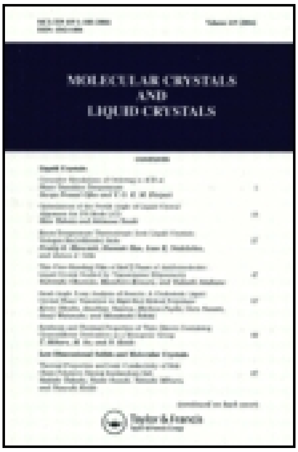

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Synthesis and Transition Temperatures of Some Ortho-Dichloroterphenyls for Ferroelectric Mixtures

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To cite this article: Michael Hird , Kenneth J. Toyne , Paul Hindmarsh , J. Clifford Jones & Victoria Minter (1995): The Synthesis and Transition Temperatures of Some Ortho-Dichloroterphenyls for Ferroelectric Mixtures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 260:1, 227-240

To link to this article: http://dx.doi.org/10.1080/10587259508038694

Mol. Cryst. Liq. Cryst. 1995, Vol. 260, pp. 227–240
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THE SYNTHESIS AND TRANSITION TEMPERATURES OF SOME *ORTHO*-DICHLOROTERPHENYLS FOR FERROELECTRIC MIXTURES

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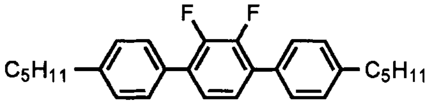
Abstract A range of *ortho*-dichloroterphenyls has been prepared and evaluated for their transition temperatures and physical properties. The analogous *ortho* difluoro-substituted materials have been very successful as ferroelectric host materials. It was expected that the dichloro-substituted compounds would provide a greater lateral dipole and confer of dielectric biaxiality. State of the art synthetic techniques were used. For example, low-temperature *ortho* directed metallations provided arylboronic acids which were used in palladium-catalysed cross-coupling reactions to provide final materials. Materials with low melting points that exhibit the S_C phase have been produced.

INTRODUCTION

The design and synthesis of ferroelectric liquid crystals (hosts and dopants) has been the subject of considerable research in recent years[1-5] because of their great potential for low-powered, fast-switching, bistable display devices that can provide high resolution over a large area. Highly promising prototype ferroelectric displays have been fabricated by both Thorn-EMI[6] and Canon,[7] however, improvements are required, most significantly in terms of a faster switching speed at a lower operating voltage, before commercial exploitation is possible. Hence, despite the synthesis of many materials and the formulation of a wide range of successful host-dopant mixtures, there is still a need for improved achiral S_C host materials and chiral dopants.

TABLE 1 Transition temperatures (°C) for some 2,3- and 2',3'-difluoroterphenyls.

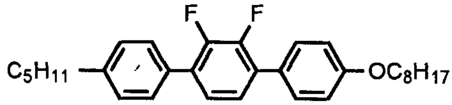


I

C 60.0 N 120.0 I

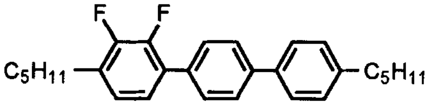
Dielectric Anisotropy
-2.0
Visocsity
35 cP

Dielectric Anisotropy
-2.1
Visocsity
60 cP



II

C 48.5 S_C 95.0 N 141.5 I

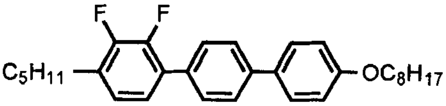


III

C 81.0 S_C 115.5 S_A 131.5 N 142.0 I

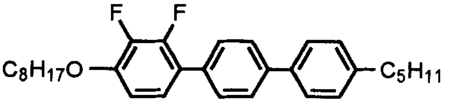
Dielectric Anisotropy
-2.0
Visocsity
80 cP

Dielectric Anisotropy
-2.1
Visocsity
130 cP



IV

C 89.0 S_C 155.5 S_A 165.0 N 166.0 I

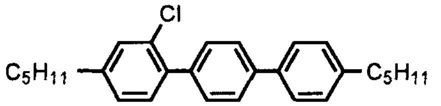


V

C 93.5 S_C 144.0 S_A 148.0 N 159.0 I

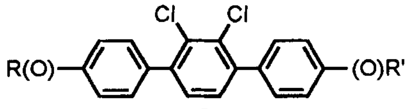
Dielectric Anisotropy
-4.2
Visocsity
130 cP

