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The synthesis and comparison of the liquid crystalline properties of certain 1-(4'-n-alkoxypolyfluorobiphenyl-4-yl)-2-(trans-4-n- pentylcyclohexyl)-ethenes and -ethanes carrying four, six or eight fluoro-substituents

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The synthesis and comparison of the liquid crystalline properties of certain 1-(4′-*n*-alkoxypolyfluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)-ethenes and -ethanes carrying four, six or eight fluoro-substituents

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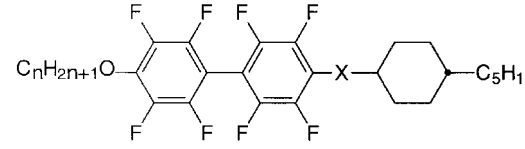
The synthesis and mesomorphic properties of a variety of polyfluorinated alkylaryl-ethanes and -ethenes are reported. The number and position of the symmetrically disposed fluoro-substituents has been varied from six to four and the mesomorphic properties of the compounds are compared with those of the analogous octafluoro-substituted compounds previously reported. All the compounds are moderately low melting, mesomorphic and the type of mesophase formed is dependent upon the number and position of the fluoro-substituents. Increasing the number of fluoro-substituents from four, to six and to eight in a series of polyfluoro-alkylarylethanes decreases the mesophase thermal stability in a stepwise manner and eliminates smectic properties whilst retaining the nematic phase.

1. Introduction

The influence of lateral fluoro-substitution on the mesomorphic properties of a wide variety of compounds has been widely investigated because the inclusion of a lateral fluoro-substituent imparts advantageous properties. For example, melting points may be lowered, nematic range may be increased, high order crystal phases may be eliminated and the occurrence of tilted smectic phases may be enhanced. In general, the properties are dependent upon the number, type and disposition of the lateral fluoro-substituents [1–18].

However, only limited studies of the effect on liquid crystal behaviour of symmetrically disposed polyfluoro-substitution within the molecular core structure have been reported [19, 20]. This may be due to the generally held notion that extensive lateral ring polysubstitution has adverse effects on thermal stability and is liable to generate high melting, non-mesomorphic compounds [1, 21]. Despite this we have recently shown that extensive lateral polyfluorination of the biphenyl nucleus does not inhibit the formation of mesomorphic compounds [22, 23]. In fact, the 4,4′-disubstituted octafluorobiphenyl core in conjunction with suitable central linking and terminal groups, e.g. (**1**), (**1a**), (**1b**), generates



X = -O.OC- (**1**); -CH=CH- (**1a**); -CH_2CH_2- (**1b**)

low melting nematogens which possess a moderately wide nematic to isotropic (N–I) range. Comparison of the mesomorphic properties of compounds (**1**), (**1a**) and (**1b**) with respect to the central linking group reveals the following group order for promoting nematic thermal stability:

$$\textit{trans}\text{–CH=CH–(}\mathbf{1a}\text{)} > \text{–O.OC–(}\mathbf{1}\text{)} > \text{–}CH_2CH_2\text{–(}\mathbf{1b}\text{)}$$

A similar trend is also observed for the melting points whereby the ethene group is associated with compounds that possess the highest melting points. In contrast, a reversed order for the nematic phase temperature range, $\Delta T_{N–I}$, is observed. Compounds comprising the ester group, i.e. (**1**), possess the largest phase range and the ethene group now shows intermediate behaviour.

The alkylaryl-ethanes (**1b**) derived from their corresponding -ethenes are of particular interest because of their low melting tendency which may be attributed to the presence of the flexible dimethylene linkage. It is envisaged that a systematic reduction in the number of lateral fluoro-substituents would improve both the mesophase thermal stability and phase range. Retention of

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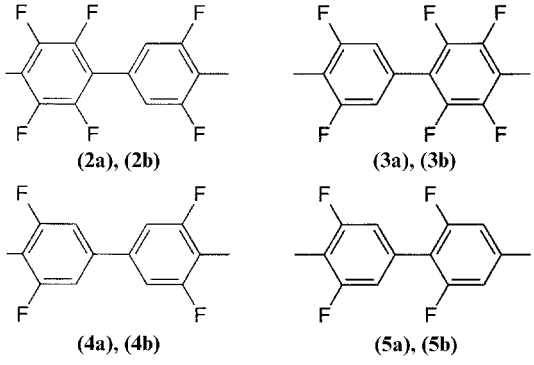
the symmetrical disposition of the remaining fluoro-substituents is particularly important since it is well known that certain non-symmetrical fluoro-substituted alkylarylethanes, e.g. *trans*-4-*n*-alkylcyclohexylethyl-substituted 2,3-difluorobiphenyls, show a high SmC tendency [12]. A symmetrical disposition of the lateral fluoro-substituents is expected to suppress smectic mesophase formation whilst maintaining nematic characteristics.

In our search for low melting nematogenic compounds, we now report further on the synthesis and liquid crystal transition temperatures of some novel 1-(4′-*n*-alkoxypolyfluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethenes and -ethanes carrying either four (**4a**, **4b**, **5a**, **5b**), six (**2a**, **2b**, **3a**, **3b**) or eight (**1a**, **1b**) fluoro-substituents. A systematic study of this type allows insight into the influence of the number and symmetrical disposition of lateral fluoro-substituents on the mesomorphic properties of polyfluoroaryl-ethenes and -ethanes.



2. Synthesis

The preparation of the alkylaryl-ethenes and -ethanes utilized the Wittig reaction [24]. Catalytic hydrogenation at room temperature and atmospheric pressure of the appropriate ethenes afforded the desired alkylaryl-ethanes. Scheme 1 shows, in generalized form, the synthetic route previously reported [23] for the 1-(4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)-ethenes (**1a**) and -ethanes (**1b**). Scheme 1 depends upon the appropriate starting materials, e.g. in the case of the octafluoro-compounds, nonafluorobiphenyl was available. Fortunately, nonafluorobiphenyl may be easily prepared from commercially available decafluorobiphenyl, but the remaining polyfluorobiphenyls (**6**), (**18**) and (**23**) were synthesized using palladium-catalysed cross-coupling reactions, e.g. Suzuki coupling [25] as indicated in scheme 2. A number of polyfluoroarylboronic acids (**13**), (**16**), prepared from the appropriate Grignard reagent and trimethyl borate, were coupled with the required polyfluorobromobenzenes (**14**), (**15**) and (**17**) to give the desired polyfluorobiphenyls (**6**), (**18**) and (**23**), in moderate to high yields.

This method was slightly modified for the preparation of members of the homologous series of (*E*)-1-(4′-*n*-alkoxy-2,3′,5′,6-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)-ethenes (**5a**) and -ethanes (**5b**). Lithiation of 2′,3,4,5,6′-pentafluorobiphenyl was inappropriate because it is liable to occur in the 2,3′,5′,6-positions, i.e. *ortho*- to the 2′,3,5,6′-fluoro-substituents, so that on subsequent carbonation undesired carboxylic acids are formed. To avoid this difficulty, the route shown in scheme 3 was adopted. (*E*)-1-(4′-bromo-2′,6′-difluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene (**32**) was synthesized at the outset via the Wittig reaction and was then cross-coupled, in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0), with 3,4,5-trifluorophenylboronic acid (**16**) to give (*E*)-1-(2,3′,4′,5′,6-pentafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)-ethene (**33**).

