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The synthesis and transition temperatures of a series of 5-(4-alkyl- and 4-alkoxy-phenyl)-2-cyanobenzo[*b*]furans and a 5-(4′-alkylbiphenyl-4-yl)-2-cyanobenzo[*b*]furan are presented. The 2-cyanobenzo[*b*]furans show similar mesophase types to the analogous biphenyl and terphenyl compounds, which are obtained by replacing the benzo[*b*]furan unit with a phenyl ring. The transition temperatures for the 2-cyanobenzo[*b*]furan compounds are always higher than for their biphenyl and terphenyl counterparts, but they are much lower than for the corresponding phenylnaphthalenes. Five mesogenic benzo[*b*]furans without a cyano group were prepared as intermediates and these compounds have lower clearing points than their biphenyl analogues.

1. Introduction

The 4-alkyl/alkoxy-4′-cyanobiphenyls (**I**) occupy a unique place in the development of liquid crystals as the first stable compounds to exhibit the nematic phase at room temperature as single components or in mixtures which were suitable for use in twisted nematic display devices [1–3]. The commercial nematic mixtures of biphenyls, which often include a small amount of a 4-alkyl-4″-cyanoterphenyl (**II**), are still used widely in display devices more than 25 years after their discovery; in such a rapidly developing and changing area it is a remarkable confirmation of the revolution in display technology which these compounds stimulated. Subsequently, many other structurally similar two-ring compounds have been synthesized and assessed for their ability to generate the nematic phase; some of the most successful systems are shown in figure 1 (**III–IX**). The structures **I**, **II**, **VI** and **VII** have the desirable features of linearity of and rotational symmetry about the molecular long axis, which are usually regarded as prime requirements for the generation of calamitic mesophases, and represent

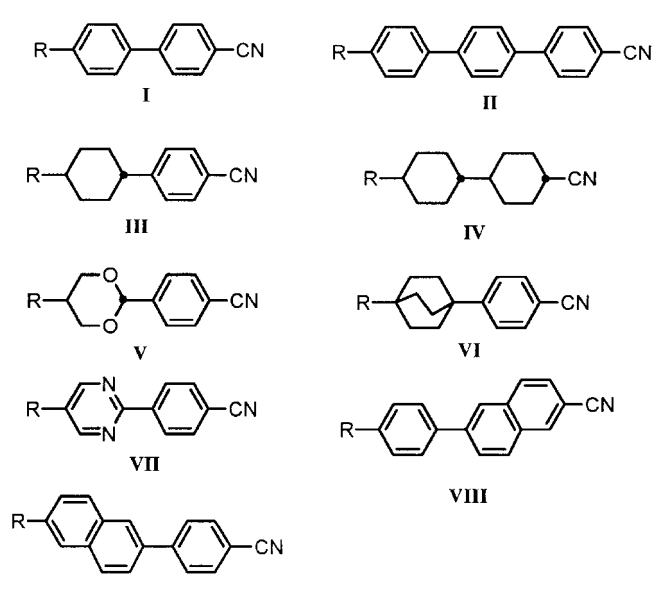

Figure 1. Biphenyls, terphenyls and general structures of some nematogens related to biphenyls. The $T_{N\text{-}I}$ values (°C) for the C_5H_{11} compounds are **I**, 35 [1]; **II**, 240 [4]; **III**, 55 [5]; **IV**, 85 [6]; **V**, (52) [7]; **VI**, 100 [8]; **VII** (52) [9]: **VIII** 130 [10]; **IX** 128 [11]; () indicates a monotropic transition.

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good nematogens. The other systems are also nematogenic even though there is an off-axis displacement of the molecular structure arising from the *trans*-1,4-cyclohexyl or *trans*-2,5-dioxanyl rings, in the case of structures **III**, **IV** and **V**, or from the 2,6-disubstituted naphthalene unit, as for structures **VIII** and **IX**.

Benzo[*b*]furans are formally related to benzene and naphthalene units in a variety of ways (as shown in figure 2), but they have not been investigated very extensively as potential core units for thermotropic liquid crystals; indeed the LiqCryst 3.2 Database [12] reports only seventeen benzo[*b*]furan systems, of which only one is a calamitic 2,5-disubstituted-benzo[*b*]furan (transition temperatures are not recorded [13]) and sixteen are discotic molecules [14, 15] (see figure 3). The 2,6-disubstituted naphthalene (**XI**) can simplistically be seen as arising from an extension of a phenyl ring to give a cinnamonitrile (**XIII**), which is then connected to the *ortho*-position to complete a ring; the extension would enhance mesogenicity with respect to the biphenyl, but the completion of the cyclic system requires what is effectively lateral substitution of the rest of the core, and this would depress mesogenicity. It is more difficult to assess the probable influence on mesogenicity of the transformation of a phenyl ring into a benzo[*b*]furan unit because of the unpredictable effects caused by the creation of a strained five-membered ring fused onto a benzene ring. Formally, the precursor **XII** has a cinnamonitrile unit attached in a *meta*-relationship to the phenyl group, whereas the attachment in **XIII** is at a more favourable *para*-position. The completion of the heterocyclic ring system by the oxygen atom introduces strain, but it may extend the polarizability of the 'biphenyl' unit of **XII**.

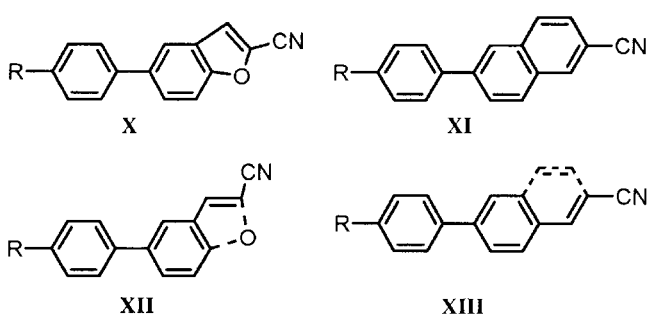


Figure 2. Representations **XII** and **XIII** showing the formal relationships of **X** and **XI**, respectively, to biphenyl systems.

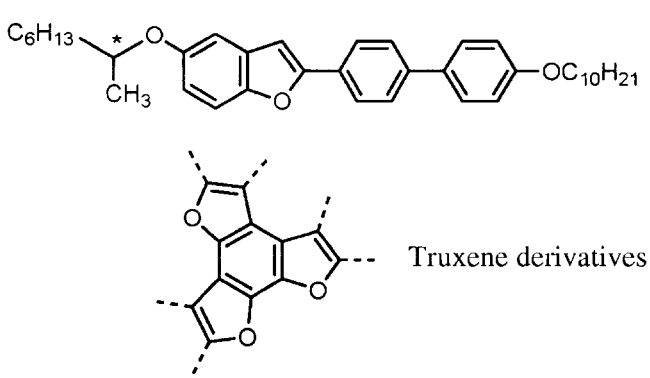


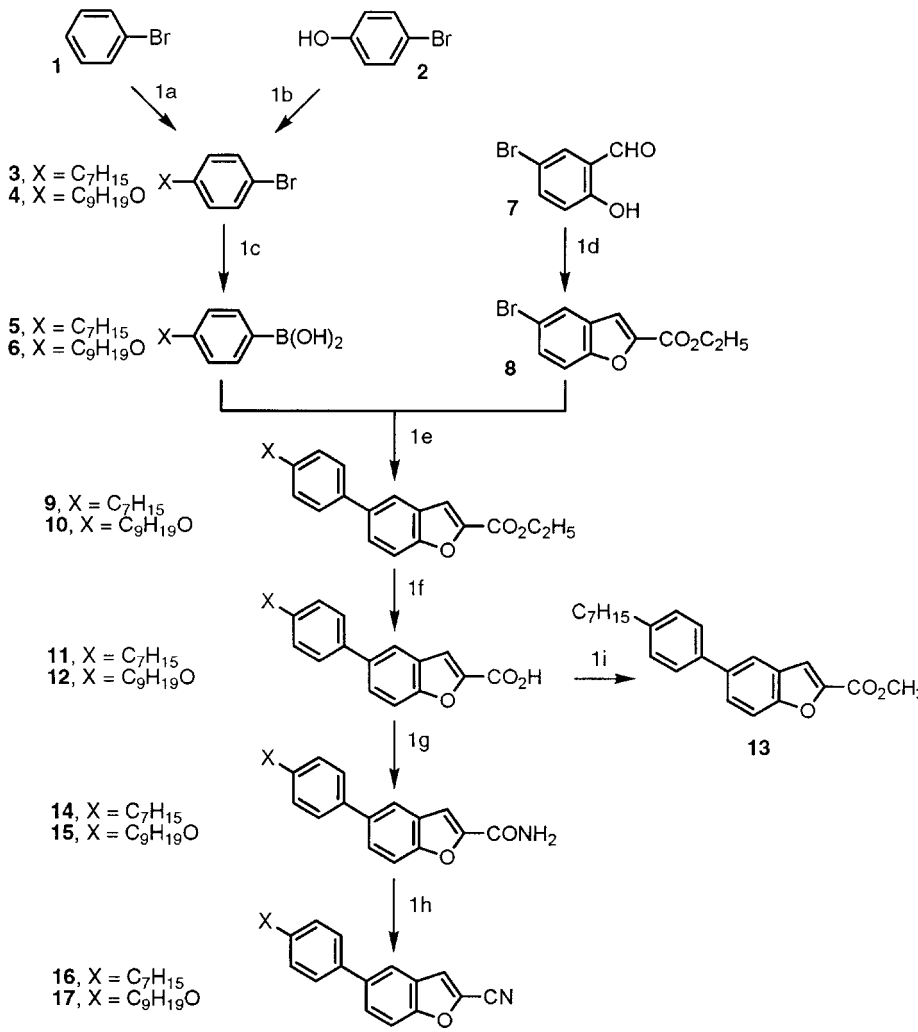
Figure 3. Benzo[*b*]furan-based liquid crystals.

