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The synthesis and transition temperatures of 2-(4-alkyl- and 4-alkoxy-phenyl)-5-cyano-1-benzofurans and related diaryl-1-benzofurans—an assessment of how deviations from linearity and conformational effects in a core unit affect mesogenicity†‡

Mark R. Friedman, 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. E-mail: K.J.Toyne@chem.hull.ac.uk

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The synthesis and transition temperatures are reported for several 2-(4-alkyl- and 4-alkoxy-phenyl)-5-cyano-1-benzofurans, 2-(4′-alkylbiphenyl-4-yl)-5-cyano- and 5-(4′-alkylbiphenyl-4-yl)-2-cyano-1-benzofurans, and for compounds with other combinations of terminal alkyl and cyano groups in 2,5-disubstituted-1-benzofurans containing two phenyl units; some isolated examples of related cyclohexane systems are also presented. The mesogenic behaviour of these compounds and several intermediates (*e.g.* amides, acids and esters) is discussed and the transition temperatures are rationalised on the following basis (a) 1-benzofuran is a superior core unit to benzene, (b) 2,5-disubstitution in 1-benzofuran gives a bent core which adversely affects mesogenicity, to an extent which depends on its position in the core, (c) antiparallel associations in terminal cyano compounds can eliminate the disadvantage of a bent core structure, (d) 2-aryl-1-benzofurans have negligible inter-annular twist but 5-aryl-1-benzofurans have similar inter-annular twist to that in biphenyls.

The initial suggestion for any new development or application of liquid crystals usually originates from the work of physical scientists who outline the general specifications of the material properties required. Chemists with the appropriate interdisciplinary knowledge may then, in collaboration with physicists, device engineers *etc.*, attempt to propose molecular structures which meet the required specification as closely as possible. In proposing a structure the chemist has to choose what he regards as the most suitable combination of molecular units to achieve as many as possible of the required properties. The variety of factors to consider for a molecular unit is immense, and includes core units, linking groups, terminal groups, lateral groups, length of chains, *etc.* At this point we are conscious of the severe limitations faced in devising suitable molecules and we have to acknowledge the deficiencies in predicting with accuracy how the range of crucial physical properties is revealed by the proposed molecular structure. In general, the prime targets for the physical properties are a specific mesophase type or a mesophase sequence, acceptable mesophase range(s), desirable viscosity (almost without exception, low), dielectric, optical properties *etc.* In some areas, other criteria need to be met; for example, with thermochromic systems, pitch lengths leading to a colour play temperature range or a specific colour may be the aim, or for ferroelectrics/antiferroelectrics, spontaneous polarisations and tilt angles over a working temperature range need to be controlled. There is no hope of achieving an 'ideal' compound (or mixture) because there is always room for improvement—the temperature range can always be greater, the viscosity lower, the switching time shorter, the colour brighter or the colour change sharper or broader. Given the above limitations, it is quite remarkable that in the majority of areas of liquid crystals, adequate materials have been provided for the desired application.

One structural parameter that has not been so extensively examined is how deviations from linearity of a core unit affect mesogenicity and to what extent they can be tolerated before mesogenicity is lost. The problem faced in considering this issue is that it is not possible to control the precise deviation from linearity one wishes to consider because the units of the molecular core only give certain 'quantised' possibilities. When a benzene ring is used as a core unit, for example, 1,4-disubstitution gives linearity, but 1,3- or 1,2-disubstitution give a 60° or 120° deviation respectively from linearity and it is impossible to choose intermediate values. A core system such as indene, 1-benzothiophene or 1-benzofuran allows disubstitution with a greater variety of deviation from linearity. However, the methylene group in indene prevents efficient molecular associations and, although discotic examples have been reported,[1] no calamitic examples have appeared. For 1-benzothiophenes and 1-benzofurans, only a few discotic and calamitic examples have been reported, but our preliminary comparison (see compounds **75** and **78** below) showed that the sulfur system had a significantly higher melting point, which may mask mesophase formation; we therefore chose 1-benzofuran (see Fig. 1) as the core unit for the basis of this study. In this unit there are several positions for disubstitution which are not linear and these allow some judgement to be made on how smaller deviations from linearity than those which arise in benzene systems, affect mesogenicity. X-Ray crystallography of 2-(4-methoxybenzoyl)-1-benzofuran[2] and

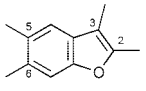
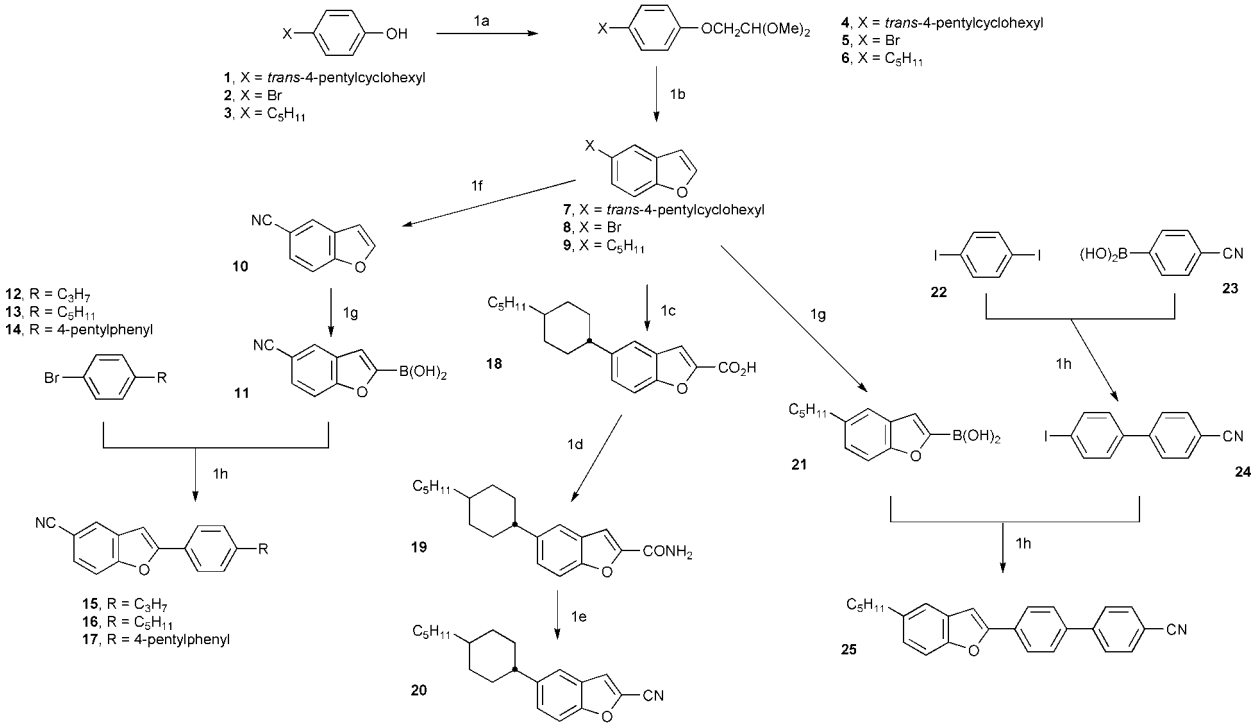


Fig. 1 Deviations from linearity arising from various substitution patterns in 1-benzofuran. Calculated from the X-ray crystallography results given in ref. 2.

†Basis of a presentation given at Materials Discussion No. 4, 11–14 September 2001, Grasmere, UK.
‡Electronic supplementary data information (ESI) available: experimental details for **5**, **6**, **8**, **9**, **21**, **24**, **34**, **36**, **40**, **41**, **47**, **50**, **52**, **54**, **57**, **58**, **61**, **62**, **63**, **64**, **72**, **73** and **74**. For direct electronic access see http://www.rsc.org/suppdata/jm/b1/b102837p/



Scheme 1 1a, $BrCH_2CH(OMe)_2$, K_2CO_3, KI, solvent; 1b, PPA, chlorobenzene; 1c, (i) n-BuLi, THF, (ii) 'Cardice', THF, (iii) AcOH; 1d, (i) thionyl chloride, benzene, (ii) ammonia, THF; 1e, thionyl chloride, DMF; 1f, $CuCN{\cdot}H_2O$, *N*-methylpyrrolidin-2-one; 1g, (i) n-BuLi, THF, (ii) trimethyl borate, (iii) HCl; 1 h, $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O.

subsequent geometrical calculations give the transposed bond angles shown in Fig. 1. The 2,5-example has the smallest deviation from linearity of $\sim 15^\circ$, the 2,6- and 3,6- have similar deviations (approximately 40°) and the 3,5-disubstitution has a severe deviation of almost 90°; the 2,6- and 3,6- cases differ in that in the former case the oxygen atom is on the inside of the bend whereas for the latter case the oxygen is on the outside. Further novel features offered by the 1-benzofuran system are that 6,7-difluoro-substitution gives three electron attracting atoms on the 'edge' of the molecule, and these may be on the exposed, outside (2,5-disubstituted core) or the sheltered, inside (2,6-disubstituted core) of the bent molecule.

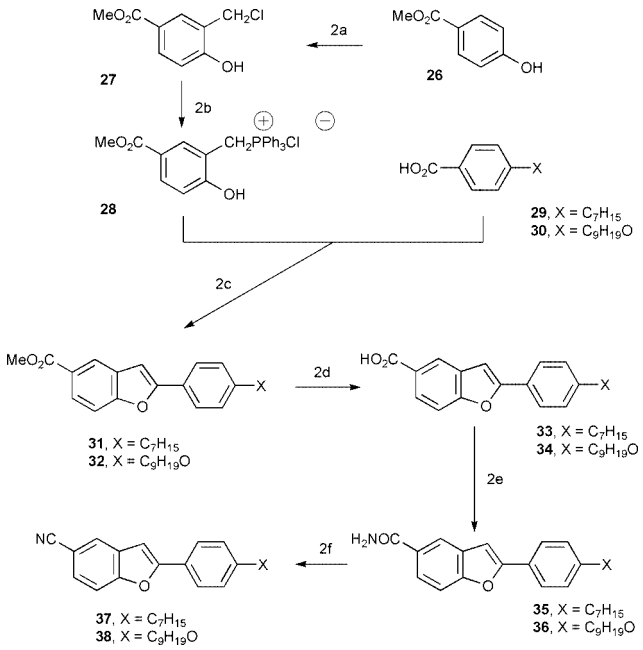
We have begun a series of studies of the different substitution patterns in 1-benzofurans and have started with 2,5-disubstituted compounds. The aims of the investigation are to consider polar (cyano) and non-polar (alkyl, alkoxy) terminal groups with the 1-benzofuran at the centre or side of an extended core unit. We have already reported some results for 5-substituted-2-cyano-1-benzofurans[3] and in this paper we present results for related 5-cyano-2-substituted-1-benzofurans and related compounds and we give some examples to elucidate the effect of altering the position of the benzofuran unit in a core system.