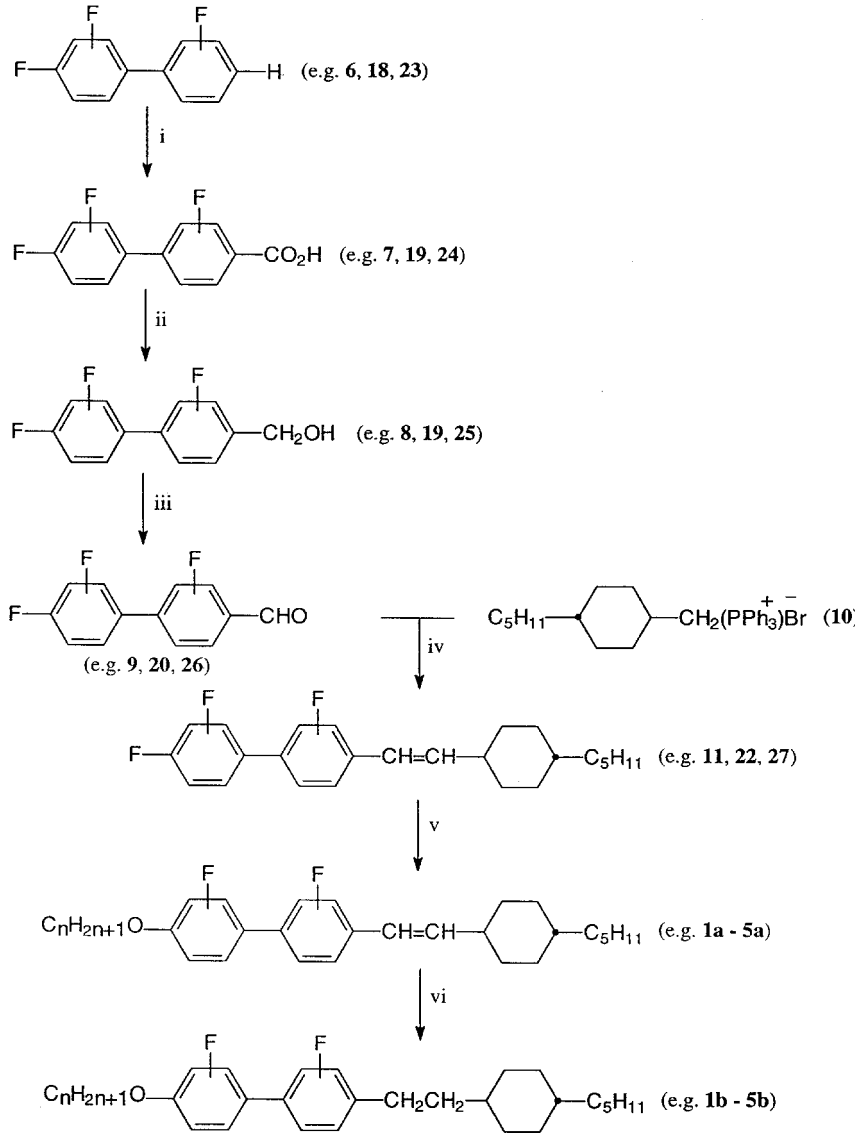
3. Results and discussion

The liquid crystal transition temperatures for members of the series of alkylaryl-ethenes (**1a**–**5b**) and their corresponding -ethanes (**1b**–**5b**) are listed in tables 1 and 2, respectively. In the presence of four fluoro-substituents, (**4a**, **4b**), (**5a**, **5b**), both nematic and smectic phases are observed, whereas with either six† (**3b**) or eight fluoro-substituents (**1b**), the smectic phase is extinguished and the nematic phase alone is observed. The presence of the SmA phase may be due to the more dominant influence of the cyclohexyl moiety which is known to promote the occurrence of orthogonal smectic phase types compared with the influence of the relatively low number of lateral fluoro-substituents. However, in general, an increase in lateral fluorination eliminates smectic properties at the expense of the nematic phase. For reference, the liquid crystal transition temperatures for members of series (**2a**) and (**2b**) are represented graphically in the form of a transition temperature plot as shown in figures 1 and 2, respectively.

Table 3 shows both the influence of replacing the central ethene linkage with the dimethylene linkage and the influence of increasing the number of fluoro-substituents from four, to six, and to eight on the mesophase thermal stability. As expected, the replacement of the ethene linkage by the more flexible dimethylene linkage reduces the mesophase thermal stability for all corresponding pairs of the homologous series, i.e. (**1a**) versus (**1b**), (**2a**) versus (**2b**), etc.

However, the influence of a systematic increase in the

† Except for (**3a**) which exhibits SmA and nematic phases.

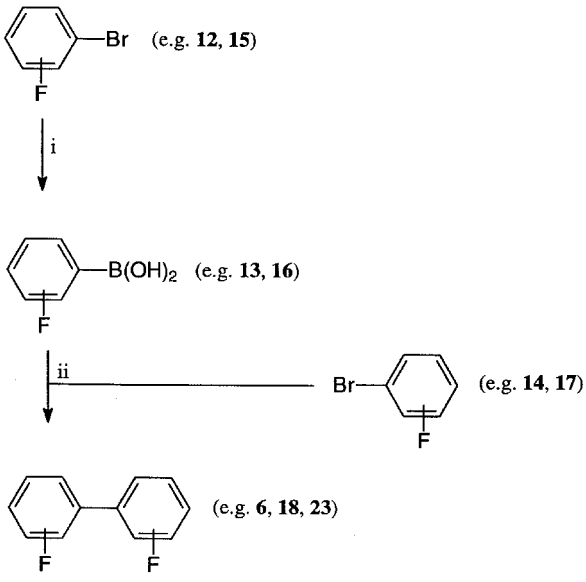


Scheme 1. i. a. 1·6M *n*-BuLi, −78°C, N_2; b. CO_2, −78°C; ii. Borane dimethylsulphide, diethyl ether, N_2; iii. Pyridinium chlorochromate, CH_2Cl_2; iv. 1·6M *n*-BuLi, THF, −10°C, N_2; v. NaH, $C_nH_{2n+1}OH$, pyridine; vi. H_2, 5 per cent Pd/C, C_2H_5OH.

number of lateral fluoro-substituents on mesophase thermal stability is best noted for the series of alkylarylethanes (**1b**–**5b**). The nematic thermal stability, T_{N-I}, decreases in a stepwise manner as the number of fluoro-substituents increases and may be rationalized in terms of molecular broadening, interannular twisting and space-filling effects. For example, when four fluoro-substituents are present, the average T_{N-I} for series (**4b**) is 10°C lower than that for its isomeric counterpart, i.e. series (**5b**), because of reduced inter-ring conjugation and molecular broadening due to enhanced interannular twisting caused by the presence of two fluoro-substituents located *ortho*- to the 1,1′-inter-ring bond.

Importantly, figure 3 summarizes the changes in the average T_{N-I} as the number of fluoro-substituents is increased from four (**4b**, **5b**) to eight (**1b**) via the hexafluoro-compound (**3b**). For example, series (**3b**) may be considered as arising from series (**5b**) by the inclusion of two extra substituents at the 3- and 5-positions. Theoretically, if these two substituents are considered merely to fill space because of their *meta*-disposition with respect to the 1,1′-inter-ring bond and hence are shielded by the existing fluoro-substituents, then there should be little or no change in the mesophase thermal stability. However, the average T_{N-I} decreases by 12·5°C. Thus, the introduction of two symmetrically disposed fluoro-substituents which do not interfere with inter-ring conjugation equates to a 12·5°C decrease in mesophase thermal stability.

Alternatively, series (**3b**) may also be derived from



Scheme 2. i. a. Mg, diethyl ether, N_2; b. Trimethyl borate, THF, $-78^{\circ}C$, N_2; ii. $Pd(PPh_3)_4$, benzene, 2M Na_2CO_3, reflux.

series (**4b**), whereby two additional fluoro-substituents are introduced into the 2- and 6-positions. From theoretical considerations, the average T_{N-I} should decrease by approximately 22·5°C (10°C for interannular twisting and 12·5°C for the introduction of two symmetrically disposed fluoro-substituents. This prediction is in very good agreement with the experimental results which show that the actual decrease in the average T_{N-I} is 22·5°C. Hence, the systematic decrease in the mesophase thermal stability as the number of fluoro-substituents increases shows an additive effect. Introducing an additional two fluoro-substituents at the 2′- and 6′-positions in series (**3b**) generates the octafluoro-compounds (**1b**). The average T_{N-I} decreases by 11·4°C which appears to be primarily due to the additive effect of introducing two symmetrically disposed fluoro-substituents rather than to further increases in interannular twisting. If both effects were operating, then the expected average mesophase thermal stability should decrease by approximately 22·5°C.

A similar rationale may also be used to explain the changes in the average T_{N-I} associated with generating the octafluoro-compounds (**1b**) from the tetrafluoro-substituted analogues (**4b** and **5b**) via the isomeric hexafluoro-compounds (**2b**).

4. Experimental

Confirmation of the structures of the intermediates and the products was obtained by ^1H NMR spectroscopy (either Hitachi Perkin-Elmer R24-b 60 MHz spectrometer or JEOL FX60Q 270 MHz spectrometer) and infrared spectroscopy (Perkin-Elmer 157 grating spectrophotometer). Thermal optical microscopy was carried out with a Vickers M75 polarizing microscope in conjunction with a Mettler FP52 hot stage and FP5 control unit. The progress of reactions was monitored by thin layer chromatography using silica gel coated on aluminium plates (Art. 5554, Merck, Darmstadt).

The preparation of compounds leading to members of the homologous series of 1-(4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)-ethenes (**1a**) and -ethanes (**1b**), as generalized in scheme 1, have been reported previously [23]. Compounds (**12**), (**14**), (**15**), (**17**) and (**28**) were obtained commercially.