All these subtle structural differences make it difficult to predict how the mesogenicities of benzo[*b*]furans will compare with those of biphenyls (the furans have the advantage of a more extensive region of polarizability, but the disadvantage of a less satisfactory shape) or of naphthyls (in this case also the furans have a worse structural shape, but the creation of the heterocyclic ring and the effect of the oxygen atom on molecular polarizability is difficult to predict). In addition, the effects of a bent structure and the presence of a hetero-atom in benzo[*b*]furans may have the advantage of causing depressions in melting points. In order to assess the potential of a 2,5-disubstituted benzo[*b*]furan moiety as a core unit, we decided to synthesize initially some 5-(4-alkylphenyl)-2-cyanobenzo[*b*]furans (**16**, **31–35**), to determine their transition temperatures and to compare the values with the corresponding 4-alkyl-4′-cyanobiphenyls. One 5-(4-alkoxyphenyl)-2-cyanobenzo[*b*]-furan (**17**) was prepared to give an example from the alkoxy series, and a 5-(4′-alkylbiphenyl-4-yl)-2-cyanobenzo[*b*]furan (**39**) was also prepared for comparison with a 4-alkyl-4″-cyanoterphenyl.

2. Synthesis

The synthetic routes to the 2-cyanobenzo[*b*]furans are shown in schemes 1–3 and the key intermediate for all these syntheses is ethyl 5-bromobenzo[*b*]furan-2-carboxylate (**8**) [16]. The initial route attempted was the more linear sequence shown in scheme 1 in which compound **8** is coupled to an arylboronic acid using a palladium-catalysed reaction which has proved to be extremely valuable for the synthesis of linked-aryl liquid crystals [10, 17–19]; the ester function was then converted into the cyano group by a standard sequence of reactions. In the alternative, more convergent approach, shown in schemes 2 and 3, the cyano compound **30** was prepared and coupled to the arylboronic acids to give the target compounds directly. The route shown in scheme 1 is less efficient than that in scheme 2, but it has the advantage of providing compounds **9–15** which may be mesogenic, and their transition temperatures can be compared with those for the nitriles.

The usual route to 4-alkyl-1-bromobenzenes is via Friedel–Crafts acylation of bromobenzene followed by Wolff–Kishner reduction of the ketone [19]. An alternative *in situ* reduction of the ketone using poly(methylhydrosiloxane) [20] was used successfully in this work



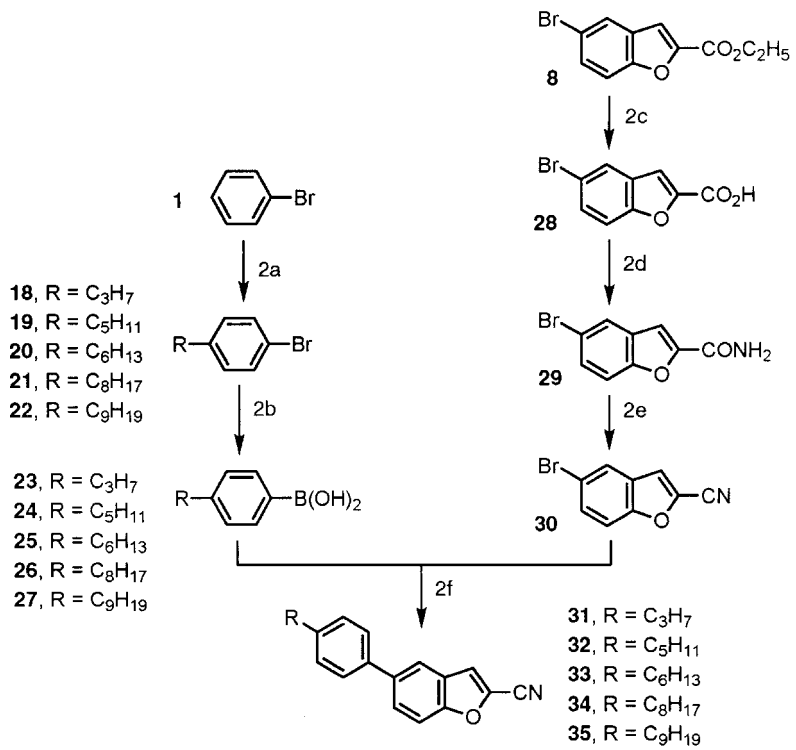
1a ... (i) heptanoyl chloride, $AlCl_3$, DCM; (ii) poly(methylhydrosiloxane)
1b ... 1-bromononane, K_2CO_3, butanone
1c ... (i) Mg, THF; (ii) trimethyl borate; (iii) aq HCl
1d ... diethyl bromomalonate, K_2CO_3, butanone
1e ... $Pd(PPh_3)_4$, Na_2CO_3, DME
1f ... (i) KOH, H_2O, EtOH; (ii) aq HCl
1g ... (i) thionyl chloride, benzene; (ii) ammonia, THF
1h ... thionyl chloride, DMF
1i ... CH_3OH, H_2SO_4

Scheme 1. A synthetic route to 2-cyano-5-(4-alkyl/alkoxyphenyl)benzo[*b*]furans.

and the method is particularly useful when the ketone contains other functional groups (e.g. I, Br, $-CO_2R$) which are sensitive to Wolff–Kishner conditions [21].

3. Discussion of transition temperatures

The transition temperatures for the benzo[*b*]furans which have been prepared are given in table 1, along with the values for the related biphenyl, terphenyl and naphthyl compounds. The $T_{N\text{-}I}$ values of the benzo[*b*]-furans are consistently higher than the values for the biphenyl or terphenyl analogues which are related by replacing a benzo[*b*]furan unit with a phenyl unit. For the 4-alkylphenyl derivatives of benzo[*b*]furan (compounds **16**, **31**–**35**), the $T_{N\text{-}I}$ values are on average 16.2°C higher than for the corresponding biphenyls and the differences gradually decrease with increasing terminal chain length; for the series with an odd number of carbon atoms in the terminal chain, the differences are 23.4, 21.1, 17.7 and 10.5°C, respectively, for the $C_3/C_5/C_7/C_9$



2a ... (i) RCOCl, $AlCl_3$, DCM; (ii) poly(methylhydrosiloxane)
2b ... (i) Mg, THF; (ii) trimethyl borate; (iii) aq HCl
2c ... (i) KOH, H_2O, EtOH; (ii) aq HCl
2d ... (i) thionyl chloride, benzene; (ii) ammonia, THF
2e ... thionyl chloride, DMF
2f ... $Pd(PPh_3)_4$, Na_2CO_3, DME

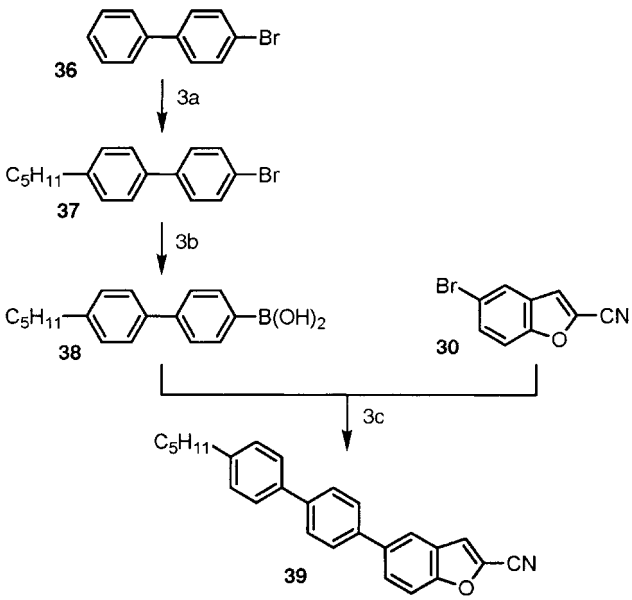
Scheme 2. An alternative synthetic route to 5-(4-alkylphenyl)-2-cyanobenzo[*b*]furans.

sequence, and 16.2 to 8.3°C, respectively, for the C_6/C_8 pair of compounds. The $T_{N\text{-}I}$ values for the odd-series of benzo[*b*]furans lie on a gradually rising curve (48.9, 56.4, 60.5, 60.0°C) which has levelled off at the C_9 compound; the two members of the even-series show a similar small increase with chain length (45.2 and 48.8°C) and the $C_5/C_6/C_7/C_8/C_9$ series shows a clear odd–even effect with the values for the odd-series, as expected, being on the higher curve.