Experimental

The synthetic routes to the compounds reported are shown in Schemes 1–6. In general the compounds are not part of a homologous series but are examples of different core systems and therefore require specific routes, although some features of the syntheses are common. Frequently connections are made between aryl rings by palladium-catalysed cross-coupling of arylboronic acids and an aryl halide [bromide (**15**–**17**, **40**, **43**, **48** and **51**) or iodide (**24**, **25**, **47** and **53**)] or aryl triflate§ (**56**).[4-7] The formation of the benzofuran unit was achieved in three different ways as illustrated for compounds **7**–**9**, **31** and **32**, and **61** respectively. The first method involves the formation of an acetal (**4**–**6**) from a *p*-substituted phenol. Protonation of the acetal generates an acylium ion which cyclises by electrophilic aromatic substitution and gives a good method of synthesis for benzofurans with a 5-substituent, since the cyclisation process gives a single product.[8] The second method was used to synthesise 2-aryl-1-benzofurans with a 5-cyano- or a 5-carboxy group and was developed by Hercouet;[9] the process is effectively an intramolecular Wittig reaction of an ester carbonyl group. The third procedure involves the reaction of a suitably substituted salicylaldehyde with diethyl bromomalonate[10] (see compound **61**, and compound **8** in ref. 3). Lithiation at the 2-position of the benzofuran [either by *n*-butyllithium (**11**, **21** and **41**) or by lithium diisopropylamide (**44**)] allows a 2-boronic acid, a 2-carboxylic acid (**18**) or 2-alkyl derivatives (**49** and **50**) to be created. The route to the thiophene compound (**75**) is based on the preparation of compound **70**[11] (*cf.* compound **8**) and the subsequent steps are similar to those in other schemes.

Confirmation of the structures of intermediates and products was obtained by ^1H NMR spectroscopy (JEOL Lambda 400 or a JEOL JNM-GX270 spectrometer; tetramethylsilane was used as the internal standard for all samples; *J* values are given in Hz), infrared spectroscopy (Perkin-Elmer 457 grating spectrophotometer or a Perkin-Elmer 1000 FT-IR Fourier transform spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 GC/MS spectrometer or a ThermoQuest Finnigan-MAT GCQ ion-trap GC/MS). The progress of reactions was frequently monitored using a Chrompack 9001 capillary gas chromatograph fitted with a WCOT fused silica column (CP-Sil 5 CB 0.12 m, 10 m long 0.25 mm internal diameter), using nitrogen as the carrier gas. Elemental analyses of products were carried out using a Fisons EA 1108 CHN analyzer. Transition temperatures were measured using a Mettler FP52 heating stage and FP5 control unit in conjunction with an Olympus BH2 polarizing microscope and were confirmed using differential scanning calorimetry (Perkin-Elmer 7 Series/Unix DSC with an indium standard and IBM data station). The purities of all final compounds were checked by GLC analysis (see above) and by HPLC analysis (Microsorb C18 80-215-C5 RP column)

§The IUPAC name for triflate is trifluoromethanesulfonate.



Scheme 2 2a, Paraformaldehyde, conc. HCl; 2b, triphenylphosphine, chloroform; 2c, for **31**: (i) DCC, DMAP, DCM, (ii) Et_3N, toluene; for **32**: (i) **30** and thionyl chloride, (ii) Et_3N, toluene; 2d, (i) KOH, EtOH, (ii) aq. HCl; 2e, (i) thionyl chloride, benzene, (ii) ammonia, THF; 2f, thionyl chloride, DMF.

and were found to be >99.5% pure. Flash (pressurised) or gravity column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh) silica gel or Aldrich Brockmann 1 Standard Grade 150 mesh neutral alumina; the eluents were as detailed in the text.

Tetrakis(triphenylphosphine)palladium(0) was prepared according to the literature procedure.[12] Arylboronic acids are difficult to obtain pure because of the possibility of anhydride formation and they were used without purification in the cross-coupling reactions.

Compounds **2**, **22**, **26**, **29**, **30**, **42**, **45**, **60**, **66**, and **68** were obtained from Aldrich, **3** from Lancaster, and **1** was supplied by Merck (Darmstadt). The syntheses of compound **12**, **13**, **14**, **39** and **71** are described in ref. 3 and **23** in ref. 13.

Molecular modelling was carried out using (a) Cerius,[2] Version 3.5, with the Smart minimiser and a UFF parameter set;[14] quantum effects were not included, (b) CS Chem3DStd™ Version 3.5.2.

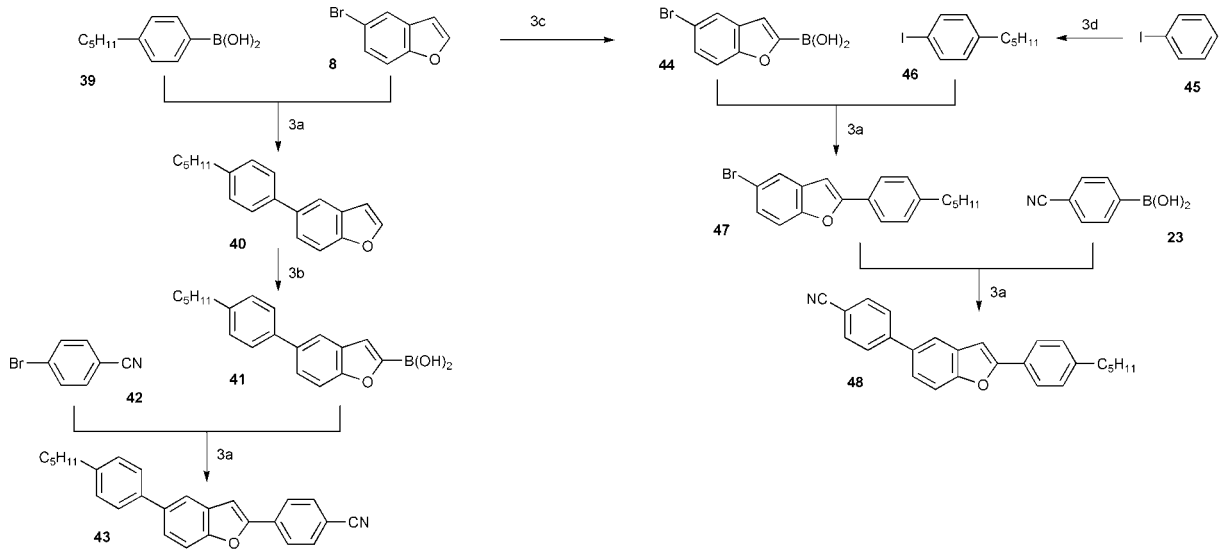
The acronyms used are DCC (*N*,*N*′-dicyclohexylcarbodiimide), DCM (dichloromethane), DMAP (4-dimethylaminopyridine), DME (1,2-dimethoxyethane), DMF (*N*,*N*-dimethylformamide), THF (tetrahydrofuran).

Representative syntheses are given below and other preparations are given as Electronic Supplementary Information.‡

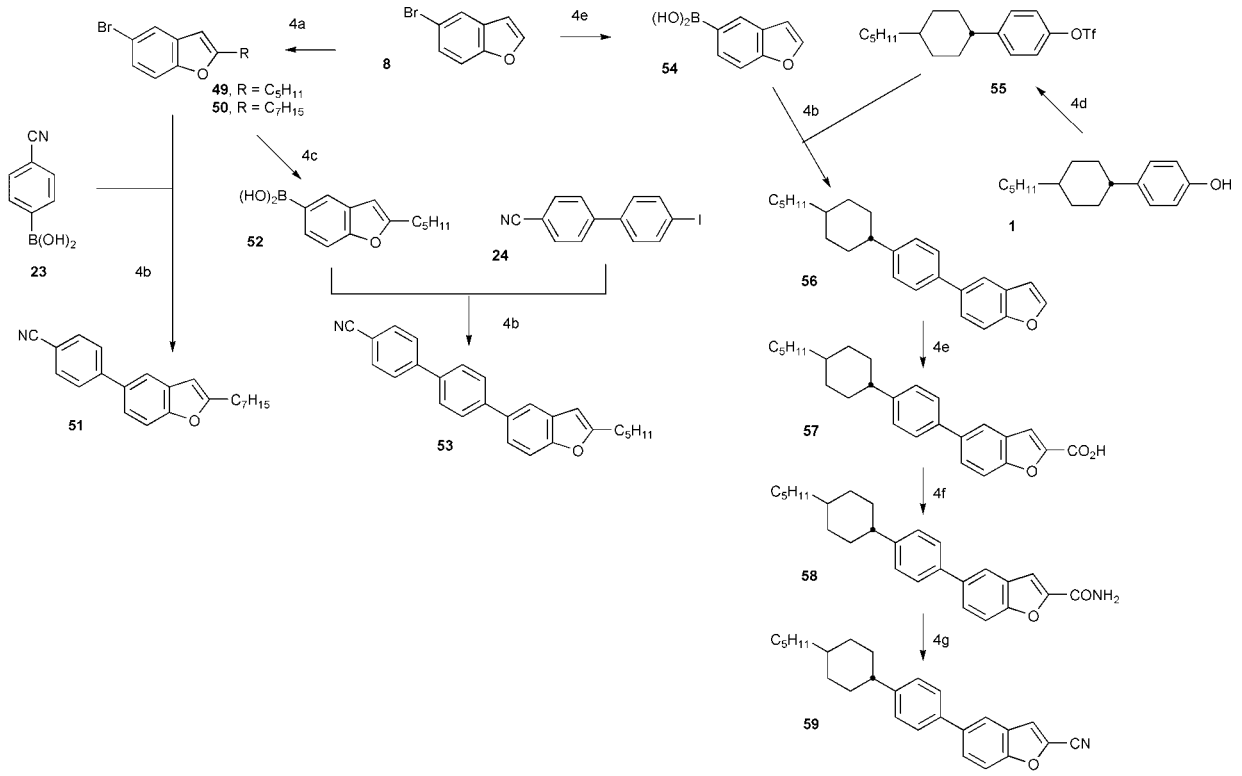
Preparations

2-[4-(*trans*-4-Pentylcyclohexyl)phenoxy]acetaldehyde dimethyl acetal 4. 4-(*trans*-4-Pentylcyclohexyl)phenol (**1**) (10.0 g, 41 mmol), bromoacetaldehyde dimethyl acetal (10.1 g, 60 mmol), potassium carbonate (11.1 g, 80 mmol) and potassium iodide (0.5 g, 3 mmol) in cyclopentanone (60 ml) were heated under reflux under nitrogen with stirring (48 h). The mixture was allowed to cool, poured into water (200 ml) and was washed with ether (2 × 200 ml). The combined organic layers were washed with sodium hydroxide solution (10%), water, dried (Na_2SO_4), and the solvent removed *in vacuo*. The crude product was purified by flash chromatography [neutral alumina, petroleum fraction (bp 40–60 °C)–DCM 1 : 1], followed by distillation. Yield 10.1 g (75%), bp 195 °C at 0.01 mmHg. ^{1}H NMR (CD_2Cl_2) δ: 7.11(2H, d, *J* 8.5), 6.82(2H, d, *J* 8.5), 4.66(1H, t, *J* 5.2), 3.94(2H, d, *J* 5.2), 3.41(6H, s), 2.83–2.80(1H, m), 1.73–1.66(4H, m), 1.45–1.38(1H, m), 1.35–1.20(10H, m), 1.08–1.02(2H, m), 0.89(3H, t, *J* 7.1). IR (KBr) ν_{max}/cm^{-1} 2928, 2860, 1709, 1644, 1514, 1139, 1081, 828. MS *m*/*z*: 334(M^+), 260, 176, 133, 75(100%).

