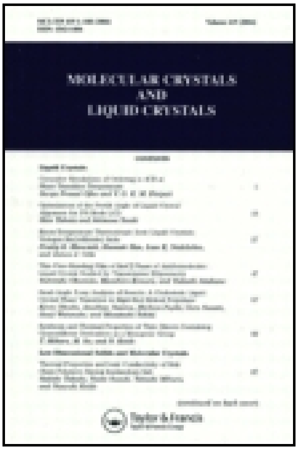

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The Synthesis and Transition Temperatures of Some Lateral Monofluoro-substituted 4,4″- Dialkyl- and 4,4″-Alkoxyalkyl- 1, 1′: 4′,1″-terphenyls

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The Synthesis and Transition Temperatures of Some Lateral Monofluoro-substituted 4,4″-Dialkyl- and 4,4″-Alkoxyalkyl-1,1′:4′,1″-terphenyls

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The tetrakis(triphenylphosphine)palladium(0)-catalysed cross-coupling of arylboronic acids with aryl halides has been used to prepare several lateral fluoro-substituted 4,4″-dialkyl- and 4,4″-alkoxyalkyl-1,1′:4′,1″-terphenyls. The melting points, mesophase types and transition temperatures of these compounds vary considerably depending on where the lateral fluoro-substituent is positioned. All the compounds have a strong tendency to form tilted smectic mesophases.

Keywords: Fluoro-substitution, 1,1′:4′,1″-terphenyls, tilted smectic mesophases.

INTRODUCTION

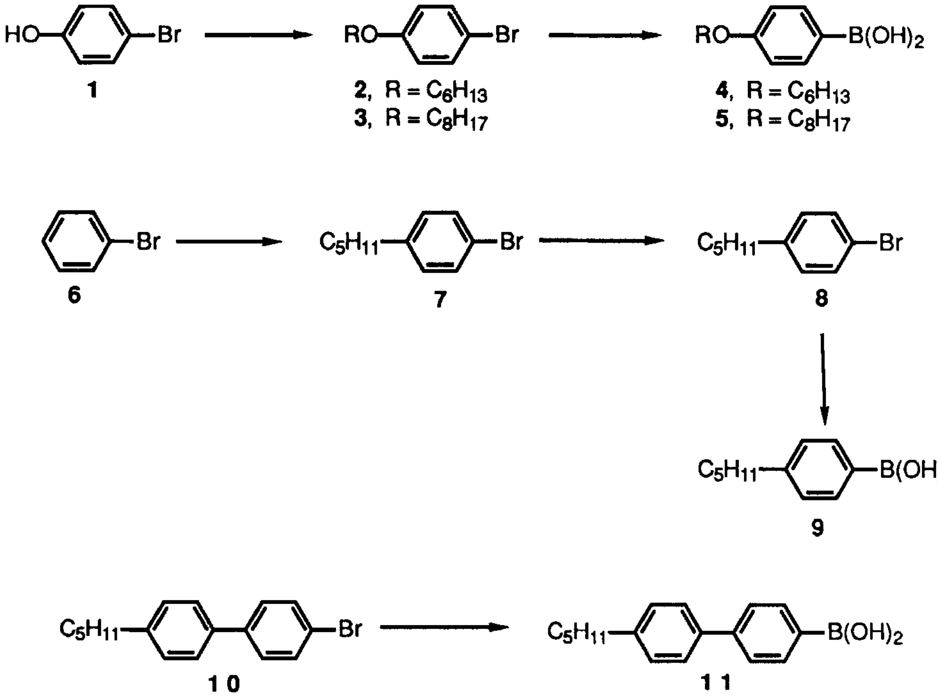
Lateral fluoro-substitution has found widespread application in liquid crystal compounds.[1–25] Because of its small size and high electronegativity, a lateral fluoro-substituent can be used to subtly modify the physical properties of liquid crystalline compounds and yet its effect is not normally so drastic as to eliminate mesophase formation.

Some examples of the usefulness of fluoro-substitution in providing non-polar, positive $\Delta\varepsilon$ and negative $\Delta\varepsilon$ materials respectively are the following: (a) a lateral fluoro-substituent has been used successfully in 4-alkyl-4′-(*trans*-4-alkylcyclohexylethyl)biphenyls[8] to give non-polar, wide-range nematic host materials (I compounds); (b) Kelly[2–6] prepared a series of cyano-substituted phenyl benzoate esters with a lateral fluoro-substituent *ortho* to the cyano-substituent and these compounds were shown[4,5] to have high positive dielectric anisotropies because of the disruption of the anti-parallel correlations found in the parent systems and in some cases because of the tendency to form parallel dimers[11,25]; subsequently, we prepared a comprehensive set of multi-fluoro-substituted cyanophenyl benzoates[18] in order to determine the necessary structural requirements for the formation of *parallel* associations which would then enable us to devise molecular structures of high positive dielectric anisotropy; (c) compounds with two fluoro-substituents *ortho* to each other have been used by us[19] and others[23,24] to obtain smectic C materials with negative dielectric anisotropies, such compounds making excellent host materials for ferroelectric (S_{C^*}) mixtures.

Our earlier work on lateral monofluoro-substituted terphenyls[13-16] has produced compounds with many different mesophase types with a particular preference for tilted smectic mesophases (*e.g.* S_C, S_I). All of these compounds had the lateral fluoro-substituent in the central ring of the terphenyl core and the terminal substituents were dialkyl or alkoxy-alkyl moieties. We now report an extension of that work to the synthesis and transition temperatures of monofluoro-substituted terphenyls with the same terminal substituents, but with the fluoro-substituent in all possible positions of the end rings. Three types of terphenyl are reported which have dipentyl, pentyl-hexoxy and pentyl-octoxy terminal moieties. This gives a total of ten compounds with a fluoro-substituent in an end-ring; their transition temperatures are discussed and compared with those for the five analogous isomeric terphenyls with the fluoro-substituent in the centre ring[13-16] and for the three parent systems.

The foundation for the synthesis of these lateral monofluoro-substituted terphenyls is the excellent palladium-catalysed cross-coupling reaction of aryl boronic acids[26,18-20] and aryl halides which was developed by Suzuki *et al.*[27] and used with