In the 4-alkyl-4′-cyanobiphenyl series the octyl compound (**44**) is the first member to show a smectic A phase. The same is true for the benzo[*b*]furans with the C_8 compound (**34**) being the first to be smectogenic, giving a smectic A phase of slightly higher thermal stability than for the biphenyl analogue; the stability of the smectic A phase increases for the C_9 compound. The bent shape of the benzo[*b*]furans would be expected detrimentally to affect the smectic phase stability more than the nematic phase stability and yet, on the contrary, the polarity of the heterocyclic oxygen might enhance smectic phase stability. From the values in table 1, it seems that shape is the more influential of the two factors as the smectic stabilities of the benzo[*b*]furans (**34**, **35**, **17**) are raised to a smaller extent (0.8, 1.6 and 9.5°C) than the nematic stabilities (8.3, 10.5 and 17.0°C), in comparison with the biphenyls (**44**, **45**, **46**, respectively).

Similar results are shown for the alkoxy example **17** which has higher smectic and nematic transition temperatures than the biphenyl analogue **46**. The similarities are continued further for the biphenylbenzo[*b*]furan (**39**) and its terphenyl relative (**48**), with the former compound again showing higher smectic and nematic phase thermal stability.

The melting point variations for the pairs of benzo[*b*]-furans and biphenyl or terphenyl analogues are less consistent than for the mesophase stabilities discussed above. In most cases the benzo[*b*]furans have higher melting points (compounds **16**, **32–34**, **39**), but usually the differences are less than 10°C. However, increases of 27.1 and 10.9°C for compounds **32** and **33**, respectively, and the decrease of 13.9°C for compound **35** show the unpredictability of melting points.



3a ... (i) pentanoyl chloride, anhydrous $AlCl_3$, DCM; (ii) poly(methylhydrosiloxane)
3b ... (i) n-BuLi, THF; (ii) trimethyl borate; (iii) aq HCl
3c ... $Pd(PPh_3)_4$, Na_2CO_3, DME

Scheme 3. A synthetic route to 2-cyano-5-(4′-pentylbiphenyl-4-yl)-benzo[*b*]furan.

The results given in table 1 show that the nematic character of a cyanobiphenyl or cyanoterphenyl is enhanced by 'grafting' the furan moiety onto the end of the biphenyl core to give a benzo[*b*]furan. It appears that, on balance, the benefits of greater polarizability arising from the additional double-bond and the oxygen atom outweigh the disadvantage of the deviation from the ideal calamitic shape. A phenylnaphthalene, in comparison with a biphenyl unit, can formally be viewed as having an extra 'diene'/aromatic ring fused onto the biphenyl core; in this case an increase in polarizability is achieved and the cyano group is still collinear with the molecular long axis, preserving a reasonable calamitic shape. For these reasons, a phenylnaphthalene (see **47** in table 1) is much superior to the benzo[*b*]furan (**32**) or biphenyl (**41**) in promoting mesogenicity.

Five of the intermediates (**9–13**) in the synthetic routes are mesogenic, and their transition temperatures are shown in table 2 along with the values for the corresponding biphenyl compounds (**49–53**). In these cases, unlike the case of the 2-cyano compounds discussed above, the benzofuran systems have clearing points that are 20–40°C lower than for the biphenyl analogues; the mesophase types are similar in both systems. A reason for the different behaviour of the cyano compounds in relation to the carboxylic acids and esters may be based on the different molecular shapes that these functional groups generate (see figure 4). The 'non-polar' esters **9**, **10** and **13** (**XIV**) exist as single molecular units and the deviation from linearity caused by the furan ring is the overriding effect which decreases mesogenicity. The acids **11** and **12** (**XV**) exist as hydrogen-bonded dimers (which give much higher transition temperatures than the esters) but the deviations from linearity are still apparent and the transition temperatures are lower than for the linear biphenyls. The cyano compounds **16**, **17**, **31–35**, **39** (**XVI** and **XVII**) will undergo anti-parallel correlation of their molecular dipoles and so the deviations from linearity are suppressed by the molecular overlap and the advantages of increased polarizability lead to higher mesophase stabilities.

All of the benzofuran esters (**9**, **10** and **13**) with short alkyloxy chains in the ester group give monotropic smectic A phases and there is no indication of the smectic AB transitions or smectic B, CrB or CrE phases which occur with the analogous biphenyl compounds (**51–54**); the angular shape of the benzofuran unit or longer, more flexible alkyloxy ester chain (**55**) seemingly prevents the occurrence of the more ordered smectic phases.

4. Experimental

4.1. *Characterization*

Confirmation of the structures of intermediates and products was obtained by ^{1}H NMR spectroscopy (JEOL Lambda 400 or a JEOL JNM-GX270 spectrometer with tetramethylsilane as the internal standard for all samples), infrared spectroscopy (Perkin-Elmer 783 spectrophotometer or a Perkin-Elmer 1000 Fourier transform FTIR 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 monitored frequently using a Chrompack

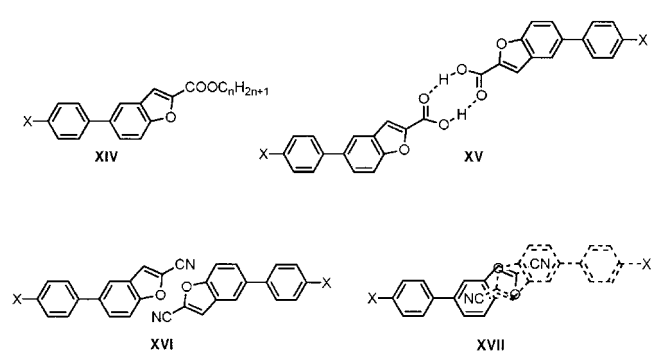
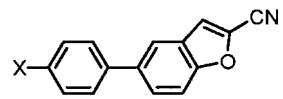
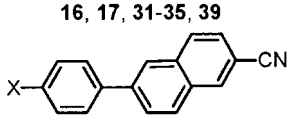


Figure 4. The shapes of ester, acid and cyano derivatives of benzo[*b*]furans. (For clarity, the antiparallel association in **XVII** is shown for separated structures in **XVI**.)

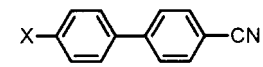
Table 1. Transition temperatures (°C) of 2-cyano-5-(4-substituted-phenyl)benzo[*b*]furans (**16**, **17**, **31–35**, **39**) and their biphenyl (**40–46**), naphthyl (**47**) and terphenyl (**48**) analogues.



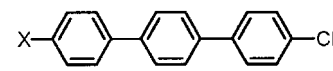
16, 17, 31-35, 39



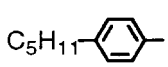
47



40-46



48

Compound	*X*	Cr		CrB		SmA		N		I
31	C_3H_7	•	58.0	—	—	—	—	(•	48.9)	•
40	C_3H_7	•	66.0	—	—	—	—	(•	25.5)	•
32	C_5H_{11}	•	51.1	—	—	—	—	•	56.4	•
41	C_5H_{11}	•	24.0	—	—	—	—	•	35.3	•
47	C_5H_{11}	•	68.0	—	—	—	—	•	130.0	•
33	C_6H_{13}	•	25.4	—	—	—	—	•	45.2	•
42	C_6H_{13}	•	14.5	—	—	—	—	•	29.0	•
16	C_7H_{15}	•	31.1	—	—	—	—	•	60.5	•
43	C_7H_{15}	•	30.0	—	—	—	—	•	42.8	•
34	C_8H_{17}	•	28.2	—	—	•	34.3	•	48.8	•
44	C_8H_{17}	•	21.5	—	—	•	33.5	•	40.5	•
35	C_9H_{19}	•	28.1	—	—	•	49.6	•	60.0	•
45	C_9H_{19}	•	42.0	—	—	•	48.0	•	49.5	•
17	$C_9H_{19}O$	•	62.0	—	—	•	87.0	•	97.0	•
46	$C_9H_{19}O$	•	64.0	—	—	•	77.5	•	80.0	•
39		•	134.0	•	147.3	—	—	•	255.6	•
48	C_5H_{11}	•	131.0	—	—	—	—	•	240.0	•

Biphenyl and terphenyl values are from reference [4].
Naphthyl value from [10].
() ... indicates a monotropic transition.