5-(*trans*-4-Pentylcyclohexyl)-1-benzofuran 7. Compound **4** (10.1 g, 31 mmol) was added dropwise to polyphosphoric acid (13.0 g) in chlorobenzene (130 ml) under reflux with stirring and the mixture was heated under reflux overnight. The solvent was removed *in vacuo* and sodium hydroxide solution (10%) (20 ml) and ether (100 ml) were added; the separated aqueous layer was washed with ether (2 × 200 ml) and the combined organic layers washed with water, brine, and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was purified by flash chromatography [silica gel, petroleum fraction (bp 40–60 °C)], followed by distillation. Yield 4.1 g (48%), bp 165 °C at 0.01 mmHg. ^{1}H NMR (CD_2Cl_2) δ: 7.51(1H, d, *J* 2.2), 7.34(1H, d, *J* 2.0), 7.31(1H, d, *J* 8.5), 7.07(1H, dd, *J* 2.0 and 8.5), 6.64(1H, dd, *J* 2.0 and 2.2), 2.48(1H, tt, *J* 3.2 and 12.2), 1.84–1.77(4H, m), 1.44(1H, dd, 3.2 and 12.7), 1.38(1H, dd, *J* 3.2 and 12.7), 1.26–1.14(9H, m),



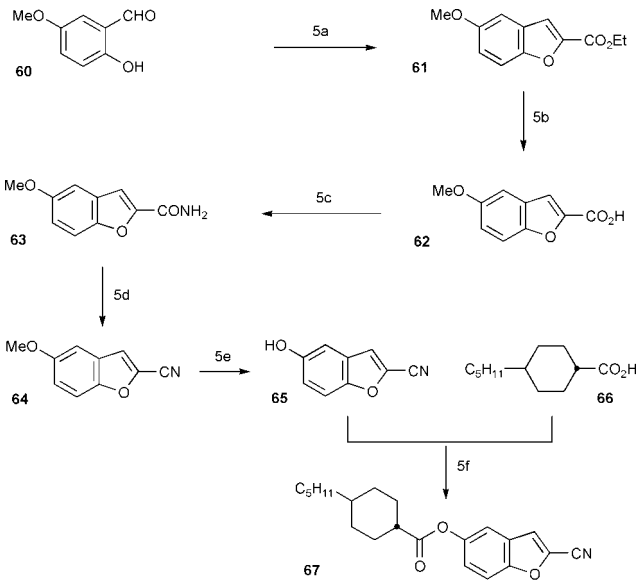
Scheme 3 3a, $Pd(PPh_3)_4$, Na_2CO_3, DME; 3b, (i) n-BuLi, THF, (ii) trimethyl borate, (iii) aq. HCl; 3c, (i) n-BuLi, Pr^i_2NH, THF, (ii) trimethyl borate, (iii) aq. HCl; 3d, (i) pentanoyl chloride, anhydrous $AlCl_3$, DCM, (ii) PMHS.



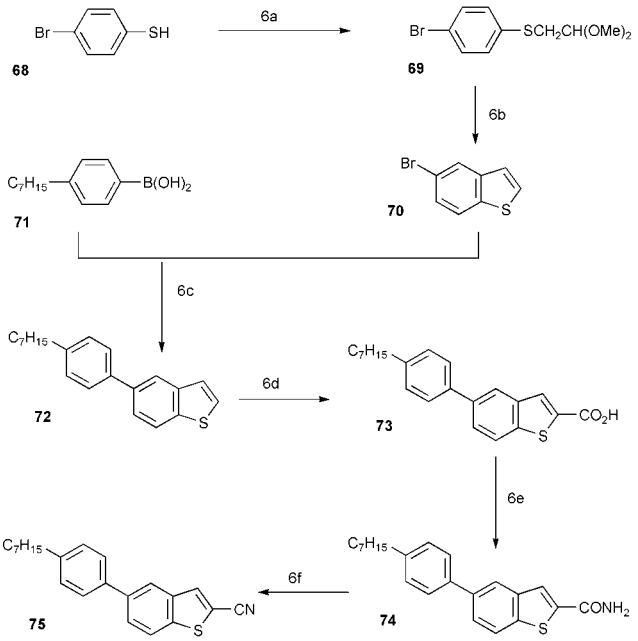
Scheme 4 4a, (i) n-BuLi, Pr^i_2NH, THF, (ii) RI; 4b, $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O; 4c, (i) Mg, THF, (ii) trimethyl borate, (iii) aq. HCl; 4d, Tf_2O, pyridine; 4e, (i) n-BuLi, THF, (ii) 'Cardice', THF, (iii) AcOH; 4f, (i) thionyl chloride, benzene, (ii) ammonia, THF; 4g, thionyl chloride, DMF.

1.02(1H, dd, *J* 4.2 and 13.7), 0.95(1H, dd, *J* 4.2 and 13.7), 0.83(3H, t, *J* 7.0). IR (KBr) ν_{max}/cm^{-1} 2927, 2856, 1514, 1455, 1197, 877, 809, 735. MS *m/z*: 270(M^+), 199, 171, 157(100%), 131.

5-Cyano-1-benzofuran 10. A mixture of compound **8** (20.0 g, 102 mmol) and cuprous cyanide monohydrate (22.0 g, 204 mmol) in *N*-methylpyrrolidin-2-one (700 ml) was heated under reflux (24 h) with stirring. The reaction mixture was allowed to cool and was filtered through a pad of 'Hyflo Supercel'. The filtrate was then poured into water (200 ml) and ether was added (200 ml). The separated aqueous layer was washed with ether (2 × 300 ml) and the combined ethereal layers were washed with water, brine, dried ($MgSO_4$), and the solvent removed *in vacuo*. The residue was recrystallised (cyclohexane). Yield 6.6 g (45%), mp 82–83 °C. ^1H NMR (CD_2Cl_2) δ: 7.98(1H, dd, *J* 1.0 and 1.6), 7.78(1H, d, *J* 2.2), 7.61(1H, d, *J* 8.8), 7.60(1H, dd, *J* 1.6 and 8.8), 6.89(1H, dd, *J* 1.0 and 2.2). IR (KBr) ν_{max}/cm^{-1}: 3150, 2200, 1755, 1600, 1550, 1185, 1010, 885, 760, 610. MS *m/z*: 143(M^+, 100%), 88, 62, 50.



Scheme 5 5a, Diethyl bromomalonate, K_2CO_3, MEK; 5b, (i) KOH, H_2O, EtOH, (ii) aq. HCl; 5c, (i) thionyl chloride, benzene, (ii) ammonia, THF; 5d, thionyl chloride, DMF; 5e, Py·HCl; 5f, (i) DCC, DMAP, DCM.



Scheme 6 6a, NaOEt, $BrCH_2CH(OMe)_2$, EtOH; 6b, PPA, chlorobenzene; 6c, $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O; 6d, (i) n-BuLi, THF, (ii) 'Cardice', THF, (iii) AcOH; 6e, (i) thionyl chloride, benzene, (ii) ammonia, THF; 6f, thionyl chloride, DMF.

5-Cyano-1-benzofuran-2-boronic acid 11. Compound **10** (6.5 g, 45 mmol) in dry THF (150 ml) was degassed and flushed with nitrogen. It was cooled (−90 °C) and *n*-butyllithium (2.5 M in hexanes, 19.1 ml, 48 mmol) was added dropwise with stirring. The mixture was stirred for a further 0.5 h, and trimethyl borate (9.4 g, 90 mmol) was added at −100 °C; the mixture was stirred (20 min), hydrochloric acid (2 M, 137 ml) was added. The mixture was stirred for a further 15 min, allowed to return to room temperature, poured into water (150 ml) and ether was added (150 ml). The separated aqueous layer was washed with ether (2 × 200 ml) and the combined organic layers were washed with water, brine, dried ($MgSO_4$), and the solvent removed *in vacuo*. Yield 7.2 g (86%). MS *m*/*z*: 187(M^+), 160, 145, 117, 43(100%).

5-Cyano-2-(4-propylphenyl)-1-benzofuran 15. Compound **15** was prepared in a similar manner to that described for the preparation of compound **9** in ref. 3. Quantities: compound **12** (1.0 g, 5.0 mmol), compound **11** (1.1 g, 5.9 mmol), sodium carbonate (1.3 g, 13 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3 g, 0.3 mmol), DME (15 ml) and water (15 ml). The product was purified by flash chromatography [neutral alumina, hexane–propionitrile 40 : 1] and recrystallisation (hexane). Yield 0.1 g (8%). Transitions/°C Cryst 98.0 Iso liq. (Found: C, 82.5; H, 5.7; N, 5.4; $C_{18}H_{15}NO$ requires C, 82.7; H, 5.8; N, 5.4%). ^{1}H NMR (CD_2Cl_2) δ: 7.93(1H, dd, *J* 0.7 and 1.7), 7.79(2H, d, *J* 8.1), 7.61(1H, d, *J* 8.6), 7.55(1H, dd, *J* 1.7 and 8.6), 7.31(2H, d, *J* 8.1), 7.06(1H, d, *J* 0.7), 2.65(2H, t, *J* 7.6), 1.68(2H, sextet, *J* 7.6), 0.96(3H, t, *J* 7.6). IR (KBr) ν_{max}/cm^{-1}: 2966, 2225, 1505, 1463, 1118, 818, 794, 738. MS *m*/*z*: 261(M^+), 232(100%), 202, 176, 58.

5-Cyano-2-(4-pentylphenyl)-1-benzofuran 16. Compound **16** was prepared in a similar manner to that described for the preparation of compound **15**. Quantities: compound **13** (1.1 g, 4.8 mmol), compound **11** (1.1 g, 5.9 mmol), sodium carbonate (1.3 g, 13 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3 g, 0.3 mmol), DME (15 ml) and water (15 ml). Yield 0.2 g (14%). Transitions/°C Cryst 99.7 (N 86.5) Iso liq. (Found: C, 82.9; H, 6.7; N, 4.9; $C_{20}H_{19}NO$ requires C, 83.0; H, 6.6; N, 4.8%). ^{1}H NMR (CD_2Cl_2) δ: 7.92(1H, dd, *J* 0.8 and 1.6), 7.89(2H, d, *J* 8.3), 7.61(1H, d, *J* 8.5), 7.55(1H, dd, *J* 1.6 and 8.5), 7.31(2H, d, *J* 8.3), 7.05(1H, d, *J* 0.8), 2.66(2H, t, *J* 7.7), 1.65(2H, quintet, *J* 7.7), 1.35(4H, m), 0.90(3H, t, *J* 7.3). IR (KBr) ν_{max}/cm^{-1}: 2933, 2865, 2224, 1504, 1461, 1185, 1115, 890, 800, 740. MS *m*/*z*: 289(M^+, 100%), 245, 232, 222, 219, 203.

5-Cyano-2-(4′-pentylbiphenyl-4-yl)-1-benzofuran 17. Compound **17** was prepared and purified in a similar manner to that described for the preparation of compound **15**. Quantities: compound **14** (1.5 g, 5.0 mmol), compound **11** (1.5 g, 8.0 mmol), sodium carbonate (1.3 g, 13 mmol), tetrakis(triphenylphosphine)palladium(0) (0.6 g, 0.6 mmol), DME (15 ml) and water (15 ml); the product was recrystallised (ethanol–DCM 5 : 1). Yield 0.3 g (16%). Transitions/°C Cryst 187.1 N 284.2 Iso liq. (Found: C, 85.4; H, 6.3; N, 3.6; $C_{26}H_{23}NO$ requires C, 85.45; H, 6.3; N, 3.8%). ^{1}H NMR (CD_2Cl_2) δ: 7.96(1H, m), 7.95(2H, d, *J* 8.5), 7.73(2H, d, *J* 8.5), 7.63(1H, d, *J* 8.5), 7.58(2H, d, *J* 8.3), 7.56(1H, dd, *J* 1.7 and 8.5), 7.30(2H, d, *J* 8.3), 7.13(1H, d, *J* 0.7), 2.66(2H, t, *J* 7.5), 1.66(2H, quintet, *J* 7.5), 1.36(4H, m), 0.91(3H, t, *J* 7.3). IR (KBr) ν_{max}/cm^{-1}: 2933, 2859, 2229, 1497, 1122, 913, 803, 746. MS *m*/*z*: 365(M^+), 308, 277, 165, 43(100%).