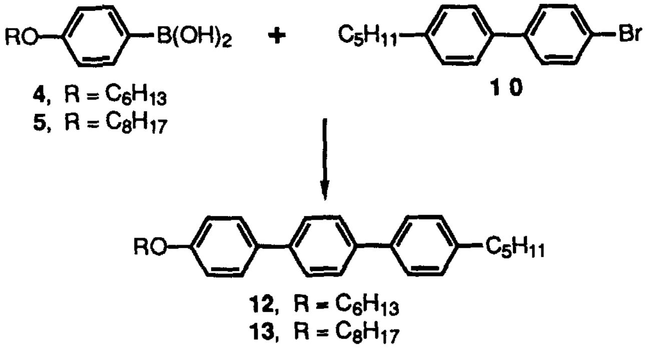
Scheme 1



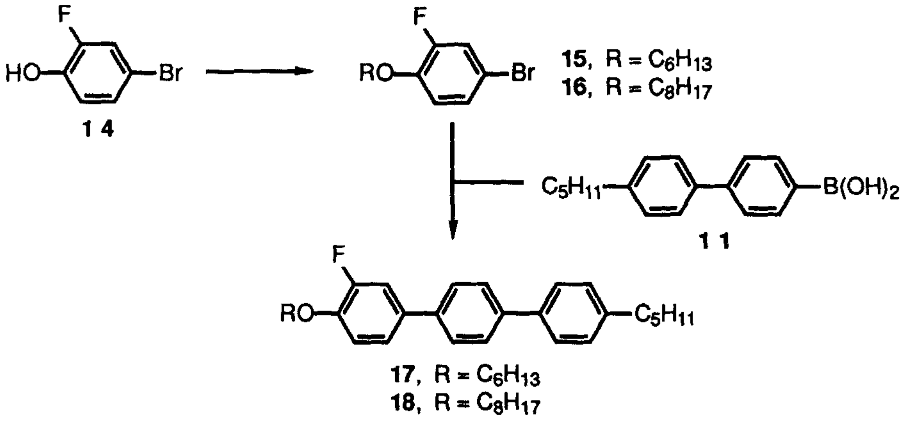
much success by the authors.[18-20] This approach to synthesis provides high yields of pure materials and is a convenient, systematic and economic method of synthesis which lends itself well to the preparation of liquid crystal compounds.

Scheme 1 shows the preparation of some simple, commonly used aryl bromides and aryl boronic acids; the boronic acids were prepared from the appropriate aryl bromides by treating the Grignard reagent with tri-isopropyl borate at −78°C. Scheme 2 illustrates the use of cross-coupling reactions involving a single ring boronic acid species with a bromobiphenyl unit to give terphenyl products (**12** and **13**). Scheme 3 shows the simple *O*-alkylation of phenol **14** to give the appropriately substituted aryl bromides **15** and **16** which were then coupled with boronic acid **11** to provide two lateral fluoro-substituted terphenyls (**17** and **18**) in excellent overall yields; Scheme 4 is identical to Scheme 3 except for the position of the fluoro-substituent and both terphenyls **22** and **23** were again obtained in a similar manner. Scheme 5 uses three different boronic acids (see Scheme 1), each being coupled

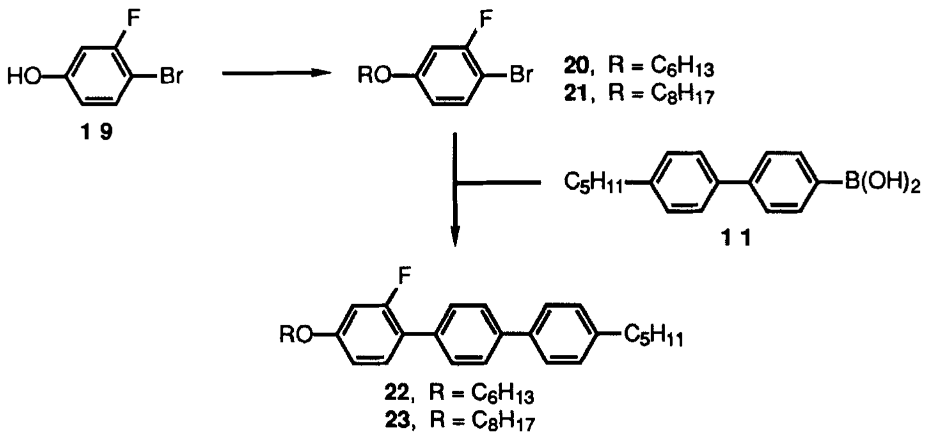
Scheme 2



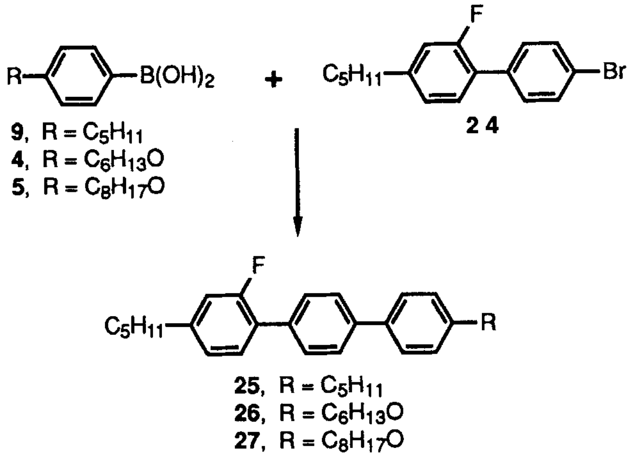
Scheme 3



Scheme 4



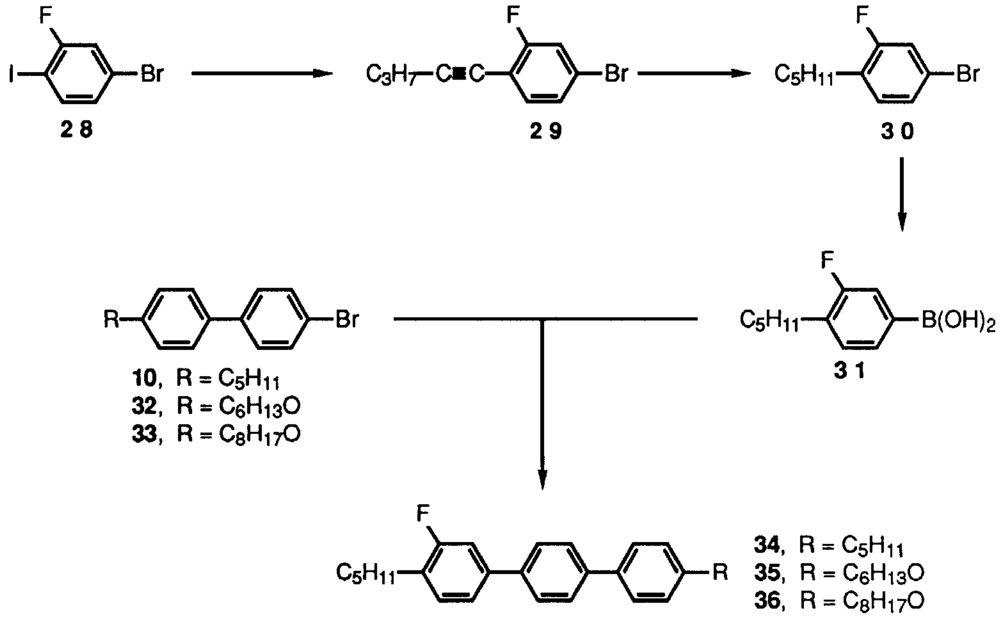
Scheme 5



to the fluoro-substituted bromobiphenyl unit **24** to give the three terphenyls (**25**, **26** and **27**).