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. 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 DSC-7 and IBM data station). DSC analyses were carried out using a Perkin-Elmer 7 Series/Unix DSC with an indium standard. The purities of all final compounds were checked by GLC analysis (see above) and by HPLC analysis (Microsorb C18 80-215-C5 RP column); they were found to be > 99.5% pure. Gravity column chromatography was carried out using Kieselgel 60 (230–400 mesh) silica gel obtained from Merck (Darmstadt); the eluents were as detailed in the text.

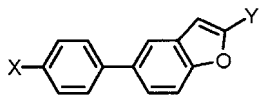
Elemental analyses of products were carried out using a Fisons EA 1108 CHN analyser and were within acceptable limits. Tetrakis(triphenylphosphine)palladium(0) was prepared according to the literature procedure [27]. Arylboronic acids are difficult to obtain pure because of the possibility of anhydride formation and they were used without purification in the cross-coupling reactions.

4.2. *Synthesis*

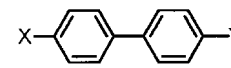
4.2.1. *1-Bromo-4-heptylbenzene (**3**)*

Anhydrous aluminium chloride (19.8 g, 148 mmol) was added to a stirred solution of heptanoyl chloride (24.2 g, 163 mmol) in dry dichloromethane (DCM) (135 ml). A solution of bromobenzene (**1**) (21.2 g, 135 mmol) in dry DCM (45 ml) was added, and the mixure was heated under reflux overnight with exclusion of moisture; GLC analysis indicated a complete reaction. The mixture

Table 2. Transition temperatures (°C) of various 2-substituted-5-(4-substituted-phenyl)benzo[*b*]furans (**9–13**) and the related biphenyl compounds (**49–53**): () indicates a monotropic transition.



9-13



49-55

Compound	X	Y	Transitions
11	C_7H_{15}	CO_2H	Cr 131.0 SmC 185.0 N 222.0 I
49[a]	C_7H_{15}	CO_2H	Cr 164.0 SmC 232.0 N 258.0 I
12	$C_9H_{19}O$	CO_2H	Cr 212.2 SmC 223.0 I
50[b]	$C_9H_{19}O$	CO_2H	Cr 176.0 SmC 256.5 N 258.5 I
13	C_7H_{15}	CO_2CH_3	Cr 76.0 (SmA 51.0) I
51	C_7H_{15}	CO_2CH_3	Cr 61.0 CrE 88.5 CrB/SmA 89.6 I
9	C_7H_{15}	$CO_2C_2H_5$	Cr 39.0 (SmA 36.8) I
52	C_7H_{15}	$CO_2C_2H_5$	Cr 13.3 CrE 41.5 CrB 65.2 I
10	$C_9H_{19}O$	$CO_2C_2H_5$	Cr 85.8 (SmA 84.6) I
53[c]	$C_9H_{19}O$	$CO_2C_2H_5$	Cr 78.0 CrE 81.0 SmB 91.0 SmA 106.0 I
54[d]	C_8H_{17}	$CO_2C_2H_5$	Cr 64 (CrB 61.4 SmA 61.4) I
55[e]	C_8H_{17}	$CO_2C_3H_7$	Cr 60.0 (SmA 57.0) I

[a] Ref. [22] (compound number 3013) gives Cr 156 Sm 243 N 262 I.
[b] Ref. [23].
[c] Ref. [24].
[d] Ref. [25].
[e] Ref. [26].

was cooled in an ice/water bath and poly(methylhydrosiloxane) (21.7 g) was added dropwise with stirring. The mixture was heated under reflux overnight, whereon GLC analysis indicated a complete reaction. The solvent was removed *in vacuo* and the residue was poured into an ice/water mixture; sodium hydroxide solution (10%, 150 ml) was added to facilitate layer separation and to remove residual acid chloride. The separated aqueous layer was washed with ether (2 × 200 ml), and the combined organic layers were washed with sodium hydroxide solution (10%, 50 ml), water and brine, and dried ($MgSO_4$). Removal of the solvent *in vacuo* gave a residue which was purified by flash chromatography (silica gel/petroleum fraction b.p. 40–60°C), followed by distillation *in vacuo* to give a colourless oil. Yield 15.1 g (44%), b.p. 117°C at 0.1 mm Hg. ^{1}H NMR ($CDCl_3$) δ 7.38 (2H, d), 7.04 (2H, d), 2.54 (2H, t), 1.57 (2H, quint) 1.28 (8H, m), 0.88 (3H, t). IR (KBr) ν_{max} 2930, 1490, 1073, 828, 799 cm^{-1}. MS *m/z* 256, 254 (M^+), 199, 185, 171 (100%), 90.

4.2.2. *4-Heptylphenylboronic acid (**5**)*

Compound **3** (20.0 g, 78 mmol) in dry tetrahydrofuran (THF) (80 ml) was added in one portion to oven-dried magnesium (2.2 g, 90 mmol) in dry THF (100 ml) with stirring under nitrogen. A crystal of iodine was added, and the mixture was heated under reflux (2.5 h) and allowed to return to room temperature. Dry THF (80 ml) was added and the mixture was cooled to −40°C. Trimethyl borate (16.2 g, 156 mmol) was added dropwise, keeping the temperature below −10°C. The mixture was allowed to return to room temperature overnight and hydrochloric acid (5M, 36 ml) was added with stirring (45 min). The mixture was then poured into water and ether (150 ml) added. The separated aqueous layer was washed twice with ether (2 × 200 ml), and the product was extracted from the combined ethereal phases as the potassium salt by washing with potassium hydroxide (2M, 80 ml). The basic solution was then washed with ether, and the product released by acidification to pH3 by adding hydrochloric acid (conc.) to the aqueous solution. The product was then extracted into ether (2 × 200 ml), and the combined ether solutions were washed with water and brine, dried ($MgSO_4$), and the solvent removed *in vacuo* to leave a pale-brown solid. Yield 15.8 g (92%). MS *m/z* 220 (M^+), 192, 135, 122, 107 (100%).

4.2.3. *4-Nonyloxybenzeneboronic acid (**6**)*

Compound **6** was prepared by a similar procedure to that described for the preparation of compound **5** using the quantities stated. 1-Bromo-4-nonyloxybenzene (**4**)

[28] (5.0 g, 17 mmol), magnesium (0.5 g, 0.021 gatom), trimethyl borate (3.5 g, 34 mmol). A pale yellow solid was obtained. Yield 4.0 g (88%). MS *m/z* 264 (M^+), 238, 220, 151, 94 (100%).

4.2.4. *Ethyl 5-bromobenzo[b]furan-2-carboxylate (**8**)*

A mixture of 5-bromosalicylaldehyde (**7**) (40.0 g, 200 mmol), diethyl bromomalonate (40.0 g, 168 mmol) and potassium carbonate (50.0 g, 360 mmol) was heated under reflux in butanone (600 ml) for 7 h; GLC analysis revealed a complete reaction. When cool, the solvent was removed *in vacuo*, and water (500 ml) and DCM (500 ml) were added. The separated aqueous layer was washed twice with DCM (2 × 250 ml) and the combined organic layers were dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue recrystallized (ethanol) to give pale yellow needle-like crystals. Yield 20.0 g (44%), m.p. 58–60°C, lit. [16] 90°C. ^{1}H NMR ($CDCl_3$) δ 7.82 (1H, d), 7.54 (1H, dd), 7.47 (1H, d), 7.46 (1H, s), 4.46 (2H, q), 1.43 (3H, t). IR (KBr) ν_{max} 1730, 1555, 1310, 1185, 855 cm^{-1}. MS *m/z* 270, 268 (M^+), 240, 225 (100%), 196, 169.