Lateral substituents have long[8] been used to modify the mesogenic and the physical properties of liquid crystal compounds and some remarkable materials have been produced.[2,4,9-11] Lateral fluoro-substitution, in particular, is of great importance because of its unique combination of small size and high electronegativity. Difluoroterphenyls have been reported with the two fluoro substituents inherently fixed on one side of the molecular core (*i.e.*, *ortho*).[2] These materials make excellent host materials for low viscosity, fast-switching ferroelectric mixtures.[12] The arrangement of fluoro-substituents serves to minimize the molecular breadth which upholds liquid crystal phase stability and minimizes viscosity. The lateral dipoles of the two fluoro substituents reinforce each other to provide a strong overall lateral dipole. The strong lateral dipole confers strong tilted S_C character and provides a negative dielectric anisotropy ($\Delta\varepsilon$). Compounds **I-V** (Table 1) are some typical examples *ortho* difluoroterphenyls.[2] Mixtures of various homologues of the *ortho* difluoroterphenyls in combination with a chiral dopant provide low viscosity ferroelectric mixtures with switching speeds of 3 μs (10 V μm^{-1}) at 30 °C.[12] The importance of dielectric biaxiality in ferroelectric switching is now becoming established.[1,13,14] There is strong evidence that the dielectric biaxiality plays and important role in AC stabilisation and enables faster ferroelectric switching.[13] Accordingly, there is a need to introduce dielectric biaxiality into ferroelectric mixtures.

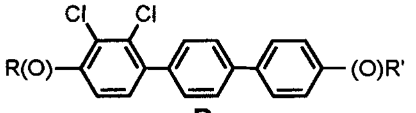


VI

C 56.0 N 60.0 I



A



B

Lateral chloro substituents are not usually employed in liquid crystal materials because of their large size which, in comparison to the analogous fluoro-substituted systems, would be detrimental to liquid crystal phase stabilities and produce a higher viscosity. However, materials have been prepared that show lateral chloro substituents to support liquid crystal phases (*e.g.*, compound **VI**).[15] The chloro substituent is known to generate a larger dipole moment than the fluoro substituent and this would be expected to provide a higher negative dielectric anisotropy; this combined with the large size of the chloro substituent may generate dielectric biaxiality.

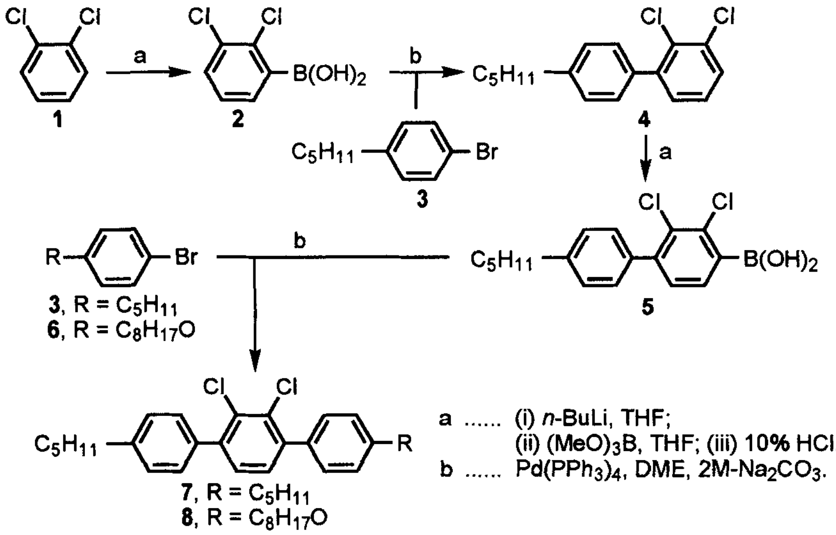
Chloro-substituted terphenyls (*e.g.*, structures **A** and **B**) have been prepared to evaluate the effect of the larger, more polar lateral substituent on physical properties when compared to the highly successful *ortho* difluoro-substituted analogues. There are obvious compromises to consider because the larger and more polar lateral substituents would be expected to confer a high viscosity to the ferroelectric mixture which would lead to slower switching speeds but the expected dielectric biaxiality of the mixture may enable faster switching speeds. With this in mind, it was not expected to produce materials for the bulk of ferroelectric host mixtures but these lateral chloro-substituted compounds are well worthy of evaluation with a view to including small to moderate quantities in ferroelectric mixtures based on *ortho* difluoroterphenyls. Additionally, those *ortho* dichloroterphenyls that are nematogens may be useful components in mixtures for electrically controlled birefringence (ECB) displays where a negative dielectric anisotropy is required.