The preparation of compound **29** (Scheme 6) involved the reaction of pent-1-ynylzinc chloride with 4-bromo-2-fluoro-1-iodobenzene (**28**) in the presence of tetrakis(triphenylphosphine)palladium(0). This type of cross-coupling procedure was developed by King *et al.*[28] and the reaction was selective at the iodo site, at room temperature, to give compound **29**. The subsequent hydrogenation (platinum(IV) oxide) provides the desired alkyl-substituted compound (**30**) in excellent overall yield. This two-step procedure is a valuable alternative for introducing an alkyl chain into an aromatic unit when it is not possible to use the normal method of Friedel-Crafts acylation followed by reduction of the ketone. The conversion of

Scheme 6



compound **30** into the boronic acid followed by the cross-coupling procedure provided the desired terphenyls (**34**, **35** and **36**).

All the terphenyls shown could have been prepared by using the boronic acid in place of the bromo-substituted compounds and the bromo-substituted system in place of the boronic acid unit (*i.e.* with the synthesis the other way round to that reported). Sometimes the possibility of a reverse synthetic route creates a dilemma, but the choice of which arylboronic acids and which aryl bromides to use is usually determined by ease of preparation and the availability of the appropriate units. For example, compounds **12** and **13** (Scheme 2) may well have been more easily prepared by using the boronic acid of compound **10** (*i.e.* compound **11**) but boronic acids **4** and **5** had already been prepared in quantity. The synthesis of compounds **22** and **23** (Scheme 4) by such a reversed procedure would have involved the unnecessary and less straightforward preparation of the two boronic acids of compounds **20** and **21** which would have involved the use of n-butyllithium at low temperatures to avoid benzyne formation. Similarly the alternative synthetic route to compounds **34**, **35** and **36** (Scheme 6) would have meant the preparation of three boronic acids instead of just one.

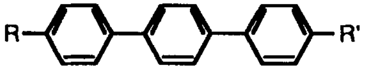
DISCUSSION OF TRANSITION TEMPERATURES

Lateral Monofluoro-substituted Terphenyls (Tables I, II, III and IV)

The two parent systems **12** and **13** were prepared so that their transition temperatures could be compared with those of the analogous fluoro-substituted systems.

TABLE I

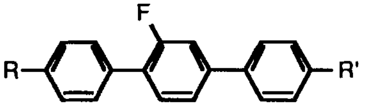
Transition Temperatures (°C) for 4-Alkoxy-4″-alkyl- and 4,4″-Dialkyl-terphenyls (**37**,[29] **12** and **13**)



Compound			Transition Temperatures (°C)						
No.	R	R'	K		S_B		S_A		I
37	C_5H_{11}	C_5H_{11}	*	192.0	--------	--------	*	213.0	*
12	C_5H_{11}	$C_6H_{13}O$	*	205.0	*	216.0	*	228.5	*
13	C_5H_{11}	$C_8H_{17}O$	*	194.5	*	211.0	*	221.5	*

TABLE II

Transition Temperatures (°C) for 4- or 4″-Alkoxy-4- or 4″-pentyl- and 4,4″-Dipentyl-2′-fluoroterphenyls (**38**–**42**) (all these compounds were prepared by L. K. M. Chan[13-16])



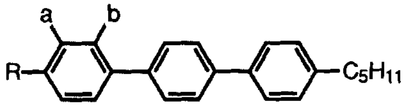
Compound			Transition Temperatures (°C)								
No.	R	R'	K	S_G	S_J	S_B	S_I	S_C	S_A	N	I
38	C_5H_{11}	C_5H_{11}	* 51.5	--------	--------	* 62.0	--------	--------	*109.5	*136.5	*
39	C_5H_{11}	$C_6H_{13}O$	* 70.0	* 78.0	--------	* 92.0	* 93.0	*118.0	*155.0	*166.5	*
40	C_5H_{11}	$C_8H_{17}O$	* 69.0	* 83.0	--------	*100.5	--------	*124.0	*158.0	*161.0	*
41	$C_6H_{13}O$	C_5H_{11}	* 62.5	--------	(* 47.5	--------	* 50.0)	*113.5	--------	*162.5	*
42	$C_8H_{17}O$	C_5H_{11}	* 47.0	--------	(* 40.0)	--------	* 53.5	*116.5	*130.0	*155.0	*

The monofluoro-substituted terphenyls prepared in this work, plus those compounds with the lateral fluoro-substituent in the centre ring which have been reported previously,[13-16] provide a full set of lateral monofluoroterphenyls to allow comparisons to be made with the parent dipentyl-substituted, hexoxy-pentyl-substituted and octoxy-pentyl-substituted terphenyls.

The transition temperatures for the parent systems reveal very high melting points (~200°C) and, as is usual, the dialkyl system[29] (compound **37**, mp 192.0°C) is lower melting than the alkyl-alkoxy systems (compounds **12** and **13**, mp 205.0 and 194.5°C

TABLE III

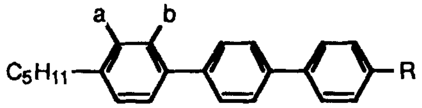
Transition Temperatures (°C) for 4-Alkoxy-4″-pentyl-2- or 3-fluoroterphenyls (**17**, **18**, **22** and **23**)



Compound				Transition Temperatures (°C)								
No.	R	a	b	K	S_K	S_G	S_J	S_B	S_C	S_A	N	I
17	$C_6H_{13}O$	F	H	*	--------	*160.0	--------	--------	*162.0	*201.0	--------	*
18	$C_8H_{17}O$	F	H	*	--------	*146.0	--------	*158.0	--------	*195.0	--------	*
22	$C_6H_{13}O$	H	F	*83.5	(* 48.5	--------	* 62.0)	--------	*105.0	--------	*166.0	*
23	$C_8H_{17}O$	H	F	*69.0	(* 25.0	--------	* 43.5)	--------	*119.0	--------	*158.0	*

TABLE IV

Transition Temperatures (°C) for 4″-Alkoxy-4-pentyl- and 4,4″-Dipentyl-2- or 3-fluoroterphenyls (**25–27** and **34–36**)



Compound				Transition Temperatures (°C)						
No.	R	a	b	K	S_G	S_I	S_C	S_A	N	I
25	C_5H_{11}	H	F	* 72.5	----------	----------	* 80.0	----------	* 136.0	*
26	$C_6H_{13}O$	H	F	* 115.0	----------	----------	* 131.5	----------	* 166.5	*
27	$C_8H_{17}O$	H	F	* 102.0	----------	(* 99.5)	* 137.5	----------	* 160.0	*
34	C_5H_{11}	F	H	*	* 156.5	----------	----------	* 185.5	----------	*
35	$C_6H_{13}O$	F	H	*	* 176.0	----------	----------	* 210.0	----------	*
36	$C_8H_{17}O$	F	H	*	* 170.5	----------	* 176.5	* 202.5	----------	*

respectively). The dialkyl compound (**37**, $T_{S_A\text{-}I}$ value 213.0°C) exhibits only one mesophase (S_A), whereas the alkyl-alkoxy-substituted terphenyls (compounds **12** and **13**, $T_{S_A\text{-}I}$ values 228.5 and 221.5°C respectively) also have a S_B phase. All three parent systems show no tendency towards tilted smectic phases and have only small mesophase ranges. The lower melting and clearing point of the octoxy compound when compared to the hexoxy homologue is a trend typical of the other systems discussed later.