4.2.5. *Ethyl 5-(4-heptylphenyl)benzo[b]furan-2-carboxylate (**9**)*

Compound **8** (2.0 g, 7.4 mmol), sodium carbonate (2.0 g, 18.9 mmol), 1,2-dimethoxyethane (DME) (10 ml) and water (30 ml), were stirred under nitrogen, and tetrakis-(triphenylphosphine)palladium(0) (0.3 g, 0.3 mmol) was added, followed by compound **5** (2.0 g, 9.1 mmol) in DME (20 ml), and the mixture was heated under reflux for 4 h; completion of the reaction was indicated by GLC and TLC analysis. The solution was allowed to cool and was poured into water; ether (150 ml) was added. The separated aqueous layer was washed with ether (2 × 100 ml), and the combined ethereal layers were washed with water and brine and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue purified by flash chromatography (silica gel/petroleum fraction b.p. 40–60°C, to collect the impurity; petroleum fraction b.p. 40–60°C: dichloromethane 7:3 to collect the product). The product was recrystallised (hexane) to give colourless needles. Yield 1.3 g (48%), transition temperatures (°C) Cr 39.0 (SmA 36.8) I. ^{1}H NMR ($CDCl_3$) δ 7.84 (1H, dd), 7.67 (1H, dd), 7.63 (1H, d), 7.56 (1H, d), 7.52 (2H, d), 7.27 (2H, d), 4.46 (2H, q), 2.65 (2H, t), 1.65 (2H, qui), 1.44 (3H, t), 1.33 (8H, m), 0.89 (3H, t). IR (KBr) ν_{max} 2930, 1725, 1560, 1160, 1095 cm^{-1}. MS *m/z* 364 (M^+) (100%), 279, 264, 251, 220.

4.2.6. *Ethyl 5-(4′-nonyloxyphenyl)benzo[b]furan-2-carboxylate (**10**)*

Compound **10** was prepared by a similar procedure to that described for the preparation of compound **9** using the quantities stated. Compound **8** (1.5 g, 5.6 mmol), compound **6** (1.8 g, 6.8 mmol), sodium carbonate (1.5 g, 14 mmol), tetrakis(tripheny lphosphine)palladium(0) (0.2 g, 0.2 mmol). A white solid was obtained. Yield 0.7 g (31%), transition temperatures (°C) Cr 85.8 (SmA 84.6) I. ^{1}H NMR (CD_2Cl_2) δ 7.83 (1H, d), 7.66 (1H, dd), 7.62 (1H, d), 7.55 (1H, s), 7.54 (2H, d), 6.98 (2H, d), 4.41 (2H, q), 4.00 (2H, t), 1.80 (2H, quint), 1.41 (3H, t), 1.30 (12H, m), 0.89 (3H, t). IR (KBr) ν_{max} 2923, 2852, 1722, 1607, 1574, 1517, 1164, 945, 839, 747 cm^{-1}. MS *m/z* 408 (M^+), 281, 227, 97, 57 (100%).

4.2.7. *5-(4-Heptylphenyl)benzo[b]furan-2-carboxylic acid (**11**)*

Potassium hydroxide (0.5 g, 8.9 mmol) in ethanol (30 ml) and water (3 ml) was added to compound **9** (1.2 g, 3.3 mmol) and the mixture was heated under reflux (5 min) with stirring. The solvent was then removed *in vacuo* and water (75 ml) was added to the residue, which was then adjusted to pH 3 by adding hydrochloric acid (2M). The precipitated white solid was filtered off and dried *in vacuo* ($CaCl_2$), then recrystallized (acetic acid) to give white, fibrous needles. Yield 0.7 g (63%), transition temperatures (°C) Cr 131.0 SmC 185.0 N 222.0 I. ^{1}H NMR ($CDCl_3$) δ 7.88 (1H, dd), 7.74 (1H, dd), 7.74 (1H, d), 7.67 (1H, d), 7.54 (2H, d), 7.28 (2H, d), 7.27 (1H, s), 2.66 (2H, t), 1.65 (2H, quint), 1.33 (8H, m), 0.89 (3H, m). IR (KBr) ν_{max} 2950, 2850, 1690, 1575, 1310, 1170, 805 cm^{-1}. MS *m/z* 336 (M^+), 292, 251 (100%), 231, 207.

4.2.8. *5-(4-Nonyloxyphenyl)benzo[b]furan-2-carboxylic acid (**12**)*

Compound **12** was prepared by a similar procedure to that described for the preparation of compound **11** using the quantities stated. Compound **10** (0.7 g, 1.7 mmol), potassium hydroxide (0.2 g, 3.6 mmol). A white crystalline solid was obtained. Yield 0.5 g, (77%), transition temperatures (°C) Cr 212.2 SmC 223.0 I. ^{1}H NMR (CD_2Cl_2) δ 7.87 (1H, d), 7.72 (1H, dd), 7.69 (1H, s), 7.65 (1H, d), 7.54 (2H, d), 6.99 (2H, d), 4.01 (2H, t), 1.80 (2H, quint), 1.48 (2H, m), 1.30 (10H, m), 0.89 (3H, t), the acidic proton was not detected. IR (KBr) ν_{max} 3420, 2920, 2840, 2547, 1690, 1515, 1174, 942, 748 cm^{-1}. MS *m/z* 380 (M^+), 254 (100%) 225, 210, 180.

4.2.9. *Methyl 5-(4-heptylphenyl)benzo[b]furan-2-carboxylate (**13**)*

A mixture of compound **11** (0.1 g, 0.3 mmol) and sulphuric acid (conc.) (0.1 ml) in methanol (5 ml) was heated under reflux (24 h) with exclusion of moisture. The mixture was allowed to cool and was then poured into water (20 ml) and washed with DCM (20 ml). The separated aqueous layer was washed again with DCM

(2 × 20 ml) and the combined organic layers were washed with water and brine, dried ($MgSO_4$), and the solvent removed *in vacuo*. The product was purified by recrystallization (hexane) to give a white, crystalline solid. Yield 0.1 g (95%), transition temperatures (°C) Cr 76.0 (SmA 51.0) I. ^{1}H NMR (CD_2Cl_2) δ 7.88 (1H, d), 7.70 (1H, dd), 7.64 (1H, d), 7.57 (1H, d), 7.53 (2H, d), 7.28 (2H, d), 3.95 (3H, s), 2.66 (2H, s), 1.65 (2H, qui), 1.32 (8H, m), 0.89 (3H, t). IR (KBr) ν_{max} 2930, 2856, 1736, 1565, 1438, 1164, 1099, 898, 847, 767 cm^{-1}. MS *m/z* 350 (M^+), 293, 265 (100%), 177, 165.

4.2.10. *5-(4-Heptylphenyl)benzo[b]furan-2-carboxamide (**14**)*

A mixture of compound **11** (0.70 g, 2.1 mmol) and thionyl chloride (0.75 g, 6.3 mmol) in dry benzene (25 ml) was heated under reflux (4 h) with exclusion of moisture. The solvent was then removed *in vacuo*, and the crude acid chloride dissolved in dry THF (20 ml). Ammonia (d 0.880, 0.7 ml) was then added with stirring. The mixture was stirred for a further 30 min, water (40 ml) was added and the precipitate was filtered off and washed with cold water; it was recrystallized (ethanol), and dried *in vacuo* overnight ($CaCl_2$) to give white crystals. Yield 0.55 g (78%), m.p. 201–202°C ^{1}H NMR ($CDCl_3$) δ 7.86 (1H, dd), 7.66 (1H, dd), 7.56 (1H, d), 7.56 (1H, d), 7.53 (2H, d), 7.27 (2H, d), 6.54 (1H, s), 5.65 (1H, s), 2.66 (2H, t), 1.66 (2H, quint), 1.31 (8H, m), 0.89 (3H, t). IR (KBr) ν_{max} 3471, 3396, 3183, 2922, 2849, 1661, 1616, 1395, 801 cm^{-1}. MS *m/z* 335 (M^+), 250 (100%), 191, 178, 165.

4.2.11. *5-(4-Nonyloxyphenyl)benzo[b]furan-2-carboxamide (**15**)*

Compound **15** was prepared by a similar procedure to that described for the preparation of compound **14** using the quantities stated. Compound **12** (0.9 g, 2.4 mmol), thionyl chloride (0.9 g, 7.6 mmol), ammonia (d 0.880, 1.4 ml). A white solid was obtained. Yield 0.8 g (82%), m.p. 201–202°C ^{1}H NMR (CD_2Cl_2) δ 7.83 (1H, dd), 7.65 (1H, dd), 7.57 (1H, d), 7.54 (2H, d), 7.49 (1H, d), 6.99 (2H, d), 6.53 (1H, s), 5.65 (1H, s), 4.00 (2H, t), 1.80 (2H, quint), 1.41 (12H, m), 0.88 (3H, t). IR (KBr) ν_{max} 3462, 2919, 2851, 1678, 1601, 1518, 1166, 941, 812 cm^{-1}. MS *m/z* 379 (M^+), 253 (100%), 225, 181, 152.