SYNTHESIS

The *ortho* difluoroterphenyls were prepared by the sequential exploitation of the acidic protons of 1,2-difluorobenzene.[2] The electron-withdrawing nature of the fluoro-substituent allows the adjacent proton to be removed by treatment with *n*-butyllithium at very low temperature (-78°C) to prevent decomposition to a benzyne derivative. The subsequent quenching of the resultant lithium salt enables a wide range of functional groups to be introduced. The appropriate combination of *ortho*-directed metallation procedures and palladium-catalysed cross-coupling materials enabled liquid crystal materials to be synthesised.

The chloro substituent is essentially identical to a fluoro substituent in terms of the acidity of adjacent protons and the wide range of functional groups that can be subsequently introduced into the position *ortho* to the chloro substituent.[16] Accordingly, the synthetic methodology employed in the preparation of the *ortho* dichloroterphenyl liquid crystals was identical to that used previously for the analogous fluoro-substituted systems.

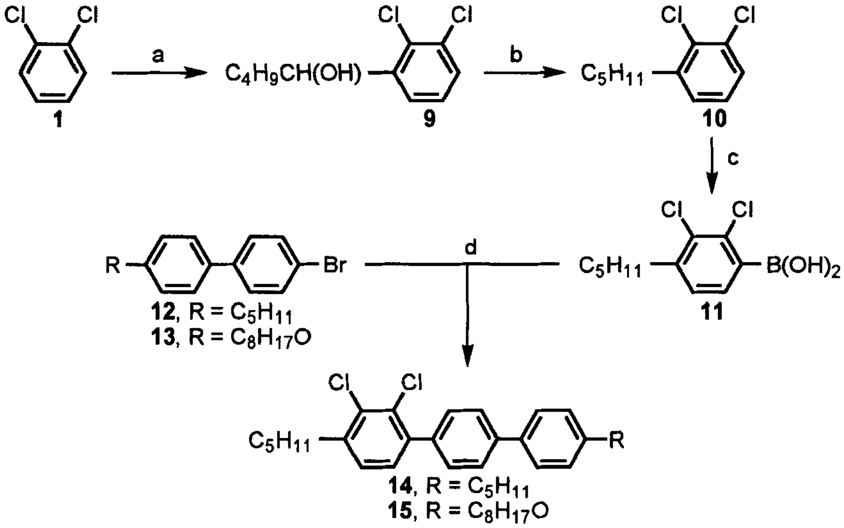
Scheme 1 clearly illustrates the scope of this synthetic strategy which involved two sequential low-temperature lithiation procedures and two palladium-catalysed cross-coupling reactions to provide unsymmetrical dichloroterphenyls with central lateral substitution. Treatment of compound **1** with *n*-butyllithium at -78 °C generated the lithium salt which was quenched with trimethyl borate to give arylboronic acid **2** which was coupled with a standard aryl bromide (**3**) to give a biphenyl (**4**). The remaining acidic proton *ortho* to the chloro substituent of compound **4** was then exploited in the manner described above. The resultant biphenylylboronic acid (**5**) was then coupled with other aryl bromides (**3** and **6**) to provide two mesogenic materials (**7** and **8**) with high overall efficiency.



SCHEME 1 The synthesis of 2',3'-dichloro-(4-octyloxy-4"-pentyl- and 4,4"-dipentyl-)terphenyls.