The transition temperatures for the monofluoroterphenyls prepared by Chan (fluorine in the centre ring) have been included here but, since their transition temperatures have been discussed elsewhere,[13-16] little will be said of these systems except in comparisons with the new compounds.

The most important and strikingly obvious effects of the monofluoro-substituent (regardless of its position) are the much reduced melting points (up to 140°C), the great variety of liquid crystal phase types exhibited and especially the tendency towards tilted smectic mesophases. This wide variety of phases makes individual phase-by-phase comparisons difficult but there are very many interesting trends which will be discussed. The presence of a lateral fluoro-substituent on the terphenyl core increases the breadth of the molecules. This tends to disrupt molecular packing and therefore melting points and mesophase thermal stabilities are much reduced when compared to the parent systems (the smectic mesophase thermal stability is most affected due to the disruption of the lamellar packing). Where the fluoro-substituent is positioned within the terphenyl core (*i.e.* not on an outer edge) then fluorine induced inter-annular twisting of the terphenyl core is possible and this allows subtle changes in mesophase type and mesophase thermal stability to be seen.

Melting points depend significantly on where the fluoro-substituent is positioned and a monofluoro-substituent (except on the edge of the core) will cause a twist in the terphenyl system about the inter-annular bond adjacent to the fluorine atom. In the case of compounds **39**, **40**, **26**, **27** the untwisted biphenyl section is alkoxy-substituted and their melting points (70.0, 69.0, 115.0, 102.0°C respectively) are higher than for their isomeric systems (compounds **41**, **42**, **22**, **23** with alkyl and alkoxy groups interchanged; mp 62.5, 47.0, 83.5, 69.0°C respectively) which have an alkyl-substituted, untwisted biphenyl moiety. For the same reason the equivalent liquid crystal phase transition temperatures (where a common phase exists) are also higher for compounds **39**, **40**, **26**, **27** when compared with compounds **41**, **42**, **22**, **23** respectively. In the comparison of compounds **22** and **23** with compounds **26** and **27** respectively, the S_C phase thermal stability is higher by 26.5°C (hexoxy) and by 18.5°C (octoxy) but in both cases the nematic phase thermal stability is only slightly higher when the untwisted moiety is alkoxy-substituted. However, the differences for the two sets of compounds are less for the mesophase transitions than for the melting points. In fact the clearing points ($T_{N\text{-}I}$ values) for all such comparable alkyl-alkoxy-substituted monofluoroterphenyls (compounds **39**–**42**, **22**, **23**, **26** and **27**) are very similar but the octoxy systems have lower clearing points (155.0–161.0°C) than the hexoxy homologues (162.5–166.5°C), which is usual.

In the cases where the fluoro-substituent is part of the untwisted biphenyl moiety (*i.e.* fluorine in the centre ring, compounds **39**–**42**; mp 70.0, 69.0, 62.5, 47.0°C respectively) then melting points, and to a smaller extent mesophase transition temperatures, are lower than when the fluorine atom is in an end ring and not part of the untwisted biphenyl moiety (compounds **26, 27, 22, 23**; mp 115.0, 102.0, 83.5, 69.0°C respectively). For example, compound **26** which has an unsubstituted, untwisted alkoxybiphenyl moiety has a higher melting point (by 45°C), a higher S_C phase thermal stability (by 13.5°C) and an identical nematic phase thermal stability when compared to compound **39** which has the fluoro-substituent in the centre ring and hence has the lateral substituent as part of the untwisted alkoxybiphenyl moiety. The same point also applies to the two dialkyl systems; compound **38** (mp 51.5°C) is of lower melting point than compound **25** (mp 72.5°C) but the clearing point ($T_{N\text{-}I}$ value) is almost identical. However, it is interesting that compound **25**, with the lateral fluoro-substituent (and hence the lateral dipole) at an end ring, exhibits an S_C mesophase of quite high thermal stability (80°C), but compound **38** (lateral fluoro-substituent in the centre ring) shows no tendency for any tilted smectic mesophases.

The S_G mesophase is common throughout the monofluoro-substituted terphenyls but in those cases where the fluoro-substituent causes an inter-annular twist to leave an untwisted alkylbiphenyl section (compounds **41, 42, 22** and **23**) the S_J mesophase is exhibited in place of the S_G mesophase.

Where the fluoro-substituent is on the edge of the terphenyl core (as in the case of compounds **17, 18, 34–36**) no inter-annular twisting at either ring connection is possible and the mutual relationships of the three rings remains as they are in the parent terphenyls. More importantly, the fluoro-substituent may more effectively fill space close to the terminal group and so provide greater potential for intermolecular associations. This would tend to counteract the disruption of the lamellar packing which is normally caused by a lateral fluoro-substituent and so smectic phase thermal stability is strongly upheld resulting in the exclusion of the nematic mesophase. Accordingly, melting points would be expected to be much higher and the presence of ordered smectic mesophases would also be expected. Remarkably no melting points have been detected for these types of compound and the DSC traces show only the mesophase-to-mesophase and mesophase-to-isotropic liquid transitions which were reversible on cooling; despite many reheats and cools and the use of new samples, no melting peaks (on heating) or recrystallisation peaks (on cooling to −20°C) were seen. Optical microscopy also revealed no visible change for the sample until the S_G to S_X transition (S_X being the appropriate mesophase above the S_G phase). This perhaps indicates that the compounds are actually in the S_G phase at room temperature and below and, bearing in mind that the S_G phase is not truly liquid crystalline but is a disordered crystal, this is not unreasonable. However, such compounds would not be expected to have such low melting points when compared to the other compounds in the tables. Possibly another explanation is of a very gradual ‘melting’ process to the disordered crystal state (S_G) which is not detected by DSC [similar in principle to the tilt angle gradually changing in an S_C phase to give an S_A phase (zero tilt); such a transition is also not always revealed by DSC analysis].

The liquid crystal phase transition temperatures of compounds **17, 18, 34–36** are, as expected, much higher when compared to those of their analogues with the fluoro-substituent positioned inside the core, and the compounds have a strong tendency to exhibit the S_G mesophase with high thermal stability. The nematic phase is not seen in these compounds because of the enhanced thermal stability of the S_A mesophase (~200°C) from which these compounds clear to the isotropic liquid. In fact the fluoro-substituent in this outer core position has had only a moderate effect on smectic mesophase type and thermal stability (except for the appearance of the S_G mesophase) and these compounds are intermediate in character between the parent systems and the monofluoroterphenyls with the fluorine positioned inside the aromatic core.

