n_{\perp}$ change only slightly as the linking unit is altered but the $n_{\parallel}$ values, and consequently the Δn values, are affected more markedly;

(d) the ester linkage decreases, but the ethynyl, ethenyl or propiolate links increase, the Δn values (the most effective unit is the ethenyl link);

(e) heterocyclic nitrogen atoms decrease $n_{\parallel}$ and increase $n_{\perp}$ so that Δn is much reduced;

(f) order parameter values lie in the range 0.61–0.79 for the

non-heterocyclic cyano and isothiocyanato compounds, with the values for -NCS terminal groups being consistently slightly lower than those for the -CN counterparts.

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