5-(*trans*-4-Pentylcyclohexyl)-1-benzofuran-2-carboxylic acid 18. Compound **7** (1.7 g, 6.3 mmol) in dry THF (70 ml) was flushed with nitrogen, degassed, flushed again with nitrogen and cooled (−70 °C). *n*-Butyllithium (2.5 M in hexanes, 2.7 ml, 6.7 mmol) was then added dropwise with stirring and kept at −70 °C for 0.5 h. The mixture was poured into a stirred slurry of 'Cardice' in dry THF (200 ml), allowed to reach room temperature with continuous stirring, and the solvent was removed *in vacuo*. The residue was dissolved in glacial acetic acid and the resulting solution was poured into water. The solid was filtered off, washed with water and dried *in vacuo* (KOH) to give a white solid. Yield 0.2 g (10%). Transitions/°C Cryst 191.5 N 217.5 Iso liq. ^{1}H NMR (CD_2Cl_2) δ: 7.47(1H, d, *J* 1.7), 7.44(1H, d, *J* 8.8), 7.39(1H, s), 7.27(1H, dd, *J* 1.7 and 8.8), 2.54(1H, tt, *J* 3.4 and 12.0), 1.89–1.83(4H, m), 1.49(1H, dd, *J* 3.2 and 12.7), 1.42(1H, dd, *J* 3.2 and 12.7), 1.31–1.19(9H, m), 1.07(1H, dd, *J* 3.9 and 13.9), 1.10(1H, dd, *J* 3.9 and 13.9), 0.86(3H, t, *J* 7.3); the acidic proton was not detected. IR (KBr) ν_{max}/cm^{-1}: 3100, 2926, 2853, 1692, 1580, 1425, 943, 828. MS *m*/*z*: 314(M^+), 260, 201, 188(100%), 175.

5-(*trans*-4-Pentylcyclohexyl)-1-benzofuran-2-carboxamide 19. Compound **19** was prepared in a similar manner to that described for the preparation of compound **14** in ref. 3. Quantities: compound **18** (0.2 g, 0.6 mmol), thionyl chloride (0.2 g, 1.8 mmol), ammonia (d 0.880, 0.4 ml), dry benzene (7 ml) and dry THF (6 ml). Yield 0.08 g (50%), mp 214–215 °C. ^{1}H NMR (CD_2Cl_2) δ: 7.51(1H, d, *J* 1.7), 7.43(1H, d, *J* 8.8), 7.41(1H, d, *J* 0.8), 7.31(1H, dd, 1.7 and 8.8), 6.51(1H, s, br), 5.69(1H, s, br), 2.59(1H, tt, *J* 3.2 and 12.2), 1.93–1.88(4H, m), 1.55–1.45(2H, m), 1.33–1.21(9H, m), 1.36–1.03(2H, m), 0.90(3H, t, *J* 7.1). IR (KBr) ν_{max}/cm^{-1}: 3424, 3167, 2926, 2854, 1659, 1613, 1449, 1198, 939, 888. MS *m*/*z*: 313(M^+), 200, 187(100%), 115.

2-Cyano-5-(*trans*-4-pentylcyclohexyl)-1-benzofuran 20. Compound **20** was prepared in a similar manner to that described for the preparation of compound **16** in ref. 3. Quantities: compound **19** (0.05 g, 0.2 mmol), thionyl chloride (0.2 g, 1.4 mmol) and dry DMF (1 ml). Yield 0.03 g (60%). Transitions/°C Cryst 77.6 (N 58.5) Iso liq. (Found: C, 81.1; H, 8.3; N, 4.6; $C_{20}H_{25}NO$ requires C, 81.3; H, 8.5; N, 4.7%). ^{1}H NMR (CD_2Cl_2) δ: 7.51(1H, dd, *J* 0.7 and 2.0), 7.47(1H, ddd, *J* 0.7, 0.7 and 8.6), 7.45(1H, d, *J* 0.7), 7.39(1H, dd, *J* 2.0 and 8.6), 2.60(1H, tt, *J* 3.2 and 12.2), 1.93–1.87(4H, m), 1.52–1.43(2H, m), 1.33–1.21(9H, m), 1.14–1.03(2H, m), 0.90(3H, t, *J* 7.3). IR (KBr) ν_{max}/cm^{-1}: 2924, 2852, 2230, 1557, 1465, 1198, 950, 874, 845, 815.

2-(4′-Cyanobiphenyl-4-yl)-5-pentyl-1-benzofuran 25. Compound **25** was prepared in a similar manner to that described for the preparation of compound **39** in ref. 3. Quantities: compound **24** (1.0 g, 3 mmol), compound **21** (0.8 g, 4 mmol), sodium carbonate (0.9 g, 8 mmol), tetrakis(triphenylphosphine)palladium(0) (0.1 g, 0.1 mmol) and DME (20 ml). The product was recrystallised (ethanol). Yield 36 mg (2%). Transitions/°C Cryst 150.8 CrB 167.0 N 280.3 Iso liq. (Found: C, 85.6; H, 6.3; N, 3.7; $C_{26}H_{23}NO$ requires C, 85.45; H, 6.3; N, 3.8%); ^{1}H NMR (CD_2Cl_2) δ: 7.97(2H, d, *J* 8.8), 7.79–7.75(4H, m), 7.72(2H, d, *J* 8.8), 7.44(1H, d, *J* 8.3), 7.42(1H, m), 7.15(1H, dd, *J* 2.0 and 8.3), 7.09(1H, d, *J* 0.8), 2.71(2H, t, *J* 7.5), 1.67(2H, quintet, *J* 7.5), 1.38–1.33(4H, m), 0.91(3H, t, *J* 6.8). IR (KBr) ν_{max}/cm^{-1}: 2927, 2858, 2229, 1603, 1493, 1465, 1189, 825, 802. MS *m*/*z*: 365(M^+), 322, 308(100%), 264, 154.

Methyl 3-(chloromethyl)-4-hydroxybenzoate 27. A suspension of methyl 4-hydroxybenzoate (**26**) (15.2 g, 100 mmol) in conc. hydrochloric acid (130 ml) was cooled (5 °C) with stirring. Paraformaldehyde (3.3 g, 11 mmol) was added, and the mixture was heated (50–55 °C) for 6 hours and then left overnight at room temperature. The solid was filtered off, washed with water, dried *in vacuo* ($CaCl_2$), and recrystallised ($CHCl_3$). Yield 8.0 g (40%), mp 144–145 °C (lit.,[15] 147–149 °C).

^{1}H NMR ($CDCl_3$) δ: 8.03(1H, d, J 1.5), 7.93(1H, dd, J 1.5 and 8.0), 6.90(1H, d, J 8.0), 6.18(1H, s), 4.68(2H, s), 3.90(3H, s). IR (KBr) ν_{max}/cm^{-1}: 3241, 2958, 1688, 1605, 1287, 1152, 844, 754, 705. MS m/z: 202, 200(M^+), 165(100%), 149, 133, 119.

[2-Hydroxy-5-(methoxycarbonyl)benzyl]triphenylphosphonium chloride 28. A mixture of compound **27** (7.9 g, 39 mmol) and triphenylphosphine (9.8 g, 37 mmol) in chloroform (100 ml) was heated under reflux (1 h). The mixture was allowed to cool, the solvent was removed *in vacuo* and on addition of a small volume of toluene, the residue solidified. The solid was filtered off and dried *in vacuo* (100 °C, 1 h) and recrystallised (H_2O). Yield 13.8 g (81%), mp 256–257 °C. ^{1}H NMR ($CDCl_3$) δ: 11.37(1H, s), 7.76(3H, dt, J 1.4 and 7.0), 7.66(1H, ddd, J 2.2, 2.2 and 8.4), 7.59(12H, m), 7.38(1H, d, J 2.2), 7.38(1H, d, J 8.4), 4.71(2H, d, J 14.0), 3.76(3H, s). IR (KBr) ν_{max}/cm^{-1}: 3400, 1693, 1606, 1435, 1291, 1113, 770, 745, 690. MS m/z: 427, 425(M^+-Cl), 395, 349, 262(100%), 183.

Methyl 2-(4-heptylphenyl)-1-benzofuran-5-carboxylate 31. DCC (1.8 g, 8.7 mmol) in dry DCM (20 ml) was added to a stirred mixture of DMAP (0.2 g, 1.6 mmol), compound **28** (3.2 g, 6.8 mmol) and 4-heptylbenzoic acid (**29**) (1.8 g, 8 mmol) in dry DCM (80 ml). The mixture was stirred for 24 h, dry toluene (350 ml) was added, the DCM was distilled off and dry triethylamine (2.0 g, 20 mmol) was added and the mixture was heated (85 °C) with stirring under nitrogen (14 h). The mixture was allowed to cool, filtered and the solvent removed from the filtrate *in vacuo*. The residue was then chromatographed [silica gel, petroleum fraction (bp 40–60 °C)–DCM 6 : 4], and recrystallised (hexane). Yield 1.3 g (55%). Transitions/°C Cryst 101.0 SmF 104.5 SmA 114.9 Iso liq. ^{1}H NMR (CD_2Cl_2) δ: 8.30(1H, dd, J 1.0 and 1.7), 7.98(1H, dd, J 1.7 and 8.5), 7.79(2H, d, J 8.4), 7.55(1H, d, J 8.5), 7.30(2H, d, J 8.4), 7.07(1H, d, J 1.0), 3.92(3H, s), 2.66(2H, t, J 7.4), 1.65(2H, quintet, J 7.4), 1.32(8H, m), 0.89(3H, t, J 6.8). IR (KBr) ν_{max}/cm^{-1}: 2927, 2852, 1717, 1590, 1300, 1160, 1086, 838, 766. MS m/z: 350(M^+), 319, 278, 265(100%), 206.

Methyl 2-(4-nonyloxyphenyl)-1-benzofuran-5-carboxylate 32. A suspension of 4-nonyloxybenzoic acid (**30**) (3.2 g, 12 mmol) in thionyl chloride (16.4 g, 138 mmol) was stirred overnight with exclusion of moisture. The solution was then heated under reflux (1 h), and allowed to cool. The excess of thionyl chloride was removed *in vacuo* and residual hydrogen chloride was removed by addition of dry toluene, followed by removal *in vacuo*. The acid chloride was then added to compound **28** (4.6 g, 10 mmol) and dry triethylamine (3.0 g, 30 mmol) in dry toluene (45 ml) under nitrogen, and the mixture was heated under reflux with stirring for 18 h. The mixture was allowed to cool, the precipitate was removed by filtration, and the solvent was removed from the filtrate *in vacuo*. The residue was purified by flash chromatography [silica gel, petroleum fraction (bp 40–60 °C)–DCM 7 : 3], followed by recrystallisation (hexane). Yield 0.9 g (22%). Transitions/°C Cryst 151.5 SmA 152.0 Iso liq. ^{1}H NMR (CD_2Cl_2) δ: 8.19(1H, d, J 1.5), 7.87(1H, dd, J 1.5 and 8.5), 7.72(2H, d, J 8.8), 7.45(1H, d, J 8.5), 6.90(2H, d, J 8.8), 6.89(1H, s), 3.93(2H, t, J 6.6), 3.83(3H s), 1.72(2H, quintet, J 7.5), 1.39(2H, quintet, J 7.5), 1.22(10H, m), 0.81(3H, t, J 7.1). IR (KBr) ν_{max}/cm^{-1}: 2920, 1722, 1612, 1506, 766. MS m/z: 394(M^+), 268(100%), 237, 210, 182.