4.1. *3,5-Difluorophenylboronic acid* (**13**), scheme 2

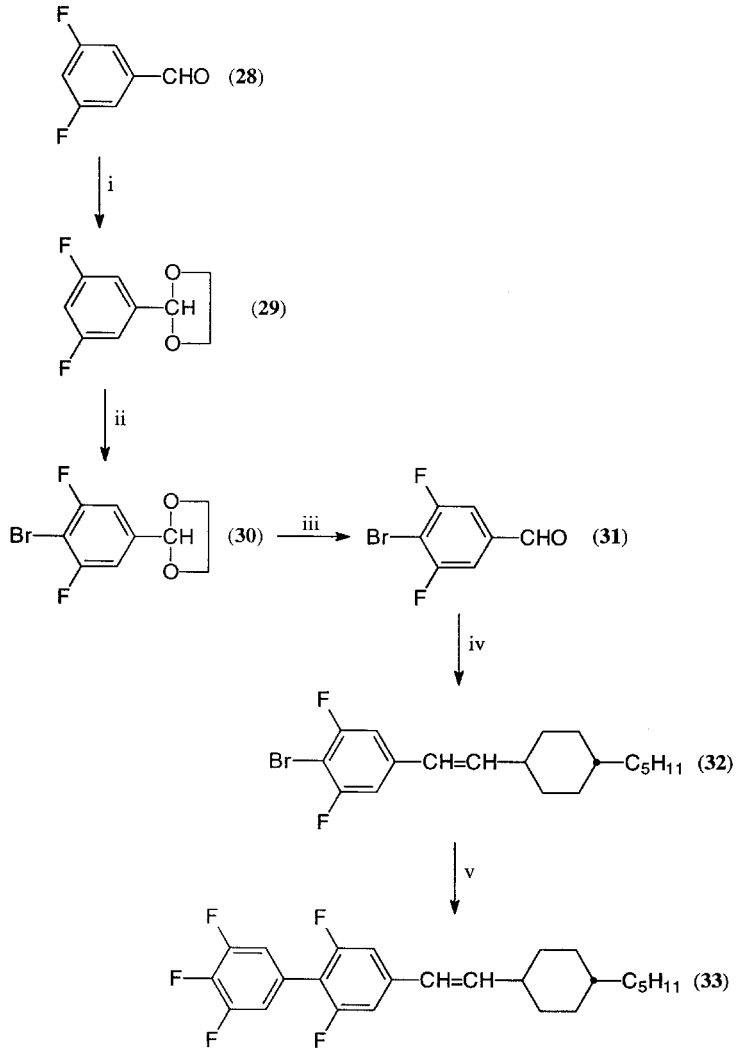
In an atmosphere of nitrogen, the Grignard reagent prepared from commercial 1-bromo-3,5-difluorobenzene (**12**) (10 g, 0·05 mol) and magnesium turnings (1·43 g, 0·06 mol) in dry diethyl ether (100 ml) was added with stirring, dropwise, to trimethyl borate (16 ml, 0·15 mol) in dry tetrahydrofuran (100 ml) at $-78^{\circ}C$. The reaction mixture was allowed to warm to room temperature, stirred overnight, and then 10% aqueous hydrochloric acid (100 ml) was added. The product was extracted into diethyl ether (3 × 100 ml) and the solution then stirred with 4M aqueous sodium hydroxide (100 ml) for 1 h. The ether layer was separated and discarded whilst the aqueous layer was acidified (4M HCl) and shaken with ether (3 × 100 ml). The combined extracts were washed with water (2 × 100 ml), dried ($MgSO_4$), and the solvent was removed *in vacuo* yielding the desired 3,5-difluorophenylboronic acid (**13**), 6·5 g (82%) as a light brown solid: m.p. 180–185°C; δ_H ($CDCl_3$/DMSO) 6·9–7·0 (5 H, m, ArH and 2 × OH) ppm; ν_{max} (KBr) 3500–3100 (O–H str.), 2950, 2850, 1640, 1600, 1480, 1000, 850 cm^{-1}.

4.2. *3,4,5-Trifluorophenylboronic acid* (**16**), scheme 2

Compound (**16**) was prepared using a procedure similar to that described for the synthesis of compound (**13**). Quantities: commercial 1-bromo-3,4,5-trifluorobenzene (**15**) (10 g, 0·05 mol), magnesium (1·4 g, 0·06 mol) and trimethyl borate (16 ml, 0·015 mol). Yield 6·5 g (78%); m.p. 285–289°C; δ_H ($CDCl_3$/DMSO) 7·3–7·5 (4 H, m, ArH and 2 × OH) ppm; ν_{max} (KBr) 3500–3300 (O–H str.), 1650, 1590, 1480, 1000, 850 cm^{-1}.

4.3. *2,3,3′,4,5,5′,6-Heptafluorobiphenyl* (**6**), schemes 1 and 2

In an atmosphere of nitrogen, a solution of 3,5-difluorophenylboronic acid (**13**) (4·3 g, 0·025 mol) in ethanol (10 ml) was added to a vigorously stirred mixture of commercial bromopentafluorobenzene (**14**) (4 g, 0·025 mol), *tetrakis*(triphenylphosphine)palladium(0) (0·17 g, 0·00015 mol), 2M aqueous sodium carbonate (30 ml) and benzene (30 ml). The stirred mixture was



Scheme 3. i. $HOCH_2CH_2OH$, toluene, *p*TSA, reflux; ii. 1·6M *n*-BuLi, Br_2, −78°C, N_2; iii. HCl(aq), dioxane, reflux; iv. (10), 1·6M *n*-BuLi, THF, −10°C, N_2; v. (**16**), $Pd(PPh_3)_4$, benzene, 2M Na_2CO_3, reflux.

heated under reflux until the bromopentafluorobenzene had been completely consumed (as indicated by TLC). The product was extracted into diethyl ether (2 × 100 ml), the extracts were combined, dried ($MgSO_4$), and the solvent was removed *in vacuo*. The resulting residue was purified by column chromatography on silica gel, eluting with light petroleum (b.p. 60–80°C), affording the desired 2,3,3′,4,5,5′,6-heptafluorobiphenyl (**6**), 5 g (71%), as a white crystalline solid, m.p. 65–66°C: δ_H ($CDCl_3$) 6·85–6·9 (2 H, m, ArH), 7·0 (1 H, m, ArH) ppm; ν_{max} (KBr) 3050, 1610, 1590, 1530, 1000, 850, 725 cm^{-1}.

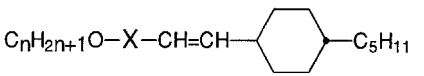
4.4. *2′,3,3′,4′,5,5′,6′-Heptafluorobiphenyl-4-carboxylic acid* (**7**), scheme 1

Commercial 1·6M *n*-butyllithium (12·2 ml, 0·019 mol) was added, dropwise, to a rapidly stirred solution of 2,3,3′,4,5,5′,6-heptafluorobiphenyl (**6**) (5 g, 0·018 mol) in dry 1:1 diethyl ether:hexane (100 ml) maintained at −78°C. After an additional 1 h at −78°C the reaction mixture was poured onto powdered solid carbon dioxide, allowed to warm to room temperature and acidified (4M HCl). The resulting acid was extracted into diethyl ether (2 × 100 ml), and the combined ether extracts were dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude residue was recrystallized from hexane to afford the desired 2′,3,3′,4′,5,5′,6′-heptafluorobiphenyl-4-carboxylic acid (**7**), 5 g (86%), as a white crystalline solid, m.p. 195–200°C: δ_H ($CDCl_3$/DMSO) 12·3 (1 H, s, CO_2H), 7·0 (2 H, m, ArH) ppm; ν_{max} (KBr) 3500–2750 (O–H str.), 1720 (C=O str.), 1530, 1500, 1480, 725 cm^{-1}.

4.5. *2′,3,3′,4′,5,5′,6′-Heptafluorobiphenyl-4-ylmethanol* (**8**), scheme 1

In an atmosphere of nitrogen, borane dimethylsulphide (4·75 ml, 0·05 mol) was added, dropwise, to a solution

Table 1. Liquid crystalline transition temperatures (°C) for members of a series of 1-(4′-*n*-alkoxypolyfluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethenes (**1a**–**5a**).



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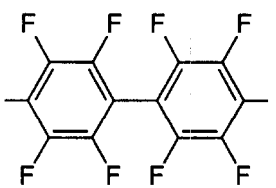
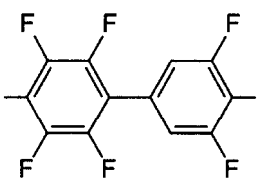
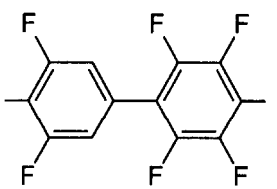


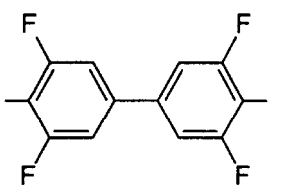
(**1a**)



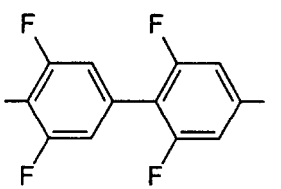
(**2a**)



(**3a**)



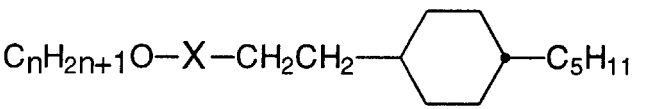
(**4a**)