It is interesting to note some of the effects caused in going from a terminal hexoxy-substituent to a longer octoxy-substituent. Where the lateral fluoro-substituent has induced an inter-annular twist to leave an untwisted alkoxybiphenyl section (compounds **39** and **40**), then the smectic phase thermal stability is little affected (3.0°C). However, in the reverse situation, the hexoxy-substituted system (compound **41**) does not show an S_A phase, but an S_A phase is induced by the longer octoxy-substituent (compound **42**) which enhances smectic phase thermal stability by 16.5°C. The longer octoxy-substituent of compound **18** has introduced an S_B mesophase but has depressed the thermal stability of the S_C phase (not seen) and S_A phase present in the hexoxy-substituted system (compound **17**). In contrast an S_C phase is not shown by compound **35** (hexoxy substituted), but increasing the chain length in compound **36** (octoxy substituted) induces an S_C phase without an S_B mesophase appearing.

Overall, the octoxy-substituted systems when compared to the analogous hexoxy-substituted systems appear to have reduced clearing points ($T_{SA\text{-}I}$ or $T_{N\text{-}I}$), increased S_A phase thermal stability (except where the S_A phase marks the clearing point), increased S_C and S_I phase thermal stabilities (except where an S_B phase has been induced to exclude S_C or S_I phase formation), reduced S_G, S_J and S_K mesophase thermal stabilities and reduced melting points.

Experimental

Confirmation of the structures of intermediates and products was obtained by ^1H nmr spectroscopy (JEOL JNM-GX270 spectrometer), infrared spectroscopy (Perkin-Elmer 457 grating spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 GC/MS spectrometer). The progress of reactions was frequently monitored using a Perkin-Elmer 8320 capillary gas chromatograph fitted with a 12 m QC2/BP1-1.0 SGE column. Transition temperatures were measured using a Mettler FP5 hot-stage and control unit in conjunction with an Olympus BH2 polarising microscope and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-2C and data station). The purity of each of the compounds in Tables I, III and IV was checked by glc analysis (see above) and by hplc analysis (Microsorb C18 80-215-C5 RP column) and all compounds were >99.9% pure.

Compounds **10**, **19**, **24**, **32** and **33** were kindly supplied by our collaborators at BDH Limited, Poole, Dorset. Compounds **2**, **3**, **7** and **8** were prepared as described in reference 19.

4-Hexoxyphenylboronic acid (**4**)

A solution of the Grignard reagent, prepared from compound **2** (72.0 g, 0.28 mol) and magnesium (7.75 g, 0.319 mol) in dry THF (220 ml) was added dropwise to a stirred, cooled (−78°C) solution of tri-isopropyl borate (109.0 g, 0.58 mol) in dry THF (40 ml) under dry nitrogen. The stirred mixture was allowed to warm to room temperature overnight and stirred with 10% hydrochloric acid (320 ml) at room temperature for 1 h. The product was extracted into ether (twice), and the combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to afford a colourless solid.

Yield 61.2 g (99%); mp 80–85°C; ^1H nmr ($CDCl_3$) δ 1.00(3H, t), 1.40(6H, m), 1.80(2H, quint), 4.10(2H, t), 7.20(2H, d), 8.40(2H, d), no obvious OH absorption; ir (KCl) ν_{max} 3500–3100, 2960, 2940, 2880, 1600, 1570, 1420, 1380, 1350, 1250, 1170, 1030, 840 cm^{-1}; ms *m/z* 382, 359, 342, 306, 298, 290, 281, 253, 239, 223, 214, 205.

4-Octoxyphenylboronic acid (**5**)

Quantities: compound **3** (42.0 g, 0.15 mol), magnesium (4.12 g, 0.170 mol), tri-isopropyl borate (53.3 g, 0.29 mol).

The experimental procedure was the same as for compound **4**. Yield 36.1 g (98%); ^1H nmr ($CDCl_3$) δ 0.85(3H, t), 1.30(8H, m), 1.45(2H, quint), 1.80(2H, quint), 4.00(2H, t), 6.95(2H, t), 7.75(1H, d), 8.15(1H, d), no obvious OH absorption; ir (KCl) ν_{max} 2950, 2860, 1610, 1360, 1255, 1180 cm^{-1}; ms *m/z* 280, 265, 248, 232, 222, 213, 206, 196, 185.

4-Pentylphenylboronic acid (**9**)

Quantities: compound **8** (24.00 g, 0.106 mol), magnesium (2.95 g, 0.121 mol), tri-isopropyl borate (39.8 g, 0.21 mol).

The experimental procedure was as described for the preparation of compound **4**. Yield 19.30 g (95%); ^1H nmr ($CDCl_3$) δ 0.90(3H, t), 1.40(4H, m), 1.65(2H, quint), 2.70(2H, t), 7.35(4H, m), no obvious OH absorption; ir (KCl) ν_{max} 3600–3200, 2960, 2940, 2860, 1610, 1410, 1370–1240, 1310, 1180, 1020, 700 cm^{-1}; ms *m/z* 247, 233, 230, 217, 211, 207.

4′-Pentylbiphenyl-4-ylboronic acid (**11**)

Quantities: compound **10** (25.00 g, 0.083 mol), magnesium (2.25 g, 0.093 mol), tri-isopropyl borate (31.0 g, 0.16 mol).

The experimental procedure was as described for the preparation of compound **4**. Yield 21.00 g (98%); ^1H nmr ($CDCl_3$) δ 0.90(3H, t), 1.35(4H, m), 1.65(2H, quint), 2.65(2H, t), 7.25(2H, d), 7.50–7.60(4H, m), 7.65(1H, d), 7.90(1H, d), no obvious OH absorption; ir (KCl) ν_{max} 3600–3100, 2960, 2940, 2860, 1610, 1450–1300, 1005, 815 cm^{-1}; ms *m/z* 446, 389, 293, 240, 224, 195, 183, 167, 152.

4-Hexoxy-4″-pentylterphenyl (**12**)

A solution of compound **4** (1.12 g, 5.05 mmol) in ethanol (15 ml) was added to a stirred mixture of compound **10** (1.15 g, 3.80 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.2646 g, 0.23 mmol) in benzene (30 ml) and 2M sodium carbonate (30 ml) at room temperature under dry nitrogen. The stirred mixture was heated under reflux (~100°C) for 23 h (*i.e.*, until glc and tlc analysis revealed a complete reaction). The product was extracted into ether (twice) and the combined ethereal extracts were washed with brine and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 3:1] to give a colourless solid which was recrystallised from ethyl acetate to yield colourless crystals.

Yield 0.96 g (63%); transitions (°C) K 205.0 S_B 216.0 S_A 228.5 I; ^{1}H nmr ($CDCl_3$) δ 0.90(6H, 2xt), 1.35(8H, m), 1.45(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 4.00(2H, t), 6.98(2H, d), 7.27(2H, d), 7.55(2H, d), 7.57(2H, d), 7.64(4H, 2xd); ir (KCl) ν_{max} 2960, 2940, 2860, 1610, 1495, 1250, 810 cm^{-1}; ms *m/z* 400(M$^+$), 371, 357, 343, 332.