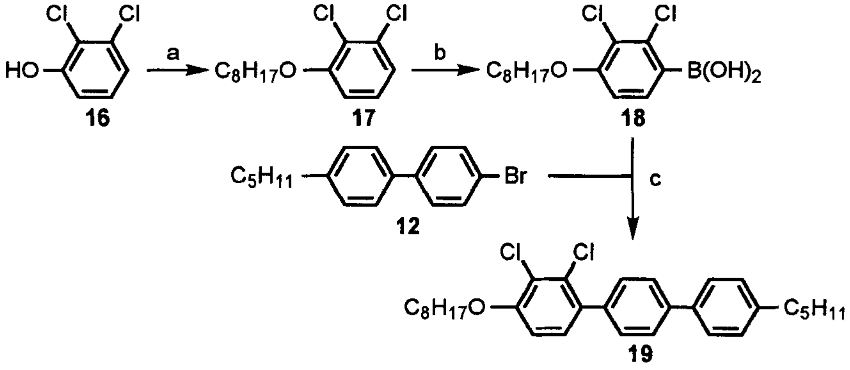
In order to introduce terminal alkyl chains (*e.g.*, pentyl) into the ring containing the lateral chloro substituents, the lithium salt was quenched with an appropriate aldehyde (Scheme 2). The resulting benzylic alcohol (**9**) was dehydrated (P_2O_5) and then hydrogenated to provide an efficient route to compound **10**. The remaining acidic proton of compound **10** was exploited to generate an arylboronic acid (**11**) which was then coupled with standard biphenylyl bromides (**12** and **13**, supplied by Merck Ltd) to provide final liquid crystalline materials (**14** and **15**) in good yields.

The commercial availability of phenol **16** provided an easy route to the dichloroterphenyls with the two chloro substituents in the alkyloxy end ring (Scheme 3). A simple *O*-alkylation provided a good yield of compound **17** which was converted into the arylboronic acid (**18**) by the same low-temperature lithiation methodology described above. A palladium-catalysed cross-coupling reaction of boronic acid **18** with bromobiphenyl **12** efficiently generated liquid crystal **19**.



a ...... (i) *n*-BuLi, THF; (ii) C_4H_9CHO, THF; (iii) NH_4Cl, H_2O.
b ...... (i) P_2O_5, petrol; (ii) H_2, PtO_2, ethanol.
c ...... (i) *n*-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl.
d ...... $Pd(PPh_3)_4$, DME, 2M-Na_2CO_3.

SCHEME 2 The synthesis of 2,3-dichloro-(4"-octyloxy-4-pentyl- and 4,4"-dipentyl-)terphenyls.



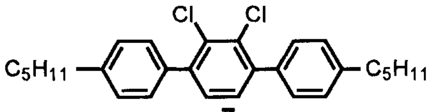
a ...... $C_8H_{17}Br$, K_2CO_3, butanone.
b ...... (i) *n*-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl.
c ...... $Pd(PPh_3)_4$, DME, 2M-Na_2CO_3.

SCHEME 3 The synthesis of 2,3-dichloro-4-octyloxy-4"-pentylterphenyl.

TRANSITION TEMPERATURES

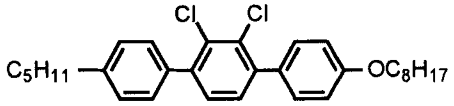
Mesogenic materials have been prepared that have the *ortho* dichloro substituents in two distinctly different molecular environments in both dialkyl and alkyl-alkyloxy forms. As with all types of lateral substitution in terphenyl mesogens, the steric effect considerably disrupts molecular packing which reduces mesogenic character, the extent of this depends upon both the size and the polarity of the lateral substituent. Where the dichloro unit is located in the centre ring, the steric disruption of molecular packing is considerable and two interannular twists are generated (reduces polarizability); hence transition temperatures tend to be dramatically reduced when compared with analogous materials with the dichloro unit located in an end ring. This situation is one commonly encountered when considering the mesogenic behaviour of liquid crystals (*e.g.*, difluoroterphenyls).

TABLE 2 Transition temperatures (°C) for 2',3'-dichloroterphenyls.