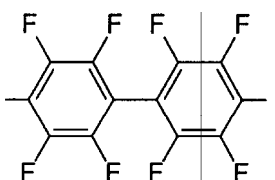
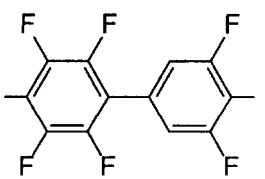
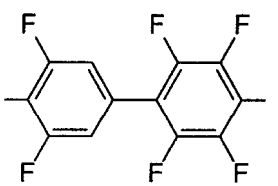
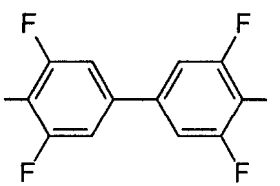
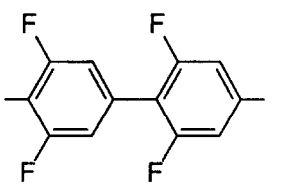


(**5a**)

n	Cr–N	N–I	Cr–N	N–I	Cr–SmA	SmA–N	N–I	Cr–SmA	SmA–N	N–I	Cr–SmA	SmA–N	N–I
3	91	135	—	—	—	—	—	32	118	178	—	—	—
4	74	134	—	—	—	—	—	33	125	177	—	—	—
5	65	125	85	136	54	112	142	31	132	168	78	112	138
6	62	123	77	136	—	—	—	32	137	165	70	110	129
7	68	118	69	121	57	104	129	34	136	157	72	106	123
8	71	115	67	123	58	105	129	—	—	—	69	107	122
9	73	113	74	118	54	97	119	—	—	—	71	101	115
10	76	112	59	118	58	101	122	—	—	—	68	104	118

Table 2. Liquid crystalline transition temperatures (°C) for members of a series of 1-(4′-*n*-alkoxypolyfluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethanes (**1b**–**5b**).



X=  (**1b**)  (**2b**)  (**3b**)  (**4b**)  (**5b**)

n	Cr–I	Cr–N	N–I	Cr–I	Cr–N	N–I	Cr–I	Cr–N	N–I	Cr–N/SmA	SmA–N	N–I	Cr–SmA	SmA–N	N–I
3	—	59	60·5	—	—	—	—	—	—	57	—	(45)	—	—	—
4	66	—	(63·5)	—	—	—	—	—	—	—	—	—	—	—	—
5	59	—	(54)	69	—	(65)	—	64·5	69	—	38	73	31	65	81
6	—	53·5	56·5	—	55	65·5	—	—	—	—	35	77	31	69	80
7	—	51	52	—	53·5	61·5	63	—	(60)	—	32	77	30	65	73
8	—	41·5	52	—	59	63	—	59·5	66	—	33	77·4	31	68	76
9	—	39·5	50·5	—	61	61	64·5	—	(59·5)	—	—	—	—	—	—
10	—	40	50	—	59	62	64	—	(63·5)	—	—	—	—	—	—

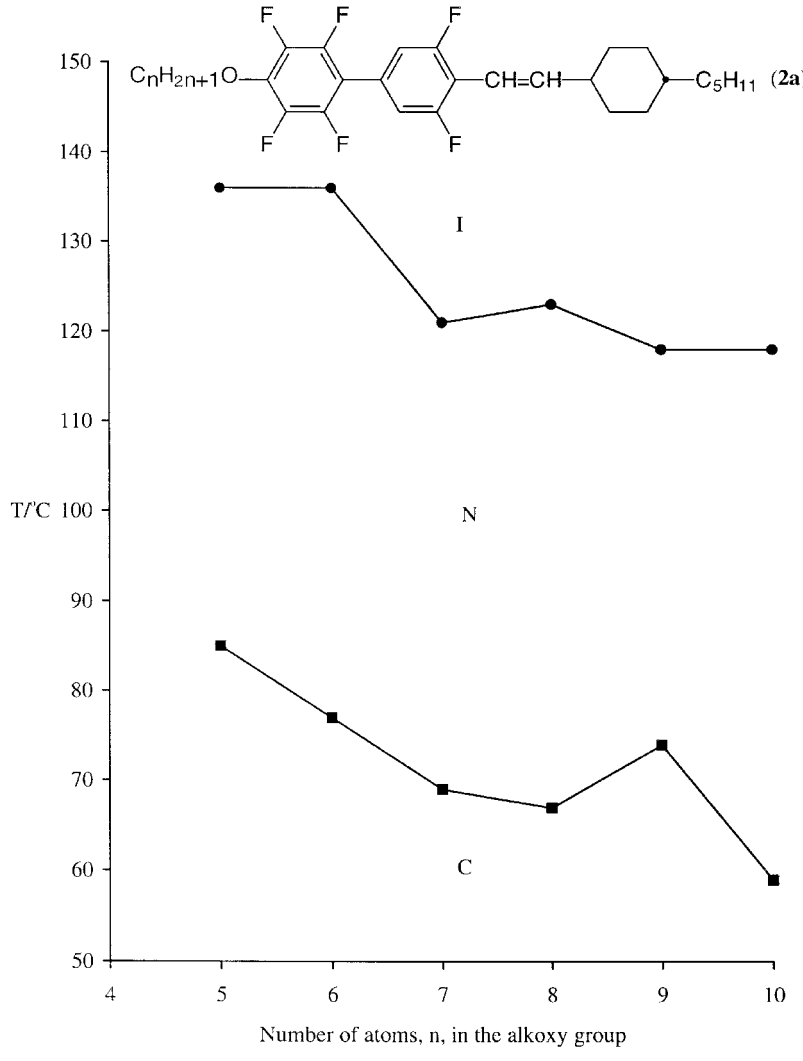


Figure 1. 1-(4′-*n*-alkoxy-2′,3,3′,5,5′,6′-hexafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethenes (**2a**); transition temperatures against *n*, the number of carbon atoms in the alkoxy group.

of 2′,3,3′,4′,5,5′,6′-heptafluorobiphenyl-4-carboxylic acid (**7**), (5 g, 0·015 mol) in dry diethyl ether (50 ml) causing vigorous effervescence and the ether to boil. On completion of the addition, the mixture was heated under reflux for 2 h. The reaction mixture was then poured into cold methanol (100 ml) and allowed to stand overnight before removal of the solvent *in vacuo*. The crude residue was not purified and was used directly in the next stage of the synthesis.

4.6. *2′,3,3′,4′,5,5′,6′-Heptafluorobiphenyl-4-carbaldehyde* (**9**), scheme 1

2′,3,3′,4′,5,5′,6′-Heptafluorobiphenyl-4-ylmethanol (**8**) (5 g, 0·017 mol) in dry dichloromethane (20 ml) was added, in portions, to a rapidly stirred suspension of pyridinium chlorochromate [10], (6 g, 0·027 mol) in dry dichloromethane (100 ml). After 24 h, dry diethyl ether (100 ml) was added and the supernatant liquid was decanted from the black gum which was washed with more dry diethyl ether (2 × 100 ml). The ether solutions were combined, filtered through 'Hyflo-supercel' and the solvent was removed under reduced pressure. The resulting dark brown oil was purified by flash chromatography on silica gel eluting with 3 : 1 light petroleum (b.p. 60–80°C): chloroform, followed by recrystallization from hexane affording the desired 2′,3,3′,4′,5,5′,6′-heptafluorobiphenyl-4-carbaldehyde (**9**), 2·5 g (54%), as a white crystalline solid, m.p. 109–110°C: δ_H ($CDCl_3$) 7·1 (2 H, m, ArH), 10·4 (1 H, s, CHO) ppm; ν_{max} (KBr) 2950, 2850, 1710 (C=O str.), 1530, 1480, 725 cm^{-1}.

4.7. *(E)-1-(2′,3,3′,4′,5,5′,6′-heptafluorobiphenyl-4-yl)-2-(trans-4-n-pentylcyclohexyl)ethene* (**11**), scheme 1

In an atmosphere of nitrogen, commercial 1·6M *n*-butyllithium (8 ml, 0·013 mol) was added, dropwise, to a