4-Octoxy-4″-pentylterphenyl (**13**)

Quantities: Compound **10** (1.15 g, 3.80 mmol), compound **5** (1.25 g, 5.00 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2401 g, 0.21 mmol).

The experimental procedure was as described for the preparation of compound **12**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 3:1] to give a colourless solid which was recrystallised from ethyl acetate to yield colourless crystals.

Yield 1.02 g (63%); transitions (°C) K 194.5 S_B 211.0 S_A 221.5 I; ^{1}H nmr ($CDCl_3$) δ 0.90(6H, 2xt), 1.30(12H, m), 1.45(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 4.00(2H, t), 6.98(2H, d), 7.27(2H, d), 7.55(2H, d), 7.57(2H, d), 7.64(4H, 2xd); ir (KCl) ν_{max} 2960, 2940, 2860, 1610, 1495, 1255, 805 cm^{-1}; ms *m/z* 428(M$^+$), 411, 400, 385, 371, 329, 316.

1-Bromo-3-fluoro-4-hexoxybenzene (**15**)

Quantities: compound **14** (10.00 g, 0.052 mol), 1-bromohexane (10.37 g, 0.063 mol), potassium carbonate (14.50 g, 0.105 mol).

The experimental procedure was as described in previous publications.[18,19] Yield 13.71 g (96%); bp 110–112°C at 0.1 mmHg; ^{1}H nmr ($CDCl_3$) δ 0.90(3H, t), 1.30(4H, m), 1.45(2H, quint), 1.80(2H, quint), 4.00(2H, t), 6.80(1H, t), 7.15(1H, oct), 7.20(1H, q); ir (film) ν_{max} 2980, 2950, 2880, 1595, 1510, 1475, 1420, 1315, 1290, 1275, 1140, 1030, 885, 870, 810 cm^{-1}; ms *m/z* 276(M$^+$), 275, 274(M$^+$), 273, 202, 189.

1-Bromo-3-fluoro-4-octoxybenzene (**16**)

Quantities: compound **14** (10.00 g, 0.052 mol), 1-bromo-octane (12.00 g, 0.062 mol), potassium carbonate (14.5 g, 0.105 mol).

The experimental procedure was as described in previous publications.[18,19] Yield 15.40 g (98%); bp 120–122°C at 0.1 mmHg; ^{1}H nmr ($CDCl_3$) δ 0.90(3H, t), 1.30(8H, m), 1.45(2H, quint), 1.80(2H, quint), 4.00(2H, t), 6.80(1H, t), 7.15(1H, oct), 7.20(1H, q); ir (film) ν_{max} 2980, 2940, 2860, 1505, 1480, 1410, 1310, 1270, 1210, 1170, 1030, 885, 870, 800 cm^{-1}; ms *m/z* 304(M$^+$), 302(M$^+$), 192, 190.

3-Fluoro-4-hexoxy-4″-pentylterphenyl (**17**)

Quantities: compound **15** (1.00 g, 3.64 mmol), compound **11** (1.27 g, 4.74 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2424 g, 0.21 mmol).

The experimental procedure was as described for the preparation of compound **12**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 5:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (1:1) to yield colourless crystals.

Yield 0.77 g (51%); transitions (°C) K ? S_G 160.0 S_C 162.0 S_A 201.0 I; ^{1}H nmr ($CDCl_3$) δ 0.90(6H, 2xt), 1.35(8H, m), 1.50(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 4.05(2H, t), 7.03(1H, t), 7.27(2H, d), 7.33(1H, q), 7.37(1H, q), 7.55(2H, d), 7.58(2H, d), 7.65(2H, d); ir (KCl) ν_{max} 2960, 2940, 2860, 1620, 1500, 1400, 1375, 1350, 1190, 1140, 805 cm^{-1}; ms *m*/*z* 418(M^+), 334, 300, 277, 243.

3-Fluoro-4-octoxy-4″-pentylterphenyl (**18**)

Quantities: compound **16** (1.36 g, 4.49 mmol), compound **11** (1.45 g, 5.41 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2101 g, 0.18 mmol).

The experimental procedure was as described for the preparation of compound **12**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 5:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (2:1) to yield colourless crystals.

Yield 1.75 g (87%); transitions (°C) K ? S_G 146.0 S_B 158.0 S_A 195.0 I; ^{1}H nmr ($CDCl_3$) δ 0.90(6H, 2xt), 1.35(12H, m), 1.45(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 4.05(2H, t), 7.02(1H, t), 7.26(2H, d), 7.33(1H, q), 7.37(1H, q), 7.54(2H, d), 7.58(2H, d), 7.64(2H, d); ir (KCl) ν_{max} 2960, 2940, 2860, 1625, 1525, 1500, 1485, 1405, 1305, 1275, 1250, 1195, 1140, 880, 810 cm^{-1}; ms *m*/*z* 446(M^+), 389, 334, 277.

1-Bromo-2-fluoro-4-hexoxybenzene (**20**)

Quantities: compound **19** (9.00 g, 0.047 mol), 1-bromohexane (9.33 g, 0.057 mol), potassium carbonate (13.50 g, 0.098 mol).

The experimental procedure was as described in previous publications.[18,19] Yield 12.71 g (98%); bp 100–105°C at 0.1 mmHg; ^{1}H nmr ($CDCl_3$) δ 0.90(3H, t), 1.30(4H, m), 1.40(2H, quint), 1.75(2H, quint), 3.90(2H, t), 6.55(1H, oct), 6.65(1H, q), 7.35(1H, t); ir (film) ν_{max} 2950, 2880, 1610, 1590, 1490, 1470, 1330, 1300, 1260, 1170, 1020, 840, 650 cm^{-1}; ms *m*/*z* 276(M^+), 274(M^+), 190, 173, 161, 151.

1-Bromo-2-fluoro-4-octoxybenzene (**21**)

Quantities: compound **19** (6.00 g, 0.031 mol), 1-bromo-octane (7.30 g, 0.038 mol), potassium carbonate (10.00 g, 0.072 mol).

The experimental procedure was as described in previous publications.[18,19] Yield 9.01 g (96%); bp 140–142°C at 0.1 mmHg; ^{1}H nmr ($CDCl_3$) δ 0.90(3H, t), 1.30(10H, m), 1.70(2H, quint), 3.90(2H, t), 6.55(1H, oct), 6.65(1H, q), 7.35(1H, t); ir (film)ν_{max} 2940, 2860, 1605, 1585, 1490, 1470, 1325, 1295, 1170, 1145 cm^{-1}; ms *m*/*z* 304(M^+), 302(M^+), 191, 189.

2-Fluoro-4-hexoxy-4″-pentylterphenyl (**22**)

Quantities: compound **20** (1.50 g, 5.45 mmol), compound **11** (1.90 g, 7.10 mmol), tetrakis(triphenylphosphine)palladium(0) (0.5010 g, 0.43 mmol).

The experimental procedure was as described for the preparation of compound **12**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 3:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (2:1), to yield colourless crystals.