7

C 48.0 I

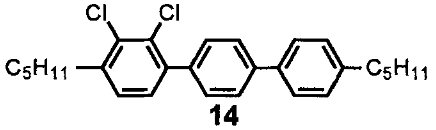


8

C 64.5 (N 54.5) I

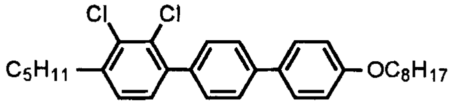
Compound 7 (Table 2) is non-mesogenic (despite a reasonably low melting point) which clearly illustrates the difference between the lateral chloro substituents and the smaller lateral fluoro substituents because the analogous fluoro-substituted materials exhibit high clearing points (*e.g.*, compound **II**); in fact those fluoro-substituted materials with longer and different terminal chains have very low melting points and wide S_C ranges.[2] The use of an alkyloxy terminal substituent (compound **8**, Table 2) increases the molecular polarizability and even though the melting point is higher than for compound 7, a monotropic nematic phase is exhibited by compound **8**. However, the nematic phase stability of compound **8** is 87 °C lower than for the analogous fluoro-substituted material (**III**). Moreover, the melting point of the chloro-substituted material is significantly higher than that of the fluoro substituted compound (**III**), indicative of increased polarity and the wide-range S_C phase generated by the difluoro-substituted system has been eliminated by the larger, more disruptive chloro substituents.

TABLE 3 Transition temperatures (°C) for 2,3-dichloroterphenyls.



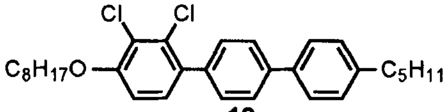
14

C 61.5 (S_C 37.0 S_A 53.5) N 73.5 I



15

C 70.0 S_C 83.5 S_A 110.0 N 112.5 I



19

C 91.5 N 103.5 I

Typically, the mesophase transition temperatures are considerably higher where a lateral substituent occupies a position at the outer edge of the core than for inner-core positions. The smectic phase stability is supported to a greater degree than the nematic phase stability because of the greater lamella packing afforded by filling of space at the edge of the core with a polar substituent; if the lateral dipoles are appropriately positioned then the tilted S_C phase is generated. Unfortunately, such substitution also tends to increase melting points, which for compound **19** has been significant because no smectic phases are exhibited. Compounds **14** and **15** (Table 3) both exhibit S_C, S_A and N phases which is welcome from the point of view of ferroelectric mixture applications. The dichloro-substituted materials with the two chloro substituents in an end ring (**14** and **15**) both exhibit the same mesophases as the difluoro-substituted analogues (S_C, S_A and N), however, the phase stabilities of these mesophases are considerably reduced for the materials with the larger chloro substituents. The dialkyl derivative (**14**) has a much lower (20 °C) melting point than the fluoro-substituted analogue (**VI**) which allows the S_A and S_C phases to be exhibited as monotropic mesophases of low stability. The nematic phase is less affected by the larger chloro substituents than the smectic phases which perhaps indicates that the steric disruption is far more significant than any difference in polarity. The reason for the lack of smectic phases in compound **19** is, in addition to the high melting point, attributed to the reduced polarizability of the alkyl-substituted untwisted biphenyl section when compared to the untwisted alkyloxy-substituted biphenyl moiety of compound **15** which is also the reason for the lower $T_{N\text{-}I}$ value of compound **19**. This structural feature also means that the groups generating the lateral dipoles are all at one end of the molecule which reduces the tilting tendency and hence a S_C phase is not exhibited in compound **19**. Overall, the mesogenic behaviour of the dichloro-susbtituted compounds is similar to the difluoro-substituted analogues in terms of the types of phases exhibited but the increased size of the chloro-substituted materials significantly reduces the liquid crystal phase transition temperatures.

PHYSICAL PROPERTIES

The most promising material (compound **15**) for inclusion in ferroelectric host mixtures from the point of view of transition temperatures has been evaluated for a limited range of physical properties (Table 4). Despite the expectation of a higher lateral dipole moment from the dichloro-substituted compound, the fluoro-substituted analogue (compound **V**) has a significantly more negative dielectric anisotropy. The parallel permittivity ($\varepsilon_{//}$) is similar for both materials (3.5) and so the more negative $\Delta\varepsilon$ of compound **V** can be attributed to the larger perpendicular permittivity ($\varepsilon_{\perp}$). As expected, the viscosity of compound **15** with the larger lateral chloro substituents is much higher than for compound **V**. A ferroelectric mixture based on the *ortho* dichloroterphenyls was formulated but the switching speed was very slow because of the very high viscosity.

TABLE 4 Physical properties of dichloroterphenyl **15**.