2-(4-Heptylphenyl)-1-benzofuran-5-carboxylic acid 33. Compound **33** was prepared in a similar manner to that described for the preparation of compound **11** in ref. 3. Quantities: compound **31** (4.2 g, 12 mmol), potassium hydroxide (1.4 g, 24 mmol), ethanol (110 ml) and water (11 ml). Yield 3.7 g (92%). Transitions/°C Cryst 200.3 SmC 255.8 Iso liq. ^{1}H NMR (DMSO-d^6) δ: 12.87(1H, s), 8.25(1H, s), 7.90(1H, d, J 8.3), 7.83(2H, d, J 8.0), 7.68(1H, d, J 8.3), 7.47(1H, s), 7.34(2H, d, J 8.0), 2.61(2H, t, J 7.1), 1.59(2H, quintet, J 7.1), 1.26(8H, m), 0.85(3H, t, J 7.1). IR (KBr) ν_{max}/cm^{-1}: 3450, 2926, 2849, 2361, 1674, 1612, 1507, 1168, 912, 836. MS m/z: 336(M^+), 264, 251(100%), 206, 178.

2-(4-Heptylphenyl)-1-benzofuran-5-carboxamide 35. Compound **35** was prepared in a similar manner to that described for the preparation of compound **14** in ref. 3. Quantities: compound **33** (1.0 g, 3 mmol), thionyl chloride (1.1 g, 9 mmol), ammonia (d 0.880, 2.0 ml), dry benzene (35 ml) and dry THF (50 ml). Yield 0.6 g (60%), mp 242–243 °C. ^{1}H NMR (DMSO-d_6) δ: 8.10(1H, d, J 1.0), 7.78(2H, d, J 8.0), 7.77(1H, d, J 8.0), 7.54(1H, d, J 8.0), 7.28(2H, d, J 8.0), 7.06(1H, d, J 1.0), 6.81(1H, s), 5.85(1H, s), 2.64(2H, t, J 7.0), 1.63(2H, quintet, J 7.0), 1.25(8H, m), 0.87(3H, t, J 7.0). IR (KBr) ν_{max}/cm^{-1}: 3419, 3192, 2922, 1646, 1608, 1391, 912, 801. MS m/z: 335(M^+), 250(100%), 217, 206, 178.

5-Cyano-2-(4-heptylphenyl)-1-benzofuran 37. Compound **37** was prepared in a similar manner to that described for the preparation of compound **16** in ref. 3. Quantities: compound **35** (0.6 g, 1.6 mmol), thionyl chloride (1.9 g, 16 mmol) and dry DMF (11 ml). Yield 0.2 g (39%). Transitions/°C Cryst 86.5 N 87.5 Iso liq. (Found: C, 83.0; H, 7.3; N, 4.3; $C_{22}H_{23}NO$ requires C, 83.2; H, 7.3; N, 4.4%). ^{1}H NMR (CD_2Cl_2) δ: 7.92(1H, d, J 1.3), 7.79(2H, d, J 8.0), 7.61(1H, d, J 8.4), 7.55(1H, dd, J 1.3 and 8.4), 7.31(2H, d, J 8.0), 7.05(1H, s), 2.66(2H, t, J 7.9), 1.65(2H, quintet, J 7.9), 1.30(8H, m), 0.89(3H, t, J 7.1). IR (KBr) ν_{max}/cm^{-1}: 2920, 2840, 2229, 1616, 1504, 1119, 881, 741. MS m/z: 317(M^+), 245, 232(100%), 203, 176.

2-(4-Nonyloxyphenyl)-5-cyano-1-benzofuran 38. Compound **38** was prepared and purified in a similar manner to that described for the preparation of compound **37**. Quantities: compound **36** (0.2 g, 0.5 mmol), thionyl chloride (0.6 g, 5 mmol) and dry DMF (4 ml). Yield 0.04 g (22%). Transitions/°C Cryst 103.0 SmA 119.7 Iso liq. (Found: C, 79.5; H, 7.5; N, 4.0; $C_{24}H_{27}NO_2$ requires C, 79.7; H, 7.5; N, 3.9%); ^{1}H NMR (CD_2Cl_2) δ: 7.90(1H, dd, J 0.8 and 1.7), 7.80(2H, d, J 9.0), 7.59(1H, d, J 8.6), 7.53(1H, dd, J 1.7 and 8.6), 7.00(2H, d, J 9.0), 6.96(1H, d, J 0.8), 4.02(2H, t, J 6.6), 1.80(2H, quintet, J 6.6), 1.47(2H, m), 1.34–1.26(10H, m), 0.89(3H, t, J 6.8). IR (KBr) ν_{max}/cm^{-1}: 2921, 2850, 2225, 1609, 1504, 1175, 1010, 875, 802. MS m/z: 361(M^+), 235(100%), 206, 190, 164.

2-(4-Cyanophenyl)-5-(4-pentylphenyl)-1-benzofuran 43. Compound **43** was prepared in a similar manner to that described for the preparation of compound **39** in ref. 3. Quantities: compound **42** (0.7 g, 4 mmol), compound **41** (1.1 g, 4 mmol), sodium carbonate (1.1 g, 10 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2 g, 0.2 mmol) and DME (14 ml). The product was recrystallised (carbon tetrachloride). Yield 0.4 g (30%). Transitions/°C Cryst 139.0 N 252.6 Iso liq. (Found: C, 85.2; H, 6.1; N, 3.9; $C_{26}H_{23}NO$ requires C, 85.45; H, 6.3; N, 3.8%); ^{1}H NMR (CD_2Cl_2) δ: 7.99(2H, d, J 8.3), 7.83(1H, dd, J 1.2 and 1.2), 7.76(2H, d, J 8.3), 7.61–7.59(2H, m), 7.55(2H, d, J 8.5), 7.29(2H, d, J 8.5), 7.27(1H, d, J 1.2), 2.66(2H, t, J 7.6), 1.66(2H, quintet, J 7.6), 1.38–1.34(4H, m), 0.92(3H, t, J 6.8). IR (KBr) ν_{max}/cm^{-1}: 2968, 2854, 2224, 1607, 1155, 842, 802. MS m/z: 365(M^+), 308(100%), 277, 252, 154.

5-Bromo-1-benzofuran-2-boronic acid 44. Dry diisopropylamine (2.0 g, 20 mmol) was added to *n*-butyllithium (2.5 M in hexanes, 8 ml, 20 mmol) at −10 °C, and the mixture was stirred under nitrogen (20 min). Compound **8** (3.5 g, 18 mmol) in dry ether (35 ml) was added and the mixture stirred (2 h) at −10 °C. Trimethyl borate (3.7 g, 36 mmol) was added at −10 °C, and the mixture was allowed to return to room temperature with stirring under nitrogen. Hydrochloric acid (5 M, 15 ml) was added with stirring and the mixture was then

poured into water (100 ml) and ether added (50 ml). The separated aqueous layer was washed with ether (2 × 50 ml) and the combined organic layers were washed with sodium hydroxide solution (10%, 30 ml). The separated aqueous layer was washed with light petroleum (bp 40–60 °C) and acidified to pH 3 with hydrochloric acid (5 M). It was then washed with ether (2 × 50 ml) and the combined organic layers were washed with water, brine, dried ($MgSO_4$), and the solvent removed *in vacuo*. A pale-orange solid was obtained. Yield 3.4 g (78%). ^{1}H NMR (DMSO-d_6) δ: 8.62(2H, s), 7.92(1H, d, *J* 2.0), 7.56(1H, d, *J* 8.8), 7.46(1H, dd, *J* 2.0 and 8.8), 7.42(1H, s). MS *m*/*z*: 197, 195($M^+ - B(OH)_2$), 165, 151, 117, 89(100%).

1-Iodo-4-pentylbenzene 46. Compound **46** was prepared in a similar manner to that described for the preparation of compound **3** in ref. 3. Quantities: iodobenzene (**45**) (20.4 g, 100 mmol), pentanoyl chloride (14.5 g, 120 mmol), aluminium chloride (14.7 g, 110 mmol), PMHS (polymethylhydrosiloxane; 16.0 g 267 mmol) and dry DCM (110 ml). A pale-yellow liquid was obtained which was stored with exclusion of light. Yield 14.4 g (53%), bp 105 °C at 0.01 mmHg (lit.,[16] 76–78 °C at 0.1 mmHg). ^{1}H NMR ($CDCl_3$) δ: 7.58(2H, d, *J* 8.0), 6.93(2H, d, *J* 8.0), 2.54(2H, t, *J* 7.0), 1.58(2H, m), 1.31(4H, m), 0.89(3H, t, *J* 7.0). IR (KBr) ν_{max}/cm^{-1}: 2962, 2862, 1486, 1118, 1065, 825, 795. MS *m*/*z*: 274(M^+), 217(100%), 203, 175, 89.

5-(4-Cyanophenyl)-2-(4-pentylphenyl)-1-benzofuran 48. Compound **48** was prepared in a similar manner to that described for the preparation of compound **9** in ref. 3. Quantities: compound **47** (0.3 g, 0.9 mmol), compound **23** (0.2 g, 1.0 mmol), sodium carbonate (0.2 g, 2 mmol), tetrakis(triphenylphosphine)-palladium(0) (0.03 g, 0.03 mmol) and DME (9 ml). The product was purified by flash chromatography (silica gel, hexane–propionitrile 40 : 1), followed by recrystallisation (ethanol). Yield 0.04 g (12%). Transitions/°C Cryst 133.8 N 230.5 Iso liq. (Found: C, 85.3; H, 6.5; N, 3.9; $C_{26}H_{23}NO$ requires C, 85.45; H, 6.3; N, 3.8%). ^{1}H NMR (CD_2Cl_2) δ: 7.74(1H, d, *J* 2.0), 7.73(2H, d, *J* 8.6), 7.69(2H, d, *J* 8.8), 7.67(2H, d, *J* 8.8), 7.53(1H, d, *J* 8.6), 7.45(1H, dd, *J* 2.0 and 8.6), 7.23(2H, d, *J* 8.6), 6.99(1H, d, *J* 0.8), 2.58(2H, t, *J* 7.6), 1.58(2H, quintet, *J* 7.6), 1.27(4H, m), 0.83(3H, t, *J* 7.1). IR (KBr) ν_{max}/cm^{-1}: 2927, 2854, 2226, 1607, 1463, 1153, 1125, 889, 841, 813. MS *m*/*z*: 365(M^+), 308(100%), 264, 176, 154.

2-Pentyl-5-bromo-1-benzofuran 49. Compound **49** was prepared and purified in a similar manner to that described for the preparation of compound **50**. Quantities: compound **8** (12.0 g, 61 mmol), dry diisopropylamine (6.8 g, 67 mmol), *n*-butyllithium (2.5 M in hexanes, 26.8 ml, 67 mmol), 1-iodopentane (24.2 g, 122 mmol) and dry THF (120 ml). Yield 2.6 g (16%), bp 198 °C at 0.6 mmHg. ^{1}H NMR (CD_2Cl_2) δ: 7.61(1H, dd, *J* 0.9 and 1.2), 7.29(2H, m), 6.36(1H, dd, *J* 0.9 and 1.0), 2.76(2H, dt, *J* 1.0 and 7.6), 1.74(2H, quintet, *J* 7.6), 1.37(4H, m), 0.91(3H, t, *J* 6.8). IR (KBr) ν_{max}/cm^{-1}: 2935, 2868, 1599, 1450, 1117, 1050, 948, 867, 671, 579. MS *m*/*z*: 268, 266(M^+), 251, 223, 208(100%), 116.