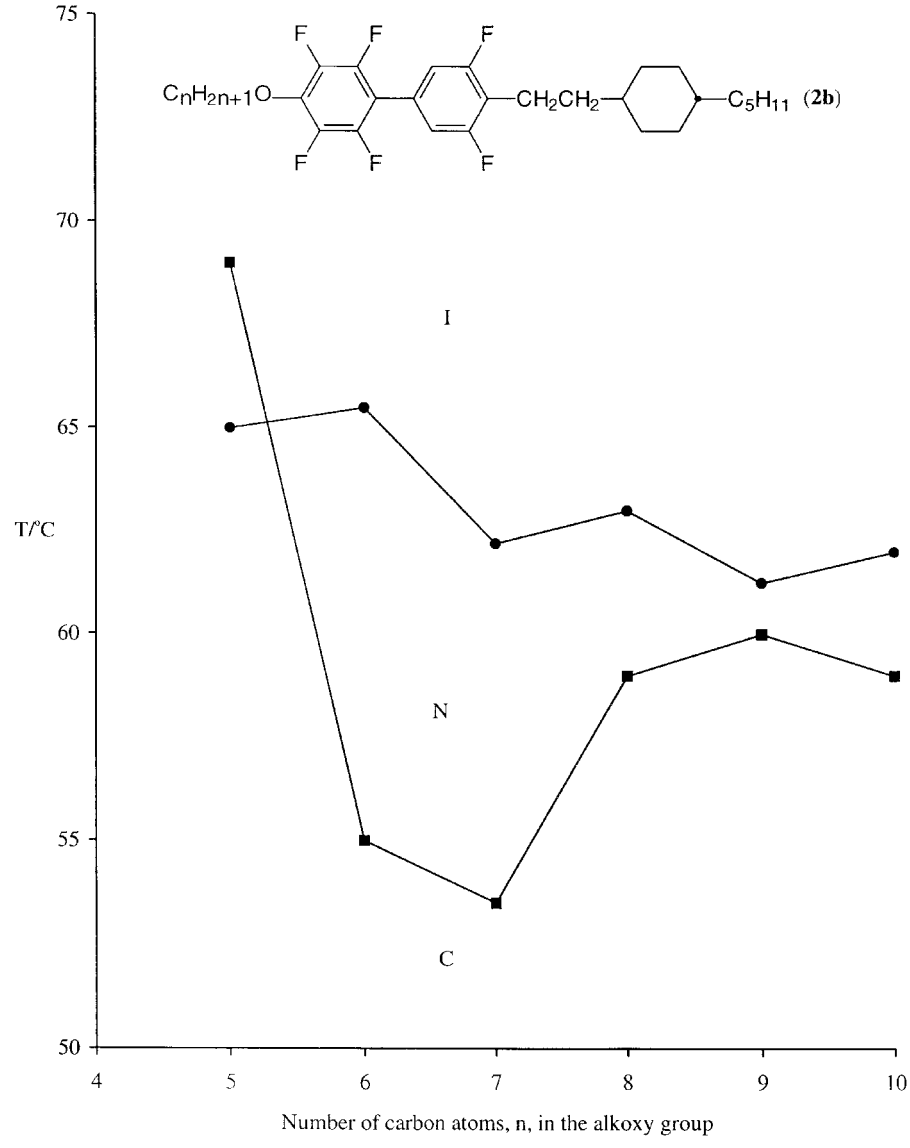


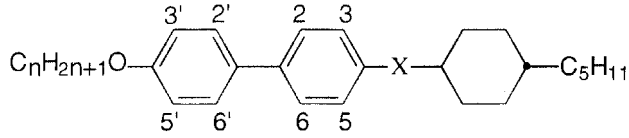
Figure 2. 1-(4′-*n*-alkoxy-2′,3,3′,5,5′,6′-hexafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethanes (**2b**); transition temperatures against *n*, the number of carbon atoms in the alkoxy group.

stirred suspension of *trans*-4-*n*-pentylcyclohexyl-1-methyltriphenylphosphonium bromide (**10**) (6·2 g, 0·012 mol) in dry tetrahydrofuran (50 ml) maintained at −10°C. On completion of the addition, the dark orange–brown solution was stirred for 1 h at 0°C. 2′,3,3′,4′,5,5′,6′-Heptafluorobiphenyl-4-carbaldehyde (**9**) (2·5 g, 0·008 mol) in dry tetrahydrofuran (10 ml) was added and the reaction mixture then stirred at 5°C for 1 h at 0°C. Water (50 ml) was added and the reaction mixture shaken with diethyl ether (3 × 50 ml). The extracts were combined, washed with water (2 × 75 ml), dried ($MgSO_4$), the solvent was removed and the residue purified by column chromatography on silica gel eluting with light petroleum (b.p. 60–80°C). The resulting clear oil, on addition of cold ethanol (10–20 ml), afforded the desired (*E*)-1-(2′,3,3′,4′,5,5′,6′-heptafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene (**11**), 1·5 g (41%), as white flakes, C–N 68–69°C, N–I 107–108·7°C: δ_H ($CDCl_3$) 0·9–1·0 (5 H, m, alkyl), 1·2–1·4 (11 H, br s, alkyl), 1·8 (4 H, m, alkyl), 2·1 (1 H, m, cyclohexyl–H), 6·3–6·4 (1 H, dd, J = 16, –CH=CH–), 6·6–6·7 (1 H, dd, J = 16, –CH=CH–), 7·0 (2 H, m, ArH) ppm; ν_{max} (KBr) 2950, 2875, 1620, 1550, 1480, 1050, 840 cm^{-1}.

4.8. *(E)-1-(4′-n-alkoxy-2′,3,3′,5,5′,6′-hexafluorobiphenyl-4-yl)-2-(trans-4-n-pentylcyclohexyl)ethenes* (**2a**), scheme 1

The appropriate sodium alkoxide (1·1 mol), prepared from the alcohol by the addition of the necessary quantity of sodium hydride, was added dropwise, with stirring,

Table 3. Influence of the position and number of fluoro-substituents on the average liquid crystalline transition temperatures (°C) of certain (n=5–8)[a] alkylaryl-ethenes (**1a**–**5a**) and -ethanes (**1b**–**5b**) containing a polyfluorinated biphenyl core.



Position of fluoro-substituents	X= CH=CH	Average m.p.	Average SmA–N	Average N–I	ΔT_{N-I}	X= CH_2CH_2	Average m.p.	Average SmA–N	Average N–I	ΔT_{N-I}
3′,2′,2,3 5′,6′,6,5	(**1a**)	66·5	—	120·3	53·8	(**1b**)	51·3	—	53·6	2·3
3′,2′,—,3 5′,6′,—,5	(**2a**)	74·5	—	129	54·5	(**2b**)	59·2	—	63·8	4·6
3′,—,2,3 5′,—,6,5	(**3a**)	56·3	107	133·3	26·3	(**3b**)	62·3	—	65	2·7
3′,—,—,3 5′,—,—,5	(**4a**)	32·3	135	163·3	28·3	(**4b**)	34·5	76·1	87·5	11·4
3′,—,2,— 5′,—,6,—	(**5a**)	72·3	108·8	128	19·2	(**5b**)	30·8	66·8	77·5	10·7

[a] n=5,7,8 for series (**3a**) and (**3b**): n=5–7 for series (**4a**).

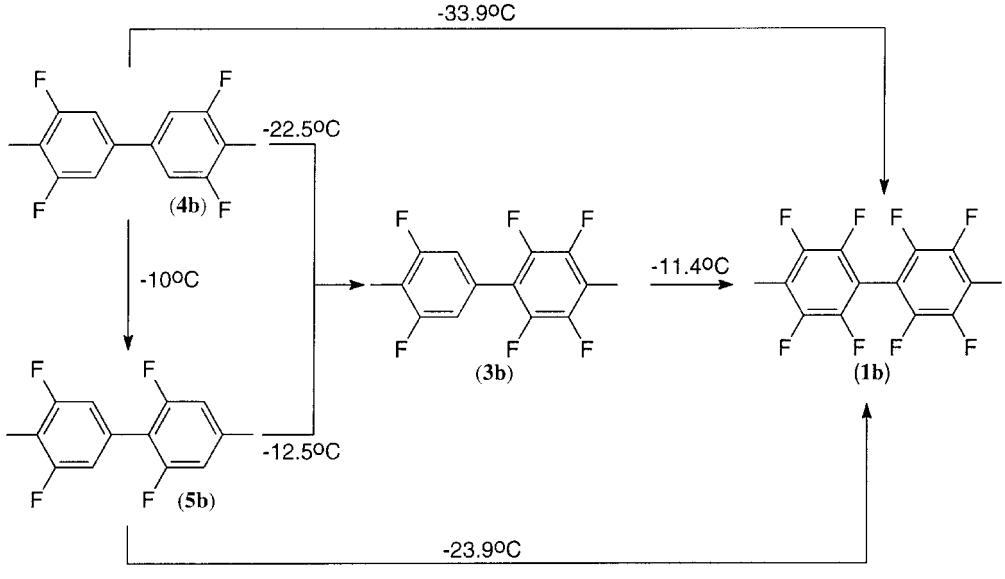


Figure 3. Flow chart to show the influence of increasing the number of fluoro-substituents. The values represent the difference in the average nematic thermal stability (T_{N-I}).

to (*E*)-1-(2′,3,3′,4′,5,5′,6′-heptafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene (**11**) (1 mol) in dry pyridine (10 ml) at −10°C. The progress of the reaction was monitored by TLC at 10 min intervals as the mixture was allowed to warm slowly to room temperature. The optimum reaction time was determined either by the complete consumption of the starting material or by the formation of undesirable side-products. The reaction mixture was then acidified by pouring into ice-cold 4M hydrochloric acid and the aqueous layer was extracted with diethyl ether (2 × 50 ml). The ether extracts were combined, washed with water (50 ml), dried ($MgSO_4$), and the solvent was removed *in vacuo*. The resulting pale yellow liquid was purified by flash chromatography on silica gel eluting with light petroleum (b.p. 60–80°C) followed by recrystallization from ethanol to give the pure (*E*)-1-(4′-*n*-alkoxy-2′,3,3′,5,5′,6′-hexafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene (**2a**) as a white

crystalline solid. The yield of the product was normally greater than 90%. Pentyloxy, Cr–N 85°, N–I 136°; hexyloxy, Cr–N 77°, N–I 136°; heptyloxy, Cr–N 69°, N–I 121°; octyloxy, Cr–N 67°, N–I 123°; nonyloxy, Cr–N 74°, N–I 118°; decyloxy, Cr–N 59°, N–I 118°C.