4.2.12. *2-Cyano-5-(4-heptylphenyl)benzo[b]furan (**16**)*

Thionyl chloride (1.8 g, 15 mmol) was added to a stirred solution of compound **14** (0.5 g, 1.5 mmol) in dry *N*,*N*-dimethylformamide (DMF) (10 ml) under nitrogen. The mixture was stirred overnight, and then poured into an ice/water mixture. The product was extracted into ether (2 × 100 ml), and the combined extracts were washed with water and saturated sodium bicarbonate solution and dried ($MgSO_4$). The solvent was removed *in vacuo* and the product purified by flash chromatography (silica gel/petroleum fraction b.p. 40–60°C: dichloromethane 1:1), followed by recrystallization (ethanol) to give colourless crystals. Yield 0.3 g (63%), transition temperatures (°C) Cr 31.1 N 60.5 I. ^{1}H NMR ($CDCl_3$) δ 7.83 (1H, d), 7.73 (1H, dd), 7.60 (1H, d), 7.51 (2H, d), 7.50 (1H, s), 7.28 (2H, d), 2.66 (2H, t), 1.65 (2H, quint), 1.33 (8H, m), 0.89 (3H, t). IR (KBr) ν_{max} 2920, 2850, 2230, 1460, 1130, 885, 800 cm^{-1}. MS *m/z* 317 (M^+), 232 (100%), 203, 190, 176.

4.2.13. *2-Cyano-5-(4-nonyloxyphenyl)benzo[b]furan (**17**)*

Compound **17** was prepared by a similar procedure to that described for the preparation of compound **16** using the quantities stated. Compound **15** (0.7 g, 1.8 mmol), thionyl chloride (2.3 g, 19 mmol). Colourless plate-like crystals were obtained. Yield 0.1 g (15%), transition temperatures (°C) Cr 62.0 SmA 87.0 N 97.0 I. ^{1}H NMR (CD_2Cl_2) δ 7.80 (1H, d), 7.70 (1H, dd), 1.58 (1H, d), 7.52 (1H, s), 7.51 (2H, d), 6.97 (2H, d), 3.98 (2H, t), 1.78 (2H, quint), 1.46 (2H, m), 1.28 (10H, m), 0.87 (3H, t). IR (KBr) ν_{max} 2930, 2859, 2236, 1688, 1517, 1182, 1032, 842, 808 cm^{-1}. MS *m/z* 361 (M^+), 248, 235 (100%), 206.

4.2.14. *1-Bromo-4-propylbenzene (**18**)*

Compounds **18–22** were prepared by a similar procedure to that described for the preparation of compound **3** using the quantities stated. Bromobenzene (**1**) (31.4 g, 200 mmol), propanoyl chloride (22.2 g, 240 mmol), aluminium chloride (29.5 g, 220 mmol), poly(methylhydrosiloxane) (32.1 g). A colourless liquid was obtained. Yield 19.2 g (48%), b.p. 115°C at 0.3 mm Hg. ^{1}H NMR ($CDCl_3$) δ 7.38 (2H, d), 7.05 (2H, d), 2.51 (2H, t), 1.61 (2H, sext), 0.92 (3H, t). IR (KBr) ν_{max} 2965, 2871, 1489, 1077, 1011, 828, 796 cm^{-1}. MS *m/z* 200, 198 (M^+), 169 (100%), 119, 103, 90.

4.2.15. *1-Bromo-4-pentylbenzene (**19**)*

Bromobenzene (**1**) (21.2 g, 135 mmol), pentanoyl chloride (19.7 g, 163 mmol), aluminium chloride (19.8 g, 148 mmol), poly(methylhydrosiloxane) (21.7 g). A colourless liquid was obtained. Yield 11.6 g (38%), b.p. 100°C at 0.2 mm Hg. ^{1}H NMR ($CDCl_3$) δ 7.38 (2H, d), 7.04 (2H, d), 2.54 (2H, t), 1.58 (2H, quint), 1.31 (4H, m), 0.88 (3H, t). IR (KBr) ν_{max} 2929, 2858, 1486, 1073, 830, 796 cm^{-1}. MS *m/z* 228, 226 (M^+), 198, 183, 171 (100%), 157.

4.2.16. *1-Bromo-4-hexylbenzene (**20**)*

Bromobenzene (**1**) (21.2 g, 135 mmol), hexanoyl chloride (20.0 g, 149 mmol), aluminium chloride (19.9 g, 149 mmol), poly(methylhydrosiloxane) (21.7 g). A colourless liquid

was obtained. Yield 10.4 g (32%), b.p. 110°C at 0.01 mm Hg. ^{1}H NMR ($CDCl_3$) δ 7.38 (2H, d), 7.03 (2H, d), 2.54 (2H, t), 1.57 (2H, quint), 1.29 (6H, m), 0.88 (3H, t). IR (KBr) ν_{max} 2933, 2861, 1489, 1075, 807, 525 cm^{-1}. MS *m/z* 242, 240 (M^+), 171 (100%), 103, 91.

4.2.17. *1-Bromo-4-octylbenzene (**21**)*

Bromobenzene (**1**) (21.2 g, 135 mmol), octanoyl chloride (24.2 g, 149 mmol), aluminium chloride (19.9 g, 149 mmol), poly(methylhydrosiloxane) (21.7 g). A colourless liquid was obtained. Yield 16.4 g (45%), b.p. 158°C at 0.9 mm Hg. ^{1}H NMR (CD_2Cl_2) δ 7.37 (2H, d), 7.06 (2H, d), 2.54 (2H, t), 1.56 (2H, quint), 1.26 (10H, m), 0.86 (3H, t). IR (KBr) ν_{max} 2932, 2859, 1489, 1074, 803, 519 cm^{-1}. MS *m/z* 270, 268 (M^+), 211, 169 (100%), 155, 89.

4.2.18. *1-Bromo-4-nonylbenzene (**22**)*

Bromobenzene (**1**) (21.2 g, 135 mmol), nonanoyl chloride (26.3 g, 149 mmol), aluminium chloride (19.9 g, 149 mmol), poly(methylhydrosiloxane) (21.7 g). A colourless liquid was obtained, which solidified to a waxy solid on standing. Yield 7.0 g (18%), b.p. 145°C at 0.01mm Hg. ^{1}H NMR ($CDCl_3$) δ 7.38 (2H, d), 7.04 (2H, d), 2.54 (2H, t), 1.58 (2H, quint), 1.27 (12H, m), 0.88 (3H, t). IR (KBr) ν_{max} 2934, 2859, 1490, 1074, 825, 798, 634, 510 cm^{-1}. MS *m/z* 284, 282 (M^+), 169, 91 (100%), 71.

4.2.19. *4-Propylbenzeneboronic acid (**23**)*

Compounds **23–27** were prepared by a similar procedure to that described for the preparation of compound **5** using the quantities stated. Compound **18** (11.0 g, 55 mmol), magnesium (1.5 g, 0.062 gatom), trimethyl borate (11.4 g, 110 mmol). An off-white solid was obtained. Yield 7.5 g (83%). MS *m/z* 164 (M^+), 147, 135, 91, 43 (100%).

4.2.20. *4-Pentylbenzeneboronic acid (**24**)* [29]

Compound **19** (15.2 g, 67 mmol), magnesium (1.9 g, 0.078 gatom), trimethyl borate (13.9 g, 134 mmol). A waxy solid was obtained. Yield 6.4 g (50%). MS *m/z* 522 ($3M^+$-$3H_2O$), 465 (100%), 409, 352, 175.

4.2.21. *4-Hexylbenzeneboronic acid (**25**)*

Compound **20** (8.0 g, 33 mmol), magnesium (1.0 g, 0.041 gatom), trimethyl borate (6.9 g, 66 mmol). A light-brown solid was obtained. Yield 4.8 g (71%). MS *m/z* 564 ($3M^+$-$3H_2O$), 535, 507, 493, 117 (100%).

4.2.22. *4-Octylbenzeneboronic acid (**26**)*

Compound **21** (6.0 g, 22 mmol), magnesium (0.7 g, 0.029 gatom), trimethyl borate (4.6 g, 44 mmol). A pale-yellow solid was obtained. Yield 4.2 g (82%). MS *m/z* 648 ($3M^+$-$3H_2O$), (100%), 551, 452, 353, 187.

4.2.23. *4-Nonylbenzeneboronic acid (**27**)*

Compound **22** (5.0 g, 18 mmol), magnesium (0.5 g, 0.021 gatom), trimethyl borate (3.7 g, 36 mmol). A waxy solid was obtained. Yield 3.7 g (83%). MS *m/z* 690 ($3M^+$-$3H_2O$), 578, 452, 354, 117 (100%).