5-(4-Cyanophenyl)-2-heptyl-1-benzofuran 51. Compound **51** was prepared and purified in a similar manner to that described for the preparation of compound **15**. Quantities: compound **23** (0.2 g, 1.5 mmol), compound **50** (0.4 g, 1.4 mmol), sodium carbonate (0.4 g, 3.5 mmol), tetrakis(triphenylphosphine)-palladium(0) (0.05 g, 0.04 mmol), DME (9 ml) and water (6 ml). Yield 0.03 g (7%). Transitions/°C Cryst 43.0 (N 30.9) Iso liq. (Found: C, 83.4; H, 7.3; N, 4.4; $C_{22}H_{23}NO$ requires C, 83.2; H, 7.3; N, 4.4%). ^{1}H NMR (CD_2Cl_2) δ: 7.71(5H, m), 7.47(1H, d, *J* 8.8), 7.43(1H, dd, *J* 1.9 and 8.8), 6.45(1H, d, *J* 1.0), 2.77(2H, t, *J* 7.4), 1.74(2H, quintet, *J* 7.4), 1.33(8H, m), 0.87(3H, t, *J* 7.1). IR (KBr) ν_{max}/cm^{-1}: 2934, 2861, 2229, 1608, 1468, 844, 808. MS *m*/*z*: 317(M^+), 274, 260, 232(100%), 190.

2-Pentyl-5-(4′-cyanobiphenyl-4-yl)-1-benzofuran 53. Compound **53** was prepared in a similar manner to that described for the preparation of compound **9** in ref. 3. Quantities: compound **52** (1.7 g, 7 mmol), compound **24** (1.7 g, 6 mmol), sodium carbonate (1.5 g, 14 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2 g, 0.2 mmol), DME (25 ml) and water (7 ml). The reaction was carried out with exclusion of light and the product was recrystallised (ethanol). Yield 0.1 g (5%). Transitions/°C Cryst 94.8 N 236.7 Iso liq. (Found: C, 85.6; H, 6.4; N, 3.9; $C_{26}H_{23}NO$ requires C, 85.45; H, 6.3; N, 3.8%); ^{1}H NMR (CD_2Cl_2) δ: 7.77–7.68(9H, m), 7.48(1H, dd, *J* 2.0 and 8.6), 7.47(1H, d, *J* 8.6), 6.45(1H, s), 2.78(2H, t, *J* 7.4), 1.76(2H, quintet, *J* 7.4), 1.40–1.34(4H, m), 0.90(3H, t, *J* 6.8). IR (KBr) ν_{max}/cm^{-1}: 2935, 2860, 2228, 1604, 1466, 1120, 948, 829, 802. MS *m*/*z*: 365(M^+), 350, 322, 308(100%), 278.

4-(*trans*-4-Pentylcyclohexyl)phenyl trifluoromethanesulfonate 55. Trifluoromethanesulfonic anhydride (6.5 g, 23 mmol) was added dropwise to a stirred, cooled (0 °C) solution of 4-(*trans*-4-pentylcyclohexyl)phenol (**1**) (5.0 g, 20 mmol) in dry pyridine (80 ml) under dry nitrogen. The mixture was stirred at room temperature overnight. It was then poured into water (150 ml) and ether added (100 ml). The separated aqueous layer was washed with ether (2 × 100 ml). The combined organic layers were washed with water, hydrochloric acid (10%) (twice), brine, dried ($MgSO_4$), and the solvent was removed *in vacuo*. The product was purified by flash chromatography [silica gel, petroleum fraction (bp 40–60 °C)–DCM 7 : 3] to give a pale-yellow oil. Yield 5.2 g (69%). ^{1}H NMR (CD_2Cl_2) δ: 7.21(2H, d, *J* 8.5), 7.10(2H, d, *J* 8.5), 2.44(1H, tt, *J* 3.2 and 12.4), 1.82–1.81(2H, m), 1.78–1.77(2H, m), 1.38–1.36(1H, m), 1.34–1.31(1H, m), 1.26–1.12(9H, m), 1.02–0.99(1H, m), 0.96–0.93(1H, m), 0.81(3H, t, *J* 7.3). IR (KBr) ν_{max}/cm^{-1}: 2929, 2858, 1503, 1427, 1143, 1018, 837, 740, 607. MS *m*/*z*: 378(M^+), 307, 252, 175, 69(100%).

5-[4-(*trans*-4-Pentylcyclohexyl)phenyl]-1-benzofuran 56. Compound **56** was prepared in a similar manner to that described for the preparation of compound **9** in ref. 3. Quantities: compound **55** (3.4 g, 9 mmol), compound **54** (1.6 g, 10 mmol), sodium carbonate (2.4 g, 23 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3 g, 0.3 mmol), DME (40 ml) and water (10 ml). Volatiles were removed by heating (95 °C) *in vacuo* (12 h) and the residue was recrystallised (hexane). Yield 1.9 g (61%). Transitions/°C Cryst 116.3 N 153.7 Iso liq. ^{1}H NMR (CD_2Cl_2) δ: 7.80–7.79(1H, m), 7.67(1H, d, *J* 2.2), 7.56–7.51(4H, m), 7.30(2H, d, *J* 8.3), 6.84(1H, dd, *J* 0.7 and 2.2), 2.53(1H, tt, *J* 3.2 and 12.4), 1.94–1.88(4H, m), 1.48(2H, ddd, *J* 3.9, 9.0 and 12.9), 1.35–1.22(9H, m), 1.08(2H, ddd, *J* 3.9, 9.0 and 12.9), 0.91(3H, t, *J* 7.0). IR (KBr) ν_{max}/cm^{-1}: 3124, 2924, 2853, 1463, 1131, 1027, 883, 742, 697. MS *m*/*z*: 346(M^+), 331, 303, 275, 233(100%).

2-Cyano-5-[4-(*trans*-pentylcyclohexyl)phenyl]-1-benzofuran 59. Compound **59** was prepared in a similar manner to that described for the preparation of compound **16** in ref. 3 using the quantities stated. Quantities: compound **58** (1.0 g, 2.6 mmol), thionyl chloride (3.2 g, 26 mmol) and dry DMF (20 ml). The product was recrystallised (ethanol). Yield 0.5 g (52%). Transitions/°C Cryst 113.0 N 240.7 Iso liq. (Found: C, 83.9; H, 8.0; N, 3.9; $C_{26}H_{29}NO$ requires C, 84.1; H, 7.9; N, 3.8%); ^{1}H NMR (CD_2Cl_2) δ: 7.86(1H, dd, *J* 0.7 and 2.0), 7.75(1H, dd, *J* 2.0 and 8.8), 7.61(1H, ddd, *J* 0.7, 0.7 and 8.8), 7.55(1H, m), 7.54(2H, d, *J* 8.0), 7.32(2H, d, *J* 8.0), 2.53(1H, tt, *J* 3.2 and 12.2), 1.93–1.87(4H, m), 1.56–1.44(4H, m), 1.35–1.19(7H, m), 1.08(2H, m), 0.90(3H, t, *J* 7.3). IR (KBr) ν_{max}/cm^{-1}: 2925, 2854, 2234, 1558, 1515, 1462, 1178, 1128, 950, 887. MS *m*/*z*: 371(M^+, 100%), 300, 245, 232, 189.

2-Cyano-5-hydroxy-1-benzofuran 65. A mixture of compound **64** (0.7 g, 4 mmol) and pyridinium chloride (4.6 g, 40 mmol) was heated under reflux (3 min). The reaction mixture was then poured into ice–water (50 ml). The precipitate was filtered off and dried *in vacuo*. The product was recrystallised (toluene–hexane 1 : 2). Yield 0.2 g (31%), mp 146.5–147.5 °C (lit.,[17] 144 °C). ^{1}H NMR (CD_2Cl_2) δ: 7.43(1H, m), 7.40(1H, d, *J* 0.7), 7.07(1H, m), 7.05(1H, dd, *J* 2.4 and 8.8), 5.07(1H, s). IR (KBr) ν_{max}/cm^{-1}: 3435, 2238, 1558, 1195, 949, 862, 608. MS *m*/*z*: 159(M^+, 100%), 130, 103, 82, 76.

2-Cyano-1-benzofuran-5-yl *trans*-4-pentylcyclohexanecarboxylate 67. Compound **65** (0.5 g, 3 mmol) and *trans*-4-pentylcyclohexanecarboxylic acid (**66**) (0.6 g, 3 mmol) were dissolved in dry DCM (30 ml), and DMAP (0.1 g, 1 mmol) was added. The mixture was stirred and DCC (0.6 g, 3 mmol) was then added, and stirring was continued (24 h). The precipitate of *N,N′*-dicyclohexylurea was filtered off, and the solvent removed *in vacuo*. The product was purified by flash chromatography [silica gel, petroleum fraction (bp 40–60 °C)–DCM 7 : 3] and recrystallisation (ethanol). Yield 0.3 g (98%). Transitions/°C Cryst 71.9 N 103.8 Iso liq. (Found: C, 74.0; H, 7.2; N, 4.1; $C_{21}H_{25}NO_3$ requires C, 74.3; H, 7.4; N, 4.1%). ^{1}H NMR (CD_2Cl_2) δ: 7.56(1H, d, *J* 9.0), 7.48(1H, d, *J* 1.0), 7.40(1H, d, *J* 2.4), 7.21(1H, dd, *J* 2.4 and 9.0), 2.50(1H, tt, *J* 3.7 and 12.2), 2.16–2.12(2H, m), 1.91–1.86(2H, m), 1.59–1.55(1H, m), 1.52–1.49(1H, m), 1.34–1.19(9H, m), 1.05–1.01(1H, m), 0.99–0.95(1H, m), 0.89(3H, t, *J* 7.1). IR (KBr) ν_{max}/cm^{-1}: 2858, 2235, 1747, 1557, 982, 884. MS *m*/*z*: 339(M^+), 198, 180, 152, 97(100%).

1-Bromo-4-[2,2-(dimethoxy)ethylsulfanyl]benzene 69. Sodium (13.8 g, 0.6 g atoms) was added to 'superdry' ethanol (400 ml) with stirring under nitrogen. 4-Bromothiophenol (**68**) (103.3 g, 0.55 mol) was added and stirring was continued (5 min). Bromoacetaldehyde dimethyl acetal (120.0 g, 0.71 mol) was then added and the mixture heated under reflux overnight with stirring under nitrogen. The mixture was then washed with DCM (3 × 100 ml) and the combined washings were washed with water, brine, dried ($MgSO_4$), the solvent removed *in vacuo* and the residue was distilled. Yield 104.3 g (69%), bp 132 °C at 2 mmHg [lit.,[18] 142–144 °C (bath temperature) at 10 mmHg]. ^{1}H NMR ($CDCl_3$) δ: 7.39(2H, d, *J* 8.0), 7.24(2H, d, *J* 8.0), 4.50(1H, t, *J* 7.0), 3.36(6H, s), 3.08(2H, d, *J* 7.0). IR (KBr) ν_{max}/cm^{-1}: 2930, 2830, 1470, 1120, 1090, 800, 480. MS *m*/*z*: 278, 276(M^+), 247, 215, 201, 189, 75(100%).