Transition Temperatures (°C)	C 70.0 S_C 83.5 S_A 110.0 N 112.5 I
Dielectric Anisotropy ($\Delta\varepsilon$)	-1.65
Viscosity (cP) at 30 °C	1400

EXPERIMENTAL

Confirmation of the structures of intermediates and products was obtained by ^{1}H and ^{13}C 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 polarizing microscope and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7 and IBM data station). The purities of intermediates were checked by GLC analysis (see above) and the purity of each final compound (**7**, **8**, **14**, **15** and **19**) was checked by HPLC analysis (Microsorb C18 80-215-C5 RP column) and were found to be >99.5% pure in each case.

Compounds **12** and **13** were kindly supplied by our collaborators at Merck Ltd, Poole, England. The preparations of intermediates **3** and **6** have been previously reported.[2] Tetrakis(triphenylphosphine)palladium(0) was prepared according to the literature procedure.[17] Compounds **1** and **9** were purchased from Aldrich Chemical Co. Ltd.

2,3-Dichlorophenylboronic acid (**2**)

A solution of *n*-butyllithium in hexanes (18.0 ml, 2.5 M, 0.045 mol) was added dropwise to a stirred, cooled (-78 °C) solution of compound **1** (6.00 g, 0.041 mol) in dry THF (100 ml) under dry nitrogen. The mixture was stirred at -78 °C for 2.5 h and a solution of trimethyl borate (8.63 g, 0.082 mol) in dry THF (60 ml) was added at -78 °C and the mixture was allowed to warm to room temperature overnight. The mixture was stirred at room temperature with 10% aqueous HCl and the product was extracted into ether (x2). The combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a colourless solid.

Yield 7.80 g (100%); no spectroscopy data were obtained for this intermediate.

2,3-Dichloro-4'-pentylbiphenyl (**4**)

Compound **2** (6.27 g, 0.033 mol) was added to a stirred mixture of compound **3** (5.79 g, 0.026 mol), tetrakis(triphenylphosphine)palladium(0) (0.98 g, 0.85 mmol), 1,2-dimethoxyethane (50 ml) and 2 M sodium carbonate (50 ml) under nitrogen. The stirred mixture was heated under reflux for 17 h (GLC and TLC analysis revealed a complete reaction). Water was added and the product was extracted into ether (x2).

The combined ethereal extracts were washed with brine and dried ($MgSO_4$). The solvent was removed *in vacuo* and the product was purified by column chromatography [silica gel / petroleum fraction (bp 40-60 °C)] to give a colourless oil.

Yield 5.05 g (66%); ^1H NMR ($CDCl_3$) δ 0.90(3H, t), 1.40(4H, m), 1.65(2H, quint), 2.65(2H, t), 7.20-7.50(7H, m); IR (film) ν_{max} 2930, 2860, 1520, 1450, 1400, 1195, 1040, 780 cm^{-1}; MS *m/z* 296(M^+), 294(M^+), 292(M^+).

2,3-Dichloro-4'-pentylbiphenyl-4-ylboronic acid (**5**)

Quantities: compound **4** (5.00 g, 0.017 mol), *n*-butyllithium (1.9 ml, 10 M, 0.019 mol), trimethyl borate (3.55 g, 0.034 mol).

The experimental procedure was as described for the preparation of compound **2**.

Yield 5.7 g (100%); no spectroscopy data were obtained for this intermediate.

2',3'-Dichloro-4,4''-dipentylterphenyl (**7**)

Quantities: compound **3** (1.34 g, 5.90 mmol), compound **5** (2.43 g, 7.21 mmol).

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

Yield 1.05 g (41%); transitions (°C) C 48.0 I; ^1H NMR ($CDCl_3$) δ 0.90(6H, t), 1.30-1.40(8H, m), 1.65(4H, quint), 2.65(4H, t), 7.27(6H, m), 7.38(4H, m); IR (KBr) ν_{max} 2940, 2860, 1520, 1455, 1360, 1190, 1020, 845, 820 cm^{-1}; MS *m/z* 442(M^+), 440(M^+), 438(M^+).

2',3'-Dichloro-4-octyloxy-4''-pentylterphenyl (**8**)

Quantities: compound **6** (1.26 g, 4.42 mmol), compound **5** (1.94 g, 5.75 mmol).