4.2.24. *5-Bromobenzo[b]furan-2-carboxylic acid (**28**)*

Compound **28** was prepared by a similar procedure to that described for the preparation of compound **11** using the quantities stated. Compound **8** (27.5 g, 102 mmol), potassium hydroxide (11.5 g, 205 mmol). White crystals were obtained. Yield 16.6 g (68%), m.p. 293°C (DSC), lit. [30] 256–260°C. ^{1}H NMR (CD_2Cl_2) δ 7.80 (1H, dd), 7.49 (1H, dd), 7.44 (1H, d), 7.38 (1H, d), the acidic proton was not detected. IR (KBr) ν_{max} 3417, 1738, 1556, 1395, 1051, 946, 873, 803, 779 cm^{-1}. MS *m/z* 242, 240 (M^+), 223, 169, 89, 62 (100%).

4.2.25. *5-Bromobenzo[b]furan-2-carboxamide acid (**29**)*

Compound **29** was prepared by a similar procedure to that described for the preparation of compound **14** using the quantities stated. Compound **28** (16.5 g, 69 mmol), thionyl chloride (24.4 g, 205 mmol), ammonia (d 0.880, 46 ml). White needles were obtained. Yield 9.9 g (60%), m.p. 212–215°C, lit. [30] 211–213°C. ^{1}H NMR (DMSO-d^6) δ 7.80 (1H, d), 7.51 (1H, d), 7.40 (1H, dd), 7.32 (2H, s), 6.95 (1H, d). IR (KBr) ν_{max} 3024, 2860, 1591, 1563, 1473, 1318, 1179, 789, 422 cm^{-1}. MS *m/z* 241, 239 (M^+), 223, 169, 89, 62 (100%).

4.2.26. *5-Bromo-2-cyanobenzo[b]furan (**30**)*

Compound **30** was prepared by a similar procedure to that described for the preparation of compound **16** using the quantities stated. Compound **29** (9.8 g, 41 mmol), thionyl chloride (49.2 g, 415 mmol). Off-white needles were obtained. Yield 4.6 g (51%), m.p. 152.5–153.5°C, lit. [30] 149–151°C. ^{1}H NMR (CD_2Cl_2) δ 7.86 (1H, dd), 7.63 (1H, dd), 7.47 (1H, dd), 7.46 (1H, d). IR (KBr) ν_{max} 2230, 1552, 1437, 1183, 949, 810, 571, 478 cm^{-1}. MS *m/z* 223, 221 (M^+), (100%), 142, 114, 87, 58.

4.2.27. *2-Cyano-5-(4-propylphenyl)benzo[b]furan (**31**)*

Compounds **31–35** were prepared by a similar procedure to that described for the preparation of compound **9** using the quantities stated. Compound **30** (1.0 g, 4.5 mmol), compound **23** (0.9 g, 5.5 mmol), sodium carbonate (1.2 g, 11.3 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3 g, 0.3 mmol). White crystals were obtained. Yield 0.3 g (26%), transition temperatures (°C) Cr 58.0 (48.9 N) I. ^{1}H NMR (CD_2Cl_2) δ 7.86 (1H, dd), 7.75 (1H, dd), 7.62 (1H, d), 7.55 (1H, d), 7.52 (2H, d), 7.29 (2H, d), 2.64 (2H, t), 1.67 (2H, sext), 0.97 (3H, t). IR (KBr) ν_{max} 2962, 2871, 2229, 1560, 1460,

1266, 1126, 885, 801, 612 cm^{-1}. MS *m/z* 261 (M^+), 232 (100%), 203, 176, 151.

4.2.28. *2-Cyano-5-(4-pentylphenyl)benzo[b]furan (**32**)*

Compound **30** (0.6 g, 2.7 mmol), compound **24** (0.6 g, 3.1 mmol), sodium carbonate (0.7 g, 6.6 mmol), tetrakis-(triphenylphosphine)palladium(0) (0.2 g, 0.2 mmol). Colourless plates were obtained. Yield 0.3 g (38%), transition temperatures (°C) Cr 51.1 N 56.4 I. ^{1}H NMR (CD_2Cl_2) δ 7.87 (1H, dd), 7.75 (1H, dd), 7.61 (1H, ddd), 7.54 (1H, d), 7.52 (2H, d), 7.28 (2H, d), 2.66 (2H, t), 1.65 (2H, quint), 1.34 (4H, m), 0.91 (3H, t). IR (KBr) ν_{max} 2965, 2861, 2232, 1558, 1439, 1187, 949, 819, 524 cm^{-1}. MS *m/z* 289 (M^+), 232 (100%), 203, 189, 176.

4.2.29. *2-Cyano-5-(4-hexylphenyl)benzo[b]furan (**33**)*

Compound **30** (1.0 g, 4.5 mmol), compound **25** (1.0 g, 4.9 mmol), sodium carbonate (1.2 g, 11 mmol), tetrakis-(triphenylphosphine)palladium(0) (0.3 g, 0.3 mmol). Colourless crystals were obtained. Yield 0.3 g (22%), transition temperatures (°C) Cr 25.4 N 45.2 I. ^{1}H NMR ($CDCl_3$) δ 7.83 (1H, d), 7.73 (1H, dd), 7.60 (1H, d), 7.51 (2H, d), 7.49 (1H, s), 7.28 (2H, d), 2.66 (2H, t), 1.66 (2H, quint), 1.39–1.31 (6H, m), 0.90 (3H, t). IR (KBr) ν_{max} 2933, 2861, 2235, 1561, 1271, 1128, 951, 808 cm^{-1}. MS *m/z* 303 (M^+), 274, 246, 232 (100%), 219.

4.2.30. *2-Cyano-5-(4-octylphenyl)benzo[b]furan (**34**)*

Compound **30** (1.6 g, 7.2 mmol), compound **26** (2.0 g, 8.5 mmol), sodium carbonate (1.9 g, 18 mmol), tetrakis-(triphenylphosphine)palladium(0) (0.2 g, 0.2 mmol). A colourless liquid crystal was obtained. Yield 0.5 g (21%), transition temperatures (°C) Cr 28.2 SmA 34.3 N 48.8 I. ^{1}H NMR (CD_2Cl_2) δ 7.87 (1H, dd), 7.45 (1H, dd), 7.62 (1H, d), 7.55 (1H, d), 7.53 (2H, d), 7.29 (2H, d), 2.66 (2H, t), 1.65 (2H, quint), 1.35–1.29 (10H, m), 0.89 (3H, t). IR (KBr) ν_{max} 2932, 2859, 2235, 1561, 1464, 1184, 951, 807 cm^{-1}. MS *m/z* 331 (M^+), 260, 232 (100%), 203, 57.

4.2.31. *2-Cyano-5-(4-nonylphenyl)benzo[b]furan (**35**)*

Compound **30** (1.0 g, 4.5 mmol), compound **27** (1.2 g, 4.8 mmol), sodium carbonate (1.2 g, 11 mmol), tetrakis-(triphenylphosphine)palladium(0) (0.3 g, 0.3 mmol). Colourless needles were obtained. Yield 0.5 g (32%), transition temperatures (°C) Cr 28.1 SmA 49.6 N 60.0 I. ^{1}H NMR (CD_2Cl_2) δ 7.86 (1H, dd), 7.75 (1H, dd), 7.61 (1H, d), 7.55 (1H, d), 7.52 (2H, d), 7.29 (2H, d), 2.66 (2H, t), 1.65 (2H, quint), 1.31 (12H, m), 0.89 (3H, t). IR (KBr) ν_{max} 2929, 2858, 2333, 1464, 1127, 950, 887, 805 cm^{-1}. MS *m/z* 345 (M^+), 231 (100%), 218, 190, 176.

4.2.32. *1-Bromo-4′-pentylbiphenyl (**37**)*

Compound **37** was prepared by a similar procedure to that described for the preparation of compound **3** using the quantities stated. 4-Bromobiphenyl (**36**) (35.0 g, 150 mmol), pentanoyl chloride (21.8 g, 181 mmol), aluminium chloride (22.0 g, 165 mmol), poly(methylhydrosiloxane) (24.0 g). Dry 1,2-dichloroethane (600 ml) was used in place of dry DCM. The product was recrystallized from ethanol to give a pale-brown solid. Yield 21.1 g (46%), m.p. 94–96°C. ^{1}H NMR (CD_2Cl_2) δ 7.56 (2H, d), 7.49 (2H, d), 7.48 (2H, d), 7.27 (2H, d), 2.64 (2H, t), 1.65 (2H, quint), 1.36 (4H, m), 0.90 (3H, t). IR (KBr) ν_{max} 2931, 2865, 1690, 1137, 1079, 803, 502 cm^{-1}. MS *m/z* 304, 302 (M^+), 247 (100%), 165, 152, 139.