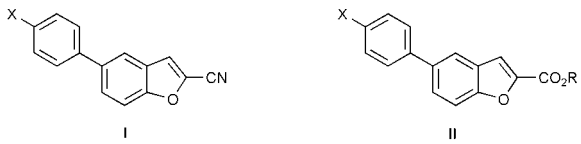
5-Bromo-1-benzothiophene 70. Compound **70** was prepared in a similar manner to that described for the preparation of compound **7**. Quantities: compound **69** (104.3 g, 376 mmol), polyphosphoric acid (156.2 g) and chlorobenzene (1000 ml). The product was recrystallised (ethanol). Yield 12.0 g (15%), mp 46–47 °C (lit.,[19] 47–48 °C). ^{1}H NMR (CD_2Cl_2) δ: 7.98(1H, dd, *J* 0.7 and 2.0), 7.77(1H, m), 7.52(1H, d, *J* 5.5), 7.44(1H, dd, *J* 2.0 and 8.5), 7.30(1H, dd, *J* 0.7 and 5.5). IR (KBr) ν_{max}/cm^{-1}: 3080, 1576, 1399, 898, 807, 472. MS *m*/*z*: 214, 212(M^+), 133(100%), 106, 89, 81.

2-Cyano-5-(4-heptylphenyl)-1-benzothiophene 75. Compound **75** was prepared in a similar manner to that described for the preparation of compound **16** in ref. 3. Quantities: compound **74** (1.0 g, 3 mmol), thionyl chloride (3.3 g, 28 mmol) and dry DMF (20 ml). The product was recrystallised (ethanol). Yield 0.4 g (43%), mp 93.2 °C (Found: C, 79.2; H, 7.1; N, 4.2; S, 9.4; $C_{22}H_{23}NS$ requires C, 79.2; H, 6.95; N, 4.2; S, 9.6%). ^{1}H NMR (CD_2Cl_2) δ: 8.10(1H, m), 7.97(1H, d, *J* 0.7), 7.94(1H, m), 7.80(1H, dd, *J* 2.0 and 8.6), 7.57(2H, d, *J* 8.3), 7.31(2H, d, *J* 8.3), 2.66(2H, t, *J* 7.5), 1.65(2H, quintet, *J* 7.5), 1.35–1.30(8H, m), 0.89(3H, t, *J* 7.1). IR (KBr) ν_{max}/cm^{-1}: 2959, 2855, 2214, 1506, 1178, 890, 800. MS *m*/*z*: 333(M^+), 290, 261, 248(100%), 221.

Results and discussion

Cyano compounds

In an earlier paper[3] we discussed the transition temperatures of 5-(4-substituted-phenyl)-2-cyano-1-benzofurans (**I**) and 5-(4-substituted-phenyl)-1-benzofuran-2-carboxylate esters (**II**) (some values for 2-cyano compounds related to the compounds reported here are given in Table 1). In these systems, the benzene ring at the 5-position of the 1-benzofuran gives a biphenyl-like situation, with respect to the extent to which inter-annular twisting occurs. The transition temperatures for the 2-cyano-5-phenyl-1-benzofurans were similar to, but consistently higher than (by approximately 10–20 °C), those for the analogous biphenyls. On the other hand, the 2-carboxylate esters have significantly lower mesophase stabilities (by approximately 20–40 °C) than the analogous compounds with phenyl replacing the benzofuran unit. We interpret these results on the basis of the benzofuran unit being intrinsically superior to phenyl in supporting mesogenicity, but the bend in the molecular core adversely affects the terminally 'non-polar' ester systems resulting in lower clearing points. For the antiparallel correlated, terminal cyano compounds,[20–25] the pair-wise associations eliminate the disadvantage of the bent core and higher clearing points result (see Fig. 3 and comments below).



X = alkyl, alkoxy;
R = H, CH_3, C_2H_5

In this paper we give a few more examples of 5-substituted-2-cyano- systems (**20**, **59**, **67**), but principally we consider the reversed 5-cyano-2-substituted systems (**15**–**17**, **37**, **38**) and present reasons for their improved mesogenicity; some other examples of closely related compounds with alternative core units are also presented (**43**, **48**, **51**, **53**), along with one example of a 1-benzothiophene (**75**). The transition temperatures for all the new compounds are given in Table 1 and are arranged to aid comparisons with the previously reported values.

Comparison of the transition temperatures for the phenyl-substituted compounds **76** and **15**, **77** and **16**, **78** and **37**, and **79** and **38**, and for the biphenyl-substituted compounds **80** and **17** shows that compounds with the cyano group at the 5-position have higher melting points (by 40.0, 48.6, 55.4, 41.0 and 53.1 °C respectively) and higher clearing points (by [no mesophase] 30.1, 27.0, 22.7 and 28.6 °C respectively) than compounds with a 2-cyano group. The types of mesophase which are present are solely nematic for the lower alkyls (C_3H_7, C_5H_{11}, C_7H_{15}), with a smectic A phase appearing for the $C_9H_{19}O$ compound; the smectic A phase is more strongly enhanced than the nematic phase for compound **38** in comparison with compound **79**. Although both sets of 2,5-disubstituted systems have a similar shape, the reason for the higher melting points, smectic A and nematic phase stabilities for the 5-cyano- systems than for the 2-cyano- counterparts is reasonably explained by the reduced inter-annular twisting effect in the compounds with a 2-phenyl substituent. Modelling shows that a 5-phenyl-1-benzofuran is structurally similar to a biphenyl or terphenyl in the nature of its connection of the two rings and indicates a dihedral angle of approximately 40° (see Fig. 2). For a 2-phenyl-1-benzofuran, the inter-ring linkage is between a phenyl ring and a five-membered furan unit in which the atoms *ortho* to the ring junction are constrained away from interference with the *ortho*-region of the phenyl unit (bond angles at the 2-position

Table 1 Transition temperatures/°C for various terminal cyano derivatives of 1-benzofuran and 1-benzothiophene

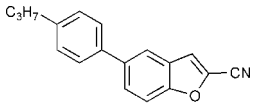
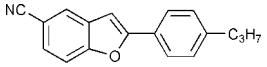
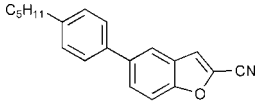
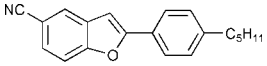
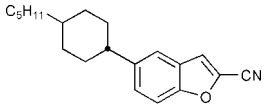
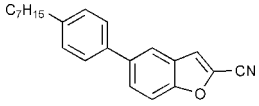
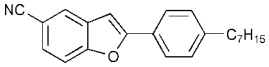
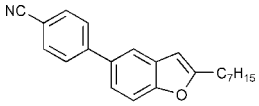
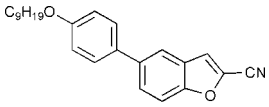
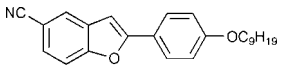
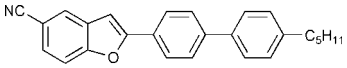
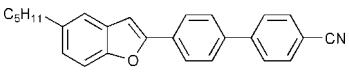
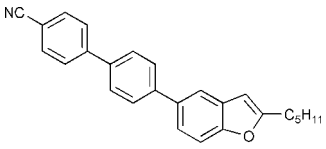
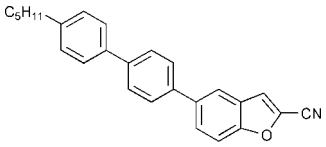
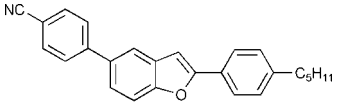
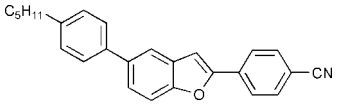
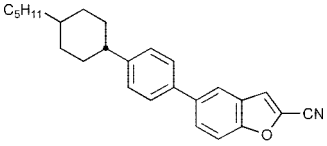
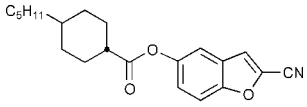
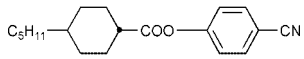
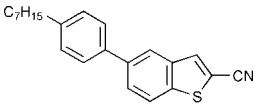
Compound	Structure	Cryst		CrB		SmA		N[a]		Iso liq.
76[b]		•	58.0	—	—	—	—	(•	48.9)	•
15		•	98.0	—	—	—	—	—	—	•
77[b]		•	51.1	—	—	—	—	•	56.4	•
16		•	99.7	—	—	—	—	(•	86.5)	•
20		•	77.6	—	—	—	—	(•	58.5)	•
78[b]		•	31.1	—	—	—	—	•	60.5	•
37		•	86.5	—	—	—	—	•	87.5	•
51		•	43.0	—	—	—	—	(•	30.9)	•
79[b]		•	62.0	—	—	•	87.0	•	97.0	•
38		•	103.0	—	—	•	119.7	—	—	•
17		•	187.1	—	—	—	—	•	284.2	•
25		•	150.8	•	167.0	—	—	•	280.3	•

Table 1 (*Continued*)

Compound	Structure	Cryst		CrB		SmA		N[a]		Iso liq.
53		•	94.8	—	—	—	—	•	236.7	•
80[b]		•	134.0	•	147.3	—	—	•	255.6	•
48		•	133.8	—	—	—	—	•	230.5	•
43		•	139.0	—	—	—	—	•	252.6	•
59		•	113.0	—	—	—	—	•	240.7	•
67		•	71.9	—	—	—	—	•	103.8	•
81[c]		•	47.2	—	—	—	—	•	79.2	•
75		•	93.2	—	—	—	—	—	—	•

[a]() denotes a monotropic transition. [b]From ref. 3. [c]From ref. 31.

of 2-phenyl-1-benzofuran are 122.4° and 127.0° for the O–C–C[phenyl] and C–C–C[phenyl] angles respectively); modelling indicates that the inter-ring dihedral angle is approximately 0–2°. The smaller the inter-annular dihedral angle, the greater the degree of polarizability between the π-systems of each ring, giving in effect an extended core region, which leads to greater mesogenicity; the more efficient packing of the more planar 2-phenyl systems in the crystal phase would also lead to higher melting points. Fig. 2 shows the general structures for the two series and the biphenyl-like structure of (a) will diminish the mesophase stabilities of these compounds in comparison with the compounds of structure (b). The importance of the extent of inter-annular twisting in understanding how the mesogenicity of terphenyl systems is influenced by lateral mono- and di-fluoro substitution has been extensively demonstrated previously.[7]

The high clearing point of 5-cyano-2-aryl-1-benzofurans is also shown for compounds analogous to terphenyls. The 2-cyano compound **80** has a higher clearing point (255.6 °C) than the terphenyl analogue (240.0 °C),[3] but the 5-cyano isomer (**17**) has the highest clearing point of 284.2 °C. The justification for these differences is similar to that given above for the biphenyl equivalents. Compound **80** has two inter-annular twists similar to those in terphenyl, but the superior benzofuran core unit, in pairwise associations, overcomes the deviation from linearity. For compound **17**, only one significant inter-annular twist is present and the compound has a higher clearing point than compound **80**.

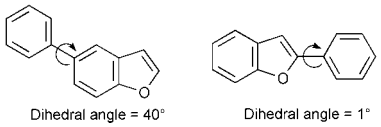


Fig. 2 The inter-annular twisting in (a) 5-phenyl-, (b) 2-phenyl-substituted-1-benzofurans.

For compounds with a benzofuran and two phenyl rings, a greater variety of structural arrangements is possible and the position in the core of the site for the deviation from linearity can be changed. All the six possible structural combinations for pentyl and cyano terminal groups have been prepared (compounds **17**, **25**, **43**, **48**, **53** and **80**). This set of compounds shows relatively simple mesophase types, all are nematogenic and two of them give a CrB phase, and their mesogenicity can be rationalised on the basis of the following factors: (a) a 2,5-disubstituted-1-benzofuran unit is superior to phenyl in promoting mesogenicity, (b) 2-aryl- is superior to 5-aryl-substitution in 1-benzofuran because of less inter-annular twisting, (c) the disadvantage of the bend in the molecule is more easily masked by anti-parallel associations if it is at the end of the molecule rather than the middle, and (d) a more extensive planar region arising from antiparallel correlations is preferred. With these points in mind, compound **17** is the best structural arrangement (one twist, bend at the end of the structure) and compound **25**, with cyano and pentyl interchanged, is similar. Although we do not know the degree to which these cyano systems overlap in their anti-parallel associations, Fig. 3 gives an indication of how the pairs can be quite linear. It is clear from these drawings that another factor which may influence mesophase stability is the effect of the position of the oxygen atoms in the core; for example, in the dimer for compound **17** the hetero atoms are closer to the centre of the structure than in compound **25**. It is also apparent that the dimer for compound **17** has a more extensive central planar region than that for compound **25**. The same observation can be made for the pairs of compounds **80**/**53** and **43**/**48**, discussed below, in which the first compound in each pair has the more extended central area.