Yield 1.46 g (64%); transitions (°C) K 83.5 (S_K 48.5 S_J 62.0) S_C 105.0 N 166.0 I; ^{1}H nmr ($CDCl_3$), δ 0.90(6H, 2xt), 1.30(8H, m), 1.45(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 3.95(2H, t), 6.72(1H, q), 6.78(1H, q), 7.27(2H, d), 7.38(1H, t), 7.54(2H, d), 7.58(2H, d), 7.64(2H, d); ir (KCl) ν_{max} 2960, 2940, 2860, 1625, 1500, 1400, 1335, 1320, 1240, 1175, 1120, 1030, 810 cm^{-1}; ms *m/z* 418(M^+), 361, 334, 277.

2-Fluoro-4-octoxy-4″-pentylterphenyl (**23**)

Quantities: compound **21** (2.00 g, 6.60 mmol), compound **11** (2.30 g, 8.58 mmol), tetrakis(triphenylphosphine)palladium(0) (0.6003 g, 0.52 mmol).

The experimental procedure was as described for the preparation of compound **12**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 3:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (2:1) to yield colourless crystals.

Yield 2.30 g (78%); transitions (°C) K 69.0 (S_K 25.0 S_J 43.5) S_C 119.0 N 158.0 I; ^{1}H nmr ($CDCl_3$) δ 0.90(6H, 2xt), 1.30(12H, m), 1.45(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 3.95(2H, t), 6.72(1H, q), 6.78(1H, q), 7.27(2H, d), 7.38(1H, t), 7.54(2H, d), 7.58(2H, d), 7.64(2H, d); ir (KCl) ν_{max} 2960, 2940, 2860, 1640, 1500, 1400, 1335, 1320, 1240, 1175, 1120, 810 cm^{-1}; ms *m/z* 446(M^+), 418, 403, 389, 361, 334, 277.

2-Fluoro-4,4″-dipentylterphenyl (**25**)

Quantities: compound **24** (1.10 g, 3.43 mmol), compound **9** (0.8721 g, 4.54 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2212 g, 0.19 mmol).

The experimental procedure was as described for the preparation of compound **12**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 5:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (2:1) to yield colourless crystals.

Yield 0.89 g (67%); transitions (°C) K 72.5 S_C 80.0 N 136.5 I; ^{1}H nmr ($CDCl_3$) δ 0.90(6H, t), 1.35(8H, m), 1.65(4H, quint), 2.60(4H, 2xt), 6.99(1H, q), 7.03(1H, q), 7.27(2H, d), 7.38(1H, t), 7.55(2H, d), 7.61(2H, q), 7.66(2H, d); ir (KCl) ν_{max} 2960, 2940, 2860, 1625, 1490, 1400, 1260, 1135, 1010, 810 cm^{-1}; ms *m/z* 388(M^+), 345, 331, 274.

2-Fluoro-4″-hexoxy-4-pentylterphenyl (**26**)

Quantities: compound **24** (1.10 g, 3.43 mmol), compound **4** (1.10 g, 4.75 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2217 g, 0.19 mmol).

The experimental procedure was as described for the preparation of compound **12**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 3:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (2:1) to yield colourless crystals.

Yield 1.02 g (71%); transitions (°C) K 115.0 S_C 131.5 N 166.5 I; ^{1}H nmr ($CDCl_3$) δ 0.90(6H, 2xt), 1.30(8H, m), 1.45(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 4.00(2H, t), 6.98(2H, d), 7.04(2H, m), 7.38(1H, t), 7.57(2H, d), 7.63(4H, d); ir (KCl) ν_{max} 2960, 2940, 2860, 1605, 1510, 1490, 1470, 1400, 1290, 1250, 1210, 1180, 820 cm^{-1}; ms m/z 418(M^+), 400, 376, 361, 347, 334, 277.

2-Fluoro-4″-octoxy-4-pentylterphenyl (**27**)

Quantities: compound **24** (1.10 g, 3.43 mmol), compound **5** (1.17 g, 4.68 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2610 g, 0.23 mmol).

The experimental procedure was as described for the preparation of compound **12**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 3:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (2:1) to yield colourless crystals.

Yield 0.90 g (59%); transitions (°C) K 102.0 (S_I 99.5) S_C 137.5 N 160.0 I; ^{1}H nmr ($CDCl_3$) δ 0.85(6H, 2xt), 1.30(12H, m), 1.45(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 4.00(2H, t), 6.98(2H, d), 7.04(2H, m), 7.38(1H, t), 7.57(2H, d), 7.63(4H, d); ir (KCl) ν_{max} 2960, 2940, 2880, 1610, 1495, 1400, 1290, 1250, 1210, 1185, 1130, 815 cm^{-1}; ms m/z 446(M^+), 418, 389, 347, 334, 277.

1-Bromo-3-fluoro-4-pent-1-ynylbenzene (**29**)

Quantities: pent-1-yne (5.00 g, 0.074 mol), n-butyllithium (7.40 ml, 10.0M in hexane, 0.074 mol), zinc chloride 10.10 g, 0.074 mol), compound **28** (20.00 g, 0.066 mol), tetrakis(triphenylphosphine)palladium(0) (2.31 g, 2.0 mmol).

The experimental procedure was as described in a previous publication.[18] Yield 14.04 g (79%); bp 128–132°C at 15 mmHg; ^{1}H nmr ($CDCl_3$) δ 1.05(3H, t), 1.65(2H, sext), 2.40(2H, t), 7.18–7.27(3H, m); ir (film) ν_{max} 2960, 2940, 2880, 2250, 1605, 1565, 1490, 1410, 1220, 1125, 1075, 870, 805 cm^{-1}; ms m/z 242(M^+), 240(M^+), 213, 211.

1-Bromo-3-fluoro-4-pentylbenzene (**30**)

A solution of compound **29** (9.95 g, 0.041 mol) in ethanol (180 ml) was hydrogenated over platinum(IV) oxide (0.45 g) at room temperature and atmospheric pressure for 5 h (glc analysis revealed a complete reaction). The catalyst was filtered off, the solvent was removed *in vacuo* and the residue was distilled to yield a red liquid.

Yield 9.52 g (95%); bp 122–124 at 15 mmHg; ^{1}H nmr ($CDCl_3$) δ 0.90(3H, t), 1.30(4H, m), 1.55(2H, quint), 2.60(2H, t), 7.04(1H, t), 7.17(2H, m); ir (film) ν_{max} 2960, 2940, 2860, 1610, 1580, 1490, 1410, 1270, 1225, 1135, 1070, 880, 860, 820 cm^{-1}; ms m/z 246(M^+), 244(M^+), 189, 187.

3-Fluoro-4-pentylphenylboronic acid (**31**)

Quantities: compound **30** (9.00 g, 0.037 mol), magnesium (1.00 g, 0.041 mol), tri-isopropyl borate (14.10 g, 0.075 mol).