4.2.33. *4′-Pentylbiphenyl-4-ylboronic acid (**38**)* [29]

n-Butyllithium (2.5M in hexanes, 23.0 ml, 57.5 mmol) was added dropwise to a stirred solution of compound **37** (10.0 g, 33.0 mmol) in dry THF (90 ml) at −70°C under nitrogen. The stirring was continued for 30 min and trimethyl borate (6.9 g, 66 mmol) was added dropwise, maintaining the temperature below −10°C. The system was allowed to return to room temperature overnight with stirring under nitogren. Hydrochloric acid (5M, 14 ml) was then added with stirring and the mixture was poured into water; ether (150 ml) was added. The separated aqueous layer was washed with ether (2 × 200 ml) and the combined organic layers were washed with water and brine, dried ($MgSO_4$), and the solvent removed *in vacuo* to give a light-brown solid. Yield 7.2 g (81%). MS *m/z* 268 (M^+), 224, 183 (100%), 167, 152.

4.2.34. *2-Cyano-5-(4′-pentylbiphenyl)benzo[b]furan (**39**)*

Compound **39** was prepared by a similar procedure to that described for the preparation of compound **9** using the quantities stated. Compound **30** (0.6 g, 2.7 mmol), compound **38** (1.1 g, 4.1 mmol), sodium carbonate (0.7 g, 6.6 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3 g, 0.3 mmol). Colourless needles were obtained. Yield 0.1 g (10%), transition temperatures (°C) Cr 134.0 CrB 147.3 N 255.6 I. ^{1}H NMR (CD_2Cl_2) δ 7.94 (1H, dd), 7.82 (1H, dd), 7.71 (2H, d), 7.69 (2H, d), 7.66 (1H, ddd), 7.58 (2H, d), 7.57 (1H, d), 7.29 (2H, d), 2.66 (2H, t), 1.66 (2H, quint), 1.36 (4H, m), 0.92 (3H, t). IR (KBr) ν_{max} 2931, 2862, 2237, 1505, 1179, 949, 805 cm^{-1}. MS *m/z* 365 (M^+, 100%), 346, 308, 252, 58.

4.2.35. *Methyl 4′-heptylbiphenyl-4-carboxylate (**51**)*

Compounds **51** and **52** were prepared by a similar procedure to that described for the preparation of compound **13** using the quantities stated. 4′-Heptylbiphenyl-4-carboxylic acid (**49**) was prepared from 4-bromo-4′-heptylbiphenyl [31] by lithiation and carboxylation; transition temperatures (°C) Cr 164.0 SmC 232.0 N 258.0 I.

4′-Heptylbiphenyl-4-carboxylic acid (**49**) (0.3 g, 1.0 mmol) and sulphuric acid (conc.) (0.1 ml) in methanol (10 ml). An off-white, crystalline solid was obtained. Yield 0.3 g (70%), transition temperatures (°C) Cr 61.0 CrE 88.5 CrB/SmA 89.6 I. ^{1}H NMR ($CDCl_3$) δ 8.09 (2H, d), 7.65 (2H, d), 7.54 (2H, d), 7.27 (2H, d), 3.95 (3H, s), 2.65 (2H, t), 1.65 (2H, qui), 1.30 (8H, m), 0.88 (3H, t). IR (KBr) ν_{max} 2925, 2860, 1727, 1609, 1112, 766 cm^{-1}. MS *m*/*z* 310 (M^+), 225, 165, 83, 43 (100%).

4.2.36. *Ethyl 4′-heptylbiphenyl-4-carboxylat e (**52**)*

4′-Heptylbiphenyl-4-carboxylic acid (**49**) (0.3 g, 1.0 mmol) and sulphuric acid (conc.) (0.1 ml) in ethanol (10 ml). A white, waxy solid was obtained. Yield 0.2 g (62%), transition temperatures (°C) Cr 13.3 CrE 41.5 CrB 65.2 I. ^{1}H NMR ($CDCl_3$) δ 8.10 (2H, d), 7.65 (2H, d), 7.55 (2H, d), 7.28 (2H, d), 4.40 (2H, q), 2.65 (2H, t), 1.65 (2H, qui), 1.41 (3H, t), 1.30 (8H, m), 0.88 (3H, t). IR (KBr) ν_{max} 2930, 2850, 1722, 1611, 1109, 823, 769 cm^{-1}. MS *m*/*z* 324 (M^+), 253, 239 (100%), 225, 211.

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References

[1] Gray, G. W., Harrison, K. J., and Nash, J. A., 1973, *Electron. Lett.*, **9,** 130.
[2] Gray, G. W., and Harrison, K. J., USP 3 947 375.
[3] Hilsum, C., 1984, in *Technology of Chemicals and Materials for Electronics*, edited by E. R. Howells (Chichester: Ellis Horwood Ltd.), Chap. 3.
[4] Gray, G. W., 1978, *Advances in liquid crystal materials for applications*, BDH Special Publication, BDH Chemicals Ltd, Poole, England.
[5] Eidenschink, R., Erdmann, D., Krause, J., and Pohl, L., 1977, *Angew. Chem., int. Ed. Engl.*, **16,** 100.
[6] Eidenschink, R., Erdmann, D., Krause, J., and Pohl, L., 1978, *Angew. Chem., int. Ed. Engl.*, **17,** 133.
[7] Demus, D., and Zaschke, H., 1981, *Mol. Cryst. liq. Cryst.*, **63,** 129.
[8] Gray, G. W., and Kelly, S. M., 1981, *J. chem. Soc., Perkin II*, 26.
[9] Boller, A., Cereghetti, M., Schadt, M., and Scherrer, H., 1977, *Mol. Cryst. liq. Cryst.*, **42,** 215.
[10] Hird, M., Gray, G. W., and Toyne, K. J., 1991, *Mol. Cryst. liq. Cryst.*, **206,** 187.
[11] Gray, G. W., and Lacey, D., 1983, *Mol. Cryst. liq. Cryst.*, **99,** 123.
[12] Vill, V., 1999, *LiqCryst Database of Liquid Crystalline Compounds for Personal Computers* (Hamburg: LCI Publisher GmbH).
[13] Chen, X.-H., Walba, D. M., Shao, R., and Clark, N. A., 1996, in Proceedings of the 16th International Liquid Crystal Conference, Kent, USA, Abstract D3P.22.
[14] Destrade, C., Nguyen, H. T., Mamlok, L., and Malthete, J., 1984, *Mol. Cryst. liq. Cryst.*, **114,** 139.
[15] Destrade, C., Nguyen, H. T., Gasparoux, H., and Mamlok, L., 1987, *Liq. Cryst.*, **2,** 229.
[16] Kurdukar, R., and Rao, N. V. S., 1963, *Proc. Indian Acad. Sci., A*, **58,** 336.
[17] Miyaura, N., Yanagi, T., and Suzuki, A., 1981, *Synth. Commun.*, **11,** 513.
[18] Miyaura, N., and Suzuki, A., 1995, *Chem. Rev.*, **95,** 2457.
[19] Gray, G. W., Hird, M., Lacey, D., and Toyne, K. J., 1989, *J. chem. Soc., Perkin Trans. 2*, 2041.
[20] Jaxa-Chamiec, A., Shah, V. P., and Kruse, L. I., 1989, *J. chem. Soc., Perkin Trans. 1*, 1705.
[21] To be published.
[22] Demus, D., Demus, H., and Zaschke, H., 1974, *Flussige Kristalle in Tabellen*, Vol. I (VEB Deutscher Verlag fur Grundstoffindustrie, Germany).
[23] Gray, G. W., Hartley, J. B., and Jones, B., 1955, *J. chem. Soc.*, 1412.
[24] Goodby, J. W., and Gray, G. W., 1976, *J. Phys. Colloq. C3*, **37,** (C3)17.
[25] Goodby, J. W., 1984, *Liq. Cryst. Ordered Fluids*, **4,** 175.
[26] Vill, V., 1986, Diploma thesis, Muenster.
[27] Coulson, D. R., 1972, *Inorg. Synth.*, **13,** 121.
[28] Lock, S. J., Goodby, J. W., Hird, M., and Toyne, K. J., 1995, *J. mater. Chem.*, **5,** 2175.
[29] Gray, G. W., Hird, M., and Toyne, K. J., 1991, *Mol. Cryst. liq. Cryst.*, **195,** 221.
[30] Dann, O., Fick, H., Pietzner, B., Walkenhorst, E., Fernbach, R., and Zeh, D., 1975, *Liebigs Ann. Chem.*, 160.
[31] Gough, N., 1999, PhD thesis, University of Hull, UK.