The experimental procedure was as described for the preparation of compound **4**. The crude product was purified by column chromatography [silica gel / petroleum fraction (bp 40-60 °C) - dichloromethane, 10:1] to give a colourless solid which was recrystallized from ethanol to yield colourless crystals.

Yield 1.70 g (77%); transitions (°C) C 64.5 (N 54.5) I; ^1H NMR ($CDCl_3$) δ 0.90(6H, 2xt), 1.30-1.40(12H, m), 1.45(2H, quint), 1.65(2H, quint), 1.85(2H, quint), 2.65(2H, t), 4.00(2H, t), 6.97(2H, d), 7.27(4H, m), 7.38(4H, m); IR (KBr) ν_{max} 2930, 2860, 1610, 1530, 1460, 1250, 840, 820 cm^{-1}; MS *m/z* 500(M^+), 498(M^+), 496(M^+).

1-(2,3-Dichlorophenyl)pentan-1-ol (**9**)

A solution of *n*-butyllithium in hexanes (5.2 ml, 10 M, 0.052 mol) was added dropwise to stirred, cooled (-78 °C) solution of compound **1** (7.00 g, 0.048 mol) in dry THF (100 ml) under dry nitrogen. The mixture was stirred at -78 °C for 2.5 h and a solution of pentanal (4.13 g, 0.048 mol) in dry THF (50 ml) was added dropwise at -78 °C. The stirred mixture was allowed to warm to room temperature overnight and aqueous ammonium chloride was added. The product was extracted into ether (x2) and the combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was distilled to yield a colourless oil.

Yield 8.54 g (76%); bp 122 °C at 0.1 mmHg; ^1H NMR ($CDCl_3$) δ 0.95(3H, t), 1.20-1.35(4H, m), 1.85(2H, m), 2.00(1H, s), 5.15(1H, t), 7.25(1H, dd), 7.38(1H, dd), 7.49(1H, dd); IR (film) ν_{max} 3600-3100, 2960, 2870, 1650, 1420, 1180, 1050, 790, 740 cm^{-1}; MS *m/z* 236(M^+), 234(M^+), 232(M^+).

1,2-Dichloro-3-pentylbenzene (**10**)

Phosphorus(V) oxide (15.5 g, 0.11 mol) was added to a stirred solution of compound **9** (8.50 g, 0.036 mol) in petroleum fraction (bp 40-60 °C) (100 ml). The mixture was stirred at room temperature overnight and the mixture was filtered. Platinum(IV) oxide (0.15 g) was added to the filtrate and the stirred mixture was hydrogenated for 4 h at room temperature and atmospheric pressure. The catalyst was filtered off and the filtrate was washed with water. The organic extract was dried ($MgSO_4$), the solvent was removed *in vacuo* and the residue was distilled to yield a colourless oil.

Yield 4.87 g (62%); bp 136-142 °C at 15 mmHg; ^1H NMR ($CDCl_3$) δ 0.90(3H, t), 1.40(4H, m), 1.65(2H, quint), 2.65(2H, t), 7.10-7.30(3H, m); IR (film) ν_{max} 2960, 2860, 1450, 1420, 1180, 1040, 780, 740 cm^{-1}; MS *m/z* 220(M^+), 218(M^+), 216(M^+).

2,3-Dichloro-4-pentylphenylboronic acid (**11**)

Quantities: compound **10** (4.80 g, 0.022 mol), *n*-butyllithium (2.5 ml, 10 M, 0.025 mol), trimethyl borate (4.60 g, 0.044 mol).

The experimental procedure was as described for the preparation of compound **2**.

Yield 5.7 g (100%); no spectroscopy data were obtained for this intermediate.

2,3-Dichloro-4,4''-dipentylterphenyl (**14**)

Quantities: compound **12** (1.52 g, 5.02 mmol), compound **11** (1.71 g, 6.54 mmol).

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

Yield 1.62 g (74%); transitions (°C) C 61.4 (S_C 37.0 S_A 53.5) N 73.5 I; ^1H NMR ($CDCl_3$) δ 0.90(6H, 2xt), 1.30-1.40(8H, m), 1.65(4H, m), 2.65(2H, t), 2.80(2H, t), 7.19-7.27(4H, m), 7.46(2H, d), 7.56(2H, d), 7.75(2H, d); IR (KBr) ν_{max} 2970, 2870, 1510, 1470, 1380, 810 cm^{-1}; MS *m/z* 442(M^+), 440(M^+), 438(M^+).