The experimental procedure was as described for the preparation of compound **4**. Yield 7.50 g (97%); ^{1}H nmr (CDCl$_3$) δ 0.85(3H, t), 1.35(4H, m), 1.65(2H, quint), 2.65(2H, t), 7.30(1H, t), 7.76(1H, d), 7.86(1H, d) no obvious OH absorption; ir (KCl) ν_{max} 3700–3100, 2960, 2940, 2860, 1415, 1400–1300, 1100, 1040, 895, 675 cm^{-1}; ms *m/z* 234, 229, 221, 207, 193, 177, 165, 161, 149, 135.

3-Fluoro-4,4''-dipentylterphenyl (**34**)

Quantities: compound **10** (1.56 g, 5.15 mmol), compound **31** (1.30 g, 6.19 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2120 g, 0.18 mmol).

The experimental procedure was as described for the preparation of compound **12**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 5:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (5:1) to yield colourless crystals.

Yield 1.54 g (77%); transitions (°C) K ? S$_G$ 156.5 S$_A$ 185.5 I; ^{1}H nmr (CDCl$_3$) δ 0.90(6H, t), 1.35(8H, m), 1.65(4H, m), 2.65(4H, 2xt), 7.25–7.31(4H, m), 7.34(1H, q) 7.56(2H, d), 7.63(2H, d), 7.68(2H, d); ir (KCl) ν_{max} 2960, 2940, 2860, 1575, 1495, 1400, 1140, 1010, 910, 880, 810 cm^{-1}; ms *m/z* 388(M$^+$), 331, 274.

3-Fluoro-4''-hexoxy-4-pentylterphenyl (**35**)

Quantities: compound **32** (1.60 g, 4.80 mmol), compound **31** (1.21 g, 5.76 mmol), tetrakis(triphenylphosphine)palladium(0) (0.1979 g, 0.17 mmol).

The experimental procedure was as described for the preparation of compound **12**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 5:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (1:3) to yield colourless crystals.

Yield 1.57 g (84%); transitions (°C) K ? S$_G$ 176.0 S$_A$ 210.0 I; ^{1}H nmr (CDCl$_3$) δ 0.90(6H, 2xt), 1.35(8H, m), 1.45(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 4.00(2H, t), 6.98(2H, d), 7.25(1H, t), 7.29(1H, q), 7.34(1H, q), 7.57(2H, d), 7.62(4H, s); ir (KCl) ν_{max} 2960, 2940, 2860, 1610, 1495, 1405, 1290, 1255, 1185, 1040, 880, 815 cm^{-1}; ms *m/z* 418(M$^+$), 361, 334, 277.

3-Fluoro-4''-octoxy-4-pentylterphenyl (**36**)

Quantities: compound **33** (1.62 g, 4.49 mmol), compound **31** (1.15 g, 5.48 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2167 g, 0.19 mmol).

The experimental procedure was as described for the preparation of compound **12**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 4:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (1:5) to yield colourless crystals.

Yield 1.76 g (88%); transitions (°C) K ? S$_G$ 170.5 S$_C$ 176.5 S$_A$ 202.5 I; ^{1}H nmr (CDCl$_3$) δ 0.90(6H, 2xt), 1.30(12H, m), 1.45(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 4.00(2H, t), 6.98(2H, d), 7.24(1H, t), 7.29(1H, q), 7.34(1H, q), 7.56(2H, d), 7.61(4H, s); ir (KCl) ν_{max} 2960, 2940, 2860, 1610, 1495, 1400, 1290, 1260, 1185, 1035, 1005, 815 cm^{-1}; ms *m/z* 446(M$^+$), 389, 334, 277.

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REFERENCES

1. G. W. Gray, C. Hogg, and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **67,** 1 (1981).
2. S. M. Kelly, *Helv. Chim. Acta*, **67,** 1572 (1984).
3. S. M. Kelly and Hp. Schad, *Helv. Chim. Acta*, **67,** 1580 (1984).
4. Hp. Schad and S. M. Kelly, *J. Chem. Phys.*, **81,** 1514 (1984).
5. Hp. Schad and S. M. Kelly, *J. Physique*, **46,** 1395 (1985).
6. S. M. Kelly and Hp. Schad, *Helv. Chim. Acta*, **68,** 1444 (1985).
7. R. Eidenschink, *Mol. Cryst. Liq. Cryst.*, **123,** 57 (1985).
8. P. H. Balkwill, D. I. Bishop, A. D. Pearson, and I. C. Sage, *Mol. Cryst. Liq. Cryst.*, **123,** 1 (1985).
9. J. E. Fearon, G. W. Gray, A. D. Ifill, and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **124,** 89 (1985).
10. M. A. Osman, *Mol. Cryst. Liq. Cryst.*, **128,** 45 (1985).
11. D. G. McDonnell, E. P. Raynes, and R. A. Smith, *Mol. Cryst. Liq. Cryst.*, **123,** 169 (1985).
12. G. W. Gray, D. Lacey, J. E. Stanton (née Fearon), and K. J. Toyne, *Liquid Crystals*, **1,** 407 (1986).
13. L. K. M. Chan, G. W. Gray, and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **123,** 185 (1985).
14. L. K. M. Chan, Ph.D. Thesis, The University of Hull, England (1987).
15. L. K. M. Chan, G. W. Gray, D. Lacey, and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **150B,** 335 (1987).
16. L. K. M. Chan, G. W. Gray, D. Lacey, and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **158B,** 209 (1988).
17. K. J. Toyne, in 'Thermotropic Liquid Crystals,' ed. G. W. Gray, Wiley, Chichester (1987).
18. G. W. Gray, M. Hird, D. Lacey, and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **172,** 165 (1989).
19. G. W. Gray, M. Hird, D. Lacey, and K. J. Toyne, *J. Chem. Soc., Perkin Trans.* **2,** 2041 (1989).
20. M. Hird, Ph.D. Thesis, The University of Hull, England (1990).
21. D. G. McDonnell, E. P. Raynes, and R. A. Smith, *Liquid Crystals*, **6,** 515 (1989).
22. M. Chambers, R. Clemitson, D. Coates, S. Greenfield, J. A. Jenner, and I. C. Sage, *Liquid Crystals*, **5,** 153 (1989).
23. V. Reiffenrath, J. Krause, H. J. Plach, and G. Weber, *Liquid Crystals*, **5,** 159 (1989).
24. S. M. Kelly, *Liquid Crystals*, **5,** 171 (1989).
25. K. Toriyama and D. A. Dunmur, *Molec. Phys.*, **56,** 479 (1985).
26. W. J. Thompson and J. Gaudino, *J. Org. Chem.*, **49,** 5237 (1984).
27. N. Miyaura, T. Yanagi, and A. Suzuki, *Synth. Commun.*, **11,** 513 (1981).
28. A. O. King, E. Negishi, F. J. Villani, and A. Silveira, *J. Org. Chem.*, **43,** 358 (1978).
29. H. Schubert, H. J. Lorenz, R. Hoffmann, and F. Franke, *Z. Chem.*, **6,** 337 (1966).