The following data for (*E*)-1-(4′-*n*-nonyloxy-2′,3,3′,5,5′,6′-hexafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene are representative of the series. Found: C 70·02, H 7·75%; $C_{34}H_4F_6O$ requires C 70·10, H 7·56%. δ_H ($CDCl_3$) 0·9–1·0 (8 H, m, alkyl), 1·2–1·4 (20 H, br s, alkyl), 1·5 (3 H, m, alkyl), 1·8 (6 H, m, alkyl), 2·1 (1 H, m, cyclohexyl–H), 4·2 (2 H, t, ArOC<u>H</u>$_2$), 6·3–6·4 (1 H, dd, J=16, –CH=CH–), 6·6–6·7 (1 H, dd, J=16, –CH=CH–), 7·0 (2 H, m, ArH) ppm; ν_{max} (KBr) 2950, 2850, 1540, 1480, 1150, 1050, 880 cm^{-1}.

4.9. *1-(4′-n-Alkoxy-2′,3,3′,5,5′,6′-hexafluorobiphenyl-4-yl)-2-(trans-4-n-pentyl-cyclohexyl)ethanes* (**2b**), scheme 1

(*E*)-1-(4′-*n*-alkoxy-2′,3,3′,5,5′,6′-hexafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene (**2a**) (0·5 g) was added to a stirred suspension of 5% palladium on charcoal (150 mg) in ethanol (20 ml), and hydrogenated at room temperature and atmospheric pressure. After uptake of the appropriate amount of hydrogen (approximately 1 h) the catalyst was filtered off and the filtrate evaporated to dryness. The residue was dissolved in hot ethanol, insoluble material was removed by hot filtration, and the solution then set aside to cool when the pure 1-(4′-*n*-alkoxy-2′,3,3′,5,5′,6′-hexafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentyl-cyclohexyl)ethane (**2b**) (100%) crystallized out as white flakes. Pentyloxy, Cr–I 69°, N–I (136°); hexyloxy, Cr–N 55°, N–I 65·5°; heptyloxy, Cr–N 53·5°, N–I 61·5°; octyloxy, Cr–N 59°, N–I 63°; nonyloxy, Cr–N 60°, N–I 61°; decyloxy, Cr–N 59°, N–I 62°C.

The following data for 1-(4′-*n*-nonyloxy-2′,3,3′,5,5′,6′-hexafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)-ethane are representative of the series. Found: C 69·64, H 8·11%; $C_{34}H_{46}F_6O$ requires C 69·86, H 7·88%. δ_H ($CDCl_3$) 0·9–1·0 (8 H, m, alkyl), 1·2–1·4 (22 H, br s, alkyl), 1·5 (4 H, m, alkyl), 1·8–2·0 (6 H, m, alkyl), 2·8 (2 H, t, Ar<u>CH</u>$_2$CH$_2$–), 4·2 (2 H, t, ArOC<u>H</u>$_2$), 7·1 (2 H, m, ArH) ppm; ν_{max} (KBr) 2950, 2850, 1540, 1480, 1150, 1050, 880 cm^{-1}.

4.10. *2,3,3′,4′,5,5′,6-Heptafluorobiphenyl* (**18**), schemes 1 and 2

Compound (**18**) was prepared using a procedure similar to that described for the synthesis of compound (**6**). Quantities: commercial 4-bromo-2,3,5,6-tetrafluorobenzene (**17**) (5 g, 0·02 mol), 3,4,5-trifluorophenylboronic acid (**16**) (4·2 g, 0·023 mol) and $Pd[P(Ph)_3]_4$ (0·15 g, 0·00013 mol). Yield 5·5 g (98%), m.p. 51·5–53°C. δ_H ($CDCl_3$) 7·1 (3 H, m, ArH) ppm; ν_{max} (KBr) 3000, 2950, 1620, 1550, 1430, 1210, 1000, 850 cm^{-1}.

4.11. *2,3,3′,4′,5,5′,6-Heptafluorobiphenyl-4-carboxylic acid* (**19**), scheme 1

Compound (**19**) was prepared using a procedure similar to that described for the synthesis of compound (**7**). Quantities: 2,3,3′,4′,5,5′,6-heptafluorobiphenyl (**18**) (5 g, 0·017 mol), 1·6M *n*-butyllithium (12·2 ml, 0·019 mol). Yield 5·3 g (96%), m.p. 177–179°C. δ_H ($CDCl_3$/DMSO) 7·2 (2 H, m, ArH), 12·0 (1 H, s, CO_2H) ppm; ν_{max} 3400–2700 (O–H str.), 1705 (C=O), 1630, 1580, 1400, 1050, 1000, 850 cm^{-1}.

4.12. *2,3,3′,4′,5,5′,6-Heptafluorobiphenyl-4-ylmethanol* (**20**), scheme 1

Compound (**20**) was prepared using a procedure similar to that described for the synthesis of compound (**8**). Quantities: 2,3,3′,4′,5,5′,6-heptafluorobiphenyl-4-carboxylic acid (**19**) (5 g, 0·015 mol), borane dimethylsulphide (4·75 ml, 0·05 mol). Yield assumed to be quantitative and compound (**20**) was used in the next stage of the synthesis without further purification.

4.13. *2,3,3′,4′,5,5′,6-Heptafluorobiphenyl-4-carbaldehyde* (**21**), scheme 1

Compound (**21**) was prepared using a procedure similar to that described for the synthesis of compound (**9**). Quantities: 2,3,3′,4′,5,5′,6-heptafluorobiphenyl-4-ylmethanol (**20**) (5 g, 0·017 mol), pyridinium chlorochromate (6·5 g, 0·03 mol). Yield 3·2 g (82%), m.p. 101–103°C. δ_H ($CDCl_3$) 7·2 (2 H, m, ArH), 10·3 (1 H, s, CHO) ppm; ν_{max} (KBr) 3050, 2950, 2850, 1700 (C=O), 1630, 1580, 1400, 1050, 1000, 850 cm^{-1}.

4.14. *(E)-1-(2,3,3′,4′,5,5′,6-heptafluorobiphenyl-4-yl)-2-(trans-4-n-pentylcyclohexyl)ethene* (**22**), scheme 1

Compound (**22**) was prepared using a procedure similar to that described for the synthesis of compound (**11**). Quantities: 2,3,3′,4′,5,5′,6-heptafluorobiphenyl-4-carbaldehyde (**21**) (3·1 g, 0·009 mol), *trans*-4-*n*-pentylcyclohexyl-1-methyltriphenylphosphonium bromide (7·5 g, 0·015 mol) and 1·6M *n*-butyllithium (10 ml, 0·016 mol). Yield 1·6 g (41%). Cr–I 71–72°, (I–N) 61–60·2°C. δ_H ($CDCl_3$) 0·9–1·0 (6 H, m, alkyl), 1·2–1·5 (10 H, br s, alkyl), 1·8 (4 H, m, alkyl), 2·1 (1 H, m, cyclohexyl–H), 6·4 (1 H, m, J=16, –CH=CH–), 6·6 (1 H, m, J=16, –CH=CH–), 7·2 (2 H, m, ArH) ppm; ν_{max} (KBr) 3050, 2950, 2850, 1630, 1580, 1400, 850 cm^{-1}.

4.15. *(E)-1-(4′-n-alkoxy-2,3,3′,5,5′,6-hexafluorobiphenyl-4-yl)-2-(trans-4-n-pentylcyclohexyl)ethenes* (**3a**), scheme 1

Members of homologous series (**3a**) were prepared using a procedure similar to that described for the

synthesis of compounds (**2a**). Transition temperatures: pentyloxy, Cr–SmA 54°, SmA–N 112°, N–I 142°; heptyloxy, Cr–SmA 57°, SmA–N 104°, N–I 129°; octyloxy, Cr–SmA 58°, SmA–N 105°, N–I 129°; nonyloxy, Cr–SmA 54°, SmA–N 97°, N–I 119°; decyloxy, Cr–SmA 58°, SmA–N 101°, N–I 122°.

The following data for (*E*)-1-(4′-*n*-decyloxy-2,3,3′,5,5′,6-hexafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene are representative of the series. Found: C 70·35, H 7·91%; $C_{35}H_{46}F_6O$ requires C 70·46, H 7·72%. δ_H ($CDCl_3$) 0·9–1·0 (8 H, m, alkyl), 1·2–1·4 (20 H, br s, alkyl), 1·5 (3 H, m, alkyl), 1·8 (6 H, m, alkyl), 2·1 (1 H, m, cyclohexyl–H), 4·2 (2 H, t, ArO$\underline{CH}_2$), 6·3–6·4 (1 H, dd, J=16, –CH=CH–), 6·6–6·7 (1 H, dd, J=16, –CH=CH–), 7·0 (2 H, m, ArH) ppm; ν_{max} (KBr) 2950, 2850, 1540, 1480, 1150, 1050, 880 cm^{-1}.