2,3-Dichloro-4''-octyloxy-4-pentylterphenyl (**15**)

Quantities: compound **13** (1.60 g, 4.43 mmol), compound **11** (1.51 g, 5.79 mmol).

The experimental procedure was as described for the preparation of compound **4**. The crude product was purified by column chromatography [silica gel / petroleum fraction (bp 40-60 °C) - dichloromethane, 10:1] to give a colourless solid which was recrystallized from ethanol to yield colourless crystals.

Yield 1.71 g (78%); transitions (°C) C 70.0 S_C 83.5 S_A 110.0 N 112.5 I; ^{1}H NMR ($CDCl_3$) δ 0.90(6H, 2xt), 1.30-1.40(12H, m), 1.45(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.80(2H, t), 4.00(2H, t), 6.98(2H, d), 7.18-7.26(4H, m), 7.45(2H, d), 7.56(2H, d); IR (KBr) ν_{max} 2930, 2860, 1760, 1610, 1510, 1460, 1250, 1180, 810 cm^{-1}; MS *m/z* 500(M^+), 498(M^+), 496(M^+).

1,2-Dichloro-3-octyloxybenzene (**17**)

A mixture of compound **16** (5.00 g, 0.031 mol), 1-bromooctane (10.39 g, 0.054 mol) and potassium carbonate (30.0 g) in dry butanone (80 ml) was heated under reflux for 24 h (GLC analysis revealed a complete reaction). The mixture was cooled and the potassium carbonate was filtered off. The solvent was removed *in vacuo* and water was added to the residue. The product was extracted into ether (x2) and the combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was distilled to yield a colourless oil.

Yield 8.30 g (98%); bp 149-151 °C at 0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.90(3H, t), 1.30-1.40(8H, m), 1.45(2H, quint), 1.80(2H, quint), 4.00(2H, t), 6.81(1H, dd), 7.04(1H, dd), 7.12(1H, dd); IR (film) ν_{max} 2960, 2940, 2860, 1575, 1450, 1290, 1260, 770 cm^{-1}; MS *m/z* 278(M^+), 276(M^+), 274(M^+).

2,3-Dichloro-4-octlyoxyphenylboronic acid (**18**)

Quantities: compound **17** (8.00 g, 0.029 mol), *n*-butyllithium (25 ml, 1.3 M, 0.033 mol), trimethyl borate (6.05 g, 0.058 mol).

The experimental procedure was as described for the preparation of compound **2**.

Yield 9.20 g (99%); no spectroscopy data were obtained for this intermediate.

2,3-Dichloro-4-octyloxy-4''-pentylterphenyl (**19**)

Quantities: compound **12** (1.22 g, 4.03 mmol), compound **18** (1.67 g, 5.23 mmol).

The experimental procedure was as described for the preparation of compound **4**. The crude product was purified by column chromatography [silica gel / petroleum fraction (bp 40-60 °C) - dichloromethane, 10:1] to give a colourless solid which was recrystallized from ethanol-ethyl acetate (20:1) to yield colourless crystals.

Yield 1.71 g (78%); transitions (°C) C 91.5 N 103.5 I; ^{1}H NMR ($CDCl_3$) δ 0.90(6H, 2xt), 1.30-1.40(12H, m), 1.50(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 4.10(2H, t), 6.91(1H, d), 7.22(1H, d), 7.28(2H, d), 7.45(2H, d), 7.56(2H, d), 7.66(2H, d); IR (KBr) ν_{max} 2960, 2940, 2860, 1610, 1490, 1460, 1300, 820 cm^{-1}; MS *m/z* 500(M^+), 498(M^+), 496(M^+).

ACKNOWLEDGEMENTS

The work reported here has been carried out with the support of the Ministry of Defence and is published by permission of the director, HMSO. We express our thanks to Mr M.R. Thomas who prepared some of the materials as part of an undergraduate research project. We thank collaborators at Merck Limited (Poole) and Dr D.F. Ewing, Mrs B. Worthington, Mr R. Knight and Mr. A.D. Roberts for various spectroscopic measurements .

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