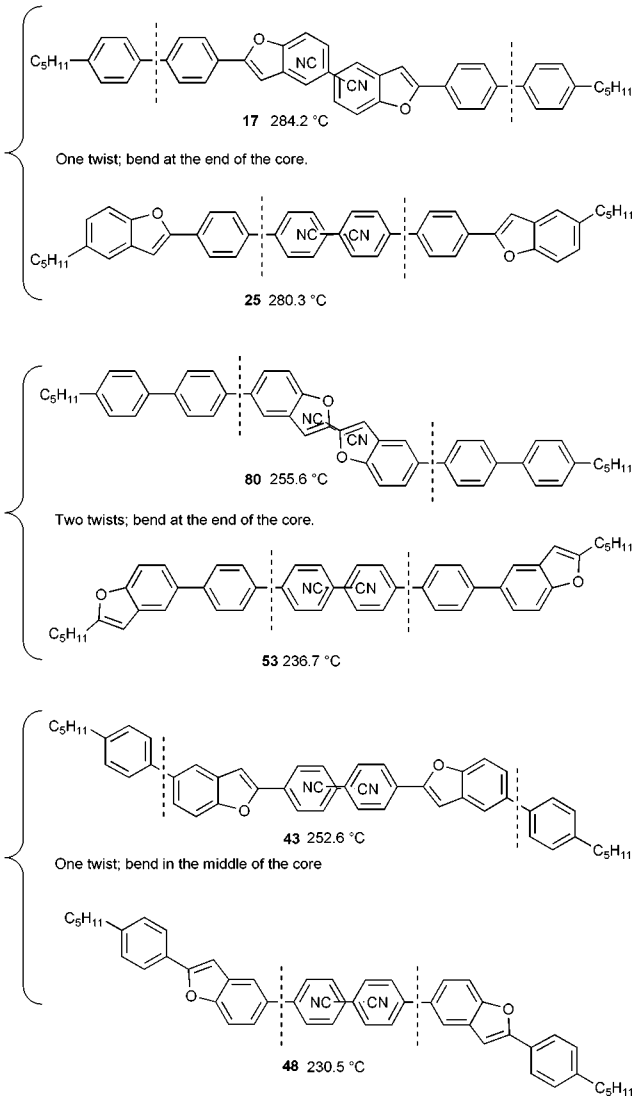


Fig. 3 Suggested structures for antiparallel associations of cyano systems. The clearing points are given and the limits of the central planar region are indicated.

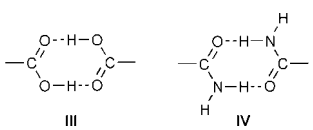
Compounds **80** and **53** (two twists, bend at the end) have lower clearing points than compounds **17** and **25**, and the anti-parallel association of **53** still leaves obvious bends whereas antiparallel association of **80** masks the deviation from linearity (see Fig. 3) and has linear terminal regions. Compounds **43** and **48** have one twist, like compounds **17** and **25**, but with a bend in the middle of the structure their clearing points are much lower than for either compound **17** or **25**. The differences between the values for compounds **43** and **48** may be justified by the larger central planar region in the dimer for compound **43**.

Compounds **20** and **67** are two further examples of 2-cyano systems and in each case they conform to the pattern shown by the related biphenyl systems.[3] Compound **20** (a cyclohexyl system) has a higher $T_{N–I}$ value than the phenyl equivalent (**77**) and although the difference is small, the relationship is similar to that for the analogous cyclohexylphenyl and biphenyl systems respectively. Compound **67** has a higher $T_{N–I}$ value than compound **81** and in this case the difference is more in keeping with the differences previously reported for phenyl and 1-benzofuran systems.

Acids, amides and esters

Several compounds (*e.g.* some acids, amides, esters) were prepared as intermediates in the synthesis of the final compounds shown in Table 1, and in many cases they were mesogenic. Several points are worth noting for these intermediates but there has not been any planned objective to produce extensive comparisons.

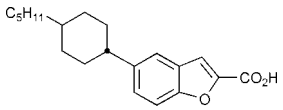
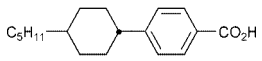
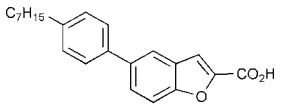
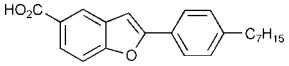
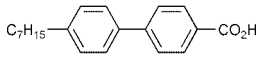
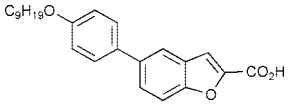
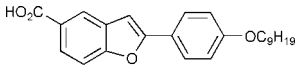
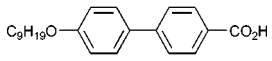
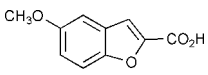
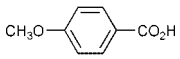
Acids **33**/**83** and **34**/**85** confirm that, as for the cyano systems, the 5-carboxylic acids show greater mesogenicity than the 2-carboxylic acids. These differences can be ascribed to greater planarity for the 2-aryl compounds (**33** and **34**) compared to the 5-aryl analogues (**83** and **85** respectively). However, with one exception, all the 1-benzofurancarboxylic acids have lower clearing points than the analogous systems with a phenyl ring replacing the 1-benzofuran unit, but the types of mesophase are the same in each set (compare **33** and **85** with **84**, **34** and **85** with **86**, and **18** with **82**). One can justify the difference in behaviour of the acids from that of the nitriles by claiming that anti-parallel associations of nitriles minimises the effect of the bend in the molecular core,[3] whereas acids have an 'end-on' formation of a dimer which does not disguise the deviation from linearity (see **III**); the collinear systems **84**, **86** and **82** therefore show greater mesogenicity. The one surprising exception to this pattern is that compound **62** has a much higher $T_{N–I}$ value than **87**.



Primary amides usually show very high melting points and consequently not many examples of calamitic amides are known. Amides can hydrogen bond to each other[26] and if they associate in a similar way to carboxylic acids (see **IV**) then the second hydrogen on each nitrogen atom of a primary amide can generate a network of hydrogen bonding leading to higher melting points. The examples in the literature of mesogenic amides are usually for systems with a bend in the structure (*e.g.*, from a Schiffs base linkage,[27] a dimethylene link[28] or flexible, non-axially symmetrical end rings[29]) and this feature may be necessary to suppress melting points. Two of the amides encountered in this work {compounds **36** [Cryst 225.0 N 235.0 Iso liq. (°C)] and **58** [Cryst 275.0 N 296.0 Iso liq. (°C)]} are mesogenic and the bend generated by a 1-benzofuran core unit may also be responsible for lowering their melting points and allowing the compounds to produce a mesophase.

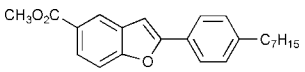
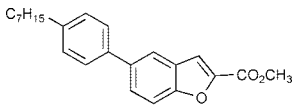
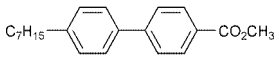
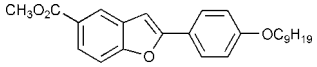
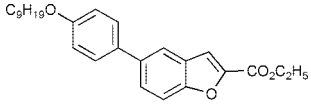
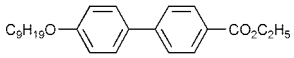
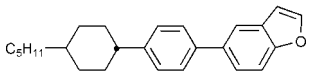
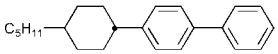
The three esters **31**, **88** and **89** also demonstrate that, relative to the biphenyl systems **89**, compound **88** has a lower clearing point (by 38.6 °C) because of the bend in the core unit, whereas compound **31** has a higher clearing point (by 25.3 °C) which indicates that the disadvantage of the molecular bend is overcome by the absence of twisting of the 2-aryl substituent in **31**; in a simplistic analysis, these effects suggest that the bend decreases mesogenicity by ~40 °C and the coplanarity at the 2-position increases mesogenicity by ~60 °C. A similar, but less precise, comparison can be made for compounds **91** (ethyl ester), **90** (ethyl ester) and **32** (methyl ester); here the bend depresses the clearing point by 21.4 °C and planarity raises it by 67.4 °C.

Table 2 Transition temperatures/°C for various 1-benzofurancarboxylic acids

Compound	Structure	Cryst		SmC		N[a]		Iso liq.
18		•	191.5	—	—	•	217.5	•
82[b]		•	180	—	—	•	265	•
83[c]		•	131.0	•	185.0	•	222.0	•
33		•	200.3	•	255.8	—	—	•
84[d]		•	156	•	243	•	262	•
85[c]		•	212.2	•	223.0	—	—	•
34		•	172.0	•	193.2	•	253.7	•
86[e]		•	176	•	256.5	•	258.5	•
62		•	208.0	—	—	•	221.0	•
87[f]		•	184	—	—	(•	156)	•

[a]( ) denotes a monotropic transition. [b]From ref. 32; entry 5669. [c]From ref. 3. [d]From ref. 33; entry 3013 [e]From ref. 33; entry 3027. [f]From ref. 33; entry 372.

Table 3 Transition temperatures/°C for various 1-benzofurancarboxylates and related compounds[a]

Compound	Structure	
31		Cryst 101.0 SmF 104.5 SmA 114.9 Iso liq.
88[b]		Cryst 76.0 (SmA 51.0) Iso liq.
89[b]		Cryst 61.0 E 88.5 B/SmA 89.6 Iso liq.
32		Cryst 151.5 SmA 152.0 Iso liq.
90[b]		Cryst 85.8 (SmA 84.6) Iso liq.
91[b]		Cryst 78.0 E 81.0 SmB 91.0 SmA 106.0 Iso liq.
56		Cryst 116.3 N 153.7 Iso liq.
92[c]		Cryst 57.9 SmB 81.9 N 97.9 Iso liq.

[a]( ) denotes a monotropic transition. [b]From ref. 3. [c]From ref. 30.

One example of a mesogenic monosubstituted 1-benzofuran (**56**) was noted which is directly comparable with **92**.[30] Fusing the furan ring onto compound **92** has not depressed mesogenicity by creating an angular structure but has significantly increased the clearing point as though a pseudo-alkoxy terminal group has been added.

Summary

Transition temperatures have been reported for several 2- and 5-cyano-1-benzofurans with one or two phenyl units or a biphenyl unit in the molecular core and for esters, amides and acids *etc.* involved in their synthesis. The mesomorphic behaviour of this set of compounds and those reported previously[3] can be explained on the basis of the following points: (a) 1-benzofuran is superior to benzene as a core unit, (b) 2,5-disubstitution in 1-benzofuran gives a bent core system which adversely affects mesogenicity, compared to 1,4-diphenyl, but the disadvantage can be minimised by the position of the bend in the core and it is overcome in cyano compounds by antiparallel correlations, (c) 2-aryl-1-benzofurans have negligible inter-annular twist but 5-aryl-1-benzofurans have similar inter-annular twist to that in biphenyls.

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