4.16. *1-(4′-n-Alkoxy-2,3,3′,5,5′,6-hexafluorobiphenyl-4-yl)-2-(trans-4-n-pentylcyclohexyl)ethanes* (**3b**), scheme 1

Members of homologous series (**3b**) were prepared using a procedure similar to that described for the synthesis of compounds (**2b**). Transition temperatures: pentyloxy, Cr–N 64·5°, N–I 69°; heptyloxy, Cr–I 63°, N–I (60°); octyloxy, Cr–N 59·5 N–I 66°; nonyloxy, Cr–I 64·5°, N–I (59·5°); decyloxy, Cr–I 64°, N–I (63·5°).

The following data for 1-(4′-*n*-nonyloxy-2,3,3′,5,5′,6-hexafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)-ethane are representative of the series. Found: C 69·64, H 8·05%; $C_{34}H_{46}F_6O$ requires C 69·86, H 7·88%. δ_H ($CDCl_3$) 0·9–1·0 (8 H, m, alkyl), 1·2–1·4 (22 H, br s, alkyl), 1·5 (4 H, m, alkyl), 1·8–2·0 (6 H, m, alkyl), 2·8 (2 H, t, Ar$\underline{CH}_2CH_2$–), 4·2 (2 H, t, ArO$\underline{CH}_2$), 7·1 (2 H, m, ArH) ppm; ν_{max} (KBr) 2950, 2850, 1540, 1480, 1150, 1050, 880 cm^{-1}.

4.17. *3,3′,4,5,5′-Pentafluorobiphenyl* (**23**), schemes 1 and 2

Compound (**23**) was prepared using a procedure similar to that described for the synthesis of compound (**6**). Quantities: commercial 1-bromo-3,4,5-trifluorobenzene (**15**) (5·7 g, 0·027 mol), 3,5-difluorophenylboronic acid (**13**) (5 g, 0·03 mol) and $Pd[P(Ph_3)]_4$ (0·2 g, 0·007 mol). Yield 6·4 g (98%), m.p. 76–78°C. δ_H ($CDCl_3$) 6·9 (1 H, m, ArH), 7·1 (2 H, m, ArH), 7·2 (2 H, m, ArH) ppm; ν_{max} (KBr) 3000, 2950, 1620, 1550, 1430, 1210, 1000, 850 cm^{-1}.

4.18. *3,3′,4′,5,5′-Pentafluorobiphenyl-4-carboxylic acid* (**24**), scheme 1

Compound (**24**) was prepared using a procedure similar to that described for the synthesis of compound (**7**). Quantities: 3,3′,4,5,5′-pentafluorobiphenyl (**23**) (5 g, 0·02 mol), 1·6M *n*-butyllithium (14 ml, 0·022 mol). Yield 5·4 g (94%), m.p. 170–172·5°C. δ_H ($CDCl_3$/DMSO) 7·0–7·2 (4 H, m, ArH), 12·1 (1 H, s, CO_2H) ppm; ν_{max} (KBr) 3400–2750 (O–H str.), 1710 (C=O), 1630, 1580, 1400, 1050, 1000, 850 cm^{-1}.

4.19. *3,3′,4′,5,5′-Pentafluorobiphenyl-4-ylmethanol* (**25**), scheme 1

Compound (**25**) was prepared using a procedure similar to that described for the synthesis of compound (**8**). Quantities: 3,3′,4′,5,5′-pentafluorobiphenyl-4-carboxylic acid (**24**) (5 g, 0·017 mol), borane dimethylsulphide (4·75 ml, 0·05 mol). Yield assumed to be quantitative and compound (**25**) was used in the next stage of the synthesis without further purification.

4.20. *3,3′,4′,5,5′-Pentafluorobiphenyl-4-carbaldehyde* (**26**), scheme 1

Compound (**26**) was prepared using a procedure similar to that described for the synthesis of compound (**9**). Quantities: 3,3′,4′,5,5′-pentafluorobiphenyl-4-ylmethanol (**25**) (5 g, 0·017 mol), pyridinium chlorochromate (6·5 g, 0·03 mol). Yield 2·9 g (63%), m.p. 153–154·5°C. δ_H ($CDCl_3$) 7·1–7·2 (4 H, m, ArH), 10·5 (1 H, s, CHO) ppm; ν_{max} (KBr) 3050, 2950, 2850, 1705 (C=O), 1630, 1580, 1400, 1050, 1000, 850 cm^{-1}.

4.21. *(E)-1-(3,3′,4′,5,5′-pentafluorobiphenyl-4-yl)-2-(trans-4-n-pentylcyclohexyl)ethene* (**27**), scheme 1

Compound (**27**) was prepared using a procedure similar to that described for the synthesis of compound (**11**). Quantities: 3,3′,4′,5,5′-pentafluorobiphenyl-4-carbaldehyde (**26**) (2·5 g, 0·009 mol), *trans*-4-*n*-pentylcyclohexyl-1-methyltriphenylphosphonium bromide (7·5 g, 0·015 mol) and 1·6M *n*-butyllithium (9·6 ml, 0·015 mol). Yield 1·0 g (26%). Cr–N 71·8–72·9°, N–I 106·7–109°C. δ_H ($CDCl_3$) 0·9–1·0 (6 H, m, alkyl), 1·2–1·5 (10 H, br s, alkyl), 1·8 (4 H, m, alkyl), 2·1 (1 H, m, cyclohexyl–H), 6·2 (1 H, m, J=16, –CH=CH–), 6·4 (1 H, m, J=16, –CH=CH–), 6·9–7·1 (4 H, m, ArH) ppm; ν_{max} (KBr) 3050, 2950, 2850, 1700, 1630, 1580, 1400, 850 cm^{-1}.

4.22. *1-(4′-n-Alkoxy-3,3′,5,5′-tetrafluorobiphenyl-4-yl)-2-(trans-4-n-pentylcyclohexyl)ethenes* (**4a**), scheme 1

Members of homologous series (**4a**) were prepared using a procedure similar to that described for the synthesis of compounds (**2a**). Transition temperatures: propyloxy, Cr–SmA 32°, SmA–N 118°, N–I 178°; butyloxy, Cr–SmA 33°, SmA–N 125°, N–I 177°; pentyloxy, Cr–SmA 31°, SmA–N 132°, N–I 168°; hexyloxy, Cr–SmA 32°, SmA–N 137°, N–I 165°; heptyloxy, Cr–SmA 34°, SmA–N 136°, N–I 157°C.

The following data for (*E*)-1-(4′-*n*-decyloxy-3,3′,5,5′-hexafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl) ethene are representative of the series. Found: C 74·66, H 8·7%; $C_{35}H_{48}F_4O$ requires C 75·00, H 8·57%. δ_H

($CDCl_3$) 0·9–1·0 (8 H, m, alkyl), 1·2–1·4 (22 H, br s, alkyl), 1·5 (3 H, m, alkyl), 1·8 (6 H, m, alkyl), 2·1 (1 H, m, cyclohexyl–H), 4·2 (2 H, t, $ArO\underline{CH_2}$), 6·3–6·4 (1 H, dd, $J=16$, –CH=CH–), 6·6–6·7 (1 H, dd, $J=16$, –CH=CH–), 7·0–7·2 (2 H, m, ArH) ppm; ν_{max} (KBr) 2950, 2850, 1540, 1480, 1150, 1050, 880 cm^{-1}.

4.23. *1-(4′-n-Alkoxy-3,3′,5,5′-tetrafluorobiphenyl-4-yl)-2-(trans-4-n-pentylcyclohexyl)ethanes* (**4b**), scheme 1

Members of homologous series (**4b**) were prepared using a procedure similar to that described for the synthesis of compounds (**2b**). Transition temperatures: propyloxy, Cr–N 57°, SmA–N (45°), N–I 97°; pentyloxy, Cr–SmA 38°, SmA–N 73°, N–I 88°; heptyloxy, Cr–I 63°, N–I (60°); octyloxy, Cr–N 59·5, N–I 66°; nonyloxy, Cr–I 64·5°, N–I (59·5°); decyloxy, Cr–I 64°, N–I (63·5°).

The following data for 1-(4′-*n*-decyloxy-3,3′,5,5′-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)-ethane are representative of the series. Found: C 74·27, H 9·12%; $C_{35}H_{50}F_4O$ requires C 74·73, H 8·89%. δ_H ($CDCl_3$) 0·9–1·0 (8 H, m, alkyl), 1·2–1·4 (22 H, br s, alkyl), 1·5 (4 H, m, alkyl), 1·8–2·0 (6 H, m, alkyl), 2·8 (2 H, t, $Ar\underline{CH_2}CH_2$–), 4·2 (2 H, t, $ArO\underline{CH_2}$), 7·1 (2 H, m, ArH) ppm; ν_{max} (KBr) 2950, 2850, 1540, 1480, 1150, 1050, 880 cm^{-1}.

4.24. *2-(3,5-Difluorophenyl)-1,3-dioxolane* (**29**), scheme 3

Commercial 3,5-difluorobenzaldehyde (**28**) (20 g, 0·14 mol), ethylene glycol (13 g, 0·21 mol), toluene (100 ml) and *p*-toluenesulphonic acid (0·3 g) were heated under reflux and the water formed during the progress of the reaction continuously removed as an azeotrope by means of a Dean–Stark trap. The reaction mixture was then poured into 10% aqueous sodium bicarbonate (200 ml) and the toluene layer was separated from the aqueous phase which was shaken with diethyl ether (2 × 50 ml). The organic phases were combined, dried ($MgSO_4$), and the solvent was removed *in vacuo* affording the desired 2-(3,5-difluorophenyl)-1,3-dioxolane (**29**), 25 g (98%), as a clear oil, b.p. 70°C/1·00 mm Hg, δ_H ($CDCl_3$) 3·9 (4 H, s, CH_2CH_2), 5·8 (1 H, s, CH), 6·9 (3 H, m, ArH) ppm; ν_{max} (film) 3050, 2950, 2850, 1620, 1600, 1310, 840, 725 cm^{-1}.

4.25. *2-(4-Bromo-3,5-difluorophenyl)-1,3-dioxolane* (**30**), scheme 3

In an atmosphere of nitrogen, commercial 1·6M *n*-BuLi (37 ml, 0·06 mol) was added with stirring, dropwise, to 2-(3,5-difluorophenyl)-1,3-dioxolane (**29**) (10 g, 0·05 mol) in dry tetrahydrofuran (100 ml) at −78°C. On completion of the addition, the reaction mixture was maintained at −78°C for an additional 1 h after which bromine (5 ml, 0·1 mol) was added dropwise. The reaction mixture was then allowed to warm to room temperature and poured into 4M sodium hydroxide (100 ml). The organic layer was separated from the aqueous phase which was shaken with diethyl ether (2 × 100 ml). The organic phases were combined, washed with aqueous sodium metabisulphite, and water (2 × 100 ml), then dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude residue was vacuum distilled to afford the desired 2-(4-bromo-3,5-difluorophenyl)-1,3-dioxolane (**30**), 11 g (82%), as a clear oil, b.p. 97°C/0·5 mm Hg. δ_H ($CDCl_3$) 4·1 (4 H, s, CH_2CH_2), 5·8 (1 H, s, CH), 7·2 (3 H, m, ArH) ppm; ν_{max} (film) 3050, 2950, 2850, 1620, 1600, 1440, 1650, 840 cm^{-1}.

4.26. *4-Bromo-3,5-difluorobenzaldehyde* (**31**), scheme 3

2-(4-Bromo-3,5-difluorophenyl)-1,3-dioxolane (**30**) (10 g, 0·04 mol), concentrated hydrochloric acid (5 ml) and dioxane (100 ml) were heated under reflux for 1 h. The reaction mixture was allowed to cool and then poured into water (200 ml). The product was extracted into diethyl ether (2 × 100 ml) and the extracts were combined, dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was recrystallized from hexane to furnish the desired 4-bromo-3,5-difluorobenzaldehyde (**31**), 8·8 g (100%), as a white solid, m.p. 83–85°C. δ_H ($CDCl_3$) 7·4 (2 H, d, ArH), 10·0 (1 H, s, CHO); ν_{max} (KBr) 3050, 2950, 2850, 1700 (C=O str.), 1500, 1440, 1000, 850 cm^{-1}.

4.27. *(E)-1-(bromo-3,5-difluorophenyl)-2-(trans-4-n-pentylcyclohexyl)ethene* (**32**), scheme 3

Compound (**32**) was prepared using a procedure similar to that described for the synthesis of compound (**11**). Quantities: 4-bromo-3,5-difluorobenzaldehyde (**31**) (5 g, 0·02 mol), *trans*-4-*n*-pentylcyclohexyl-1-methyltriphenylphosphonium bromide (15 g, 0·03 mol) and 1·6M *n*-butyllithium (19 ml, 0·033 mol). Yield 3·5 g (43%), b.p. 160°C/0·05 mm Hg. δ_H 0·9 (5 H, m, alkyl), 1·2–1·4 (11 H, br s, alkyl), 1·9 (4 H, m, alkyl), 2·1 (1 H, m, cyclohexyl–H), 6·0 (1 H, m, $J=16$, –CH=CH–), 6·2 (1 H, m, $J=16$, –CH=CH–), 7·1 (2 H, m, ArH) ppm; ν_{max} (KBr) 3050, 2950, 2850, 1610, 1580, 1400, 1050, 850 cm^{-1}.

4.28. *(E)-1-(2,3′,4′,5′,6-Pentafluorobiphenyl-4-yl)-2-(trans-4-n-pentylcyclohexyl)ethene* (**33**), scheme 3

Compound (**33**) was prepared using a procedure similar to that described for the synthesis of compound (**6**). Quantities: (*E*)-1-(bromo-3,5-difluorophenyl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene (**32**) (3 g, 0·008 mol), 3,4,5-trifluorophenylboronic acid (**16**) (1·6 g, 0·0088 mol) and $Pd[(PPh_3)]_4$ (0·1 g, 0·00008 mol). Yield 0·9 g (27%). Cr–I 87–89°, (I–N) 80–77·5°C, b.p. 185°C/0·2 mm Hg. δ_H ($CDCl_3$) 0·9–1·0 (5 H, m, alkyl), 1·32–1·4 (1 H, br s,

alkyl), 1·8 (6 H, m, alkyl), 2·1 (1 H, m, cyclohexyl–H), 6·1–6·3 (2 H, m, J=16, –CH=CH–), 6·9–7·1 (4 H, m, ArH) ppm; ν_{max} (KBr) 2950, 2850, 1540, 1500, 1480, 1150, 1050, 880 cm^{-1}.

4.29. *(E)-1-(4′-n-alkoxy-2,3′,5′,6-tetrafluorobiphenyl-4-yl)-2-(trans-4-n-pentylcyclohexyl)ethenes* (**5a**), scheme 1

Members of homologous series (**5a**) were prepared using a procedure similar to that described for the synthesis of compounds (**2a**). Transition temperatures: pentyloxy, Cr–SmA 78°, SmA–N 112°, N–I 138°; hexyloxy, Cr–SmA 70°, SmA–N 110°, N–I 129°; heptyloxy, Cr–SmA 72°, SmA–N 106°, N–I 123°; octyloxy, Cr–SmA 69°, SmA–N 107°, N–I 122°; nonyloxy, Cr–SmA 71°, SmA–N 101°, N–I 115°; decloxy, Cr–SmA 68°, SmA–N 104°, N–I 118°C.

The following data for (*E*)-1-(4′-*n*-decyloxy-2,3′,5′,6-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)-ethene are representative of the series. Found: C 74·78, H 8·85%; $C_{35}H_{48}F_4O$ requires C 75·00, H 8·57%, δ_H ($CDCl_3$) 0·9–1·0 (8 H, m, alkyl), 1·2–1·4 (22 H, br s, alkyl), 1·5 (3 H, m, alkyl), 1·8 (6 H, m, alkyl), 2·1 (1 H, m, cyclohexyl–H), 4·2 (2 H, t, ArO<u>CH</u>$_2$), 6·1–6·3 (2 H, m, J=16, –CH=CH–), 6·9–7·1 (4 H, m, ArH) ppm; ν_{max} (KBr) 2950, 2850, 1540, 1480, 1150, 1050, 880 cm^{-1}.

4.30. *1-(4′-n-Alkoxy-2,3′,5′,6-tetrafluorobiphenyl-4-yl)-2-(trans-4-n-pentylcyclohexyl)ethanes* (**5b**), scheme 1

Members of homologous series (**5b**) were prepared using a procedure similar to that described for the synthesis of compounds (**2b**). Transition temperatures: pentyloxy, Cr–SmA 31°, SmA–N 65°, N–I 81°; hexyloxy, Cr–SmA 31°, SmA–N 69°, N–I 80°; heptyloxy, Cr–SmA 30°, SmA–N 65°, N–I 73°; octyloxy, Cr–N 31°, SmA–N 68°, N–I 76°.

The following data for 1-(4′-*n*-nonyloxy-2,3′,5′,6-tetrafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethane are representative of the series. Found: C 74·26, H 8·85%; $C_{34}H_{48}F_4O$ requires C 74·45, H 8·76% δ_H ($CDCl_3$) 0·9–1·0 (8 H, m, alkyl), 1·2–1·4 (22 H, br s, alkyl), 1·5 (4 H, m, alkyl), 1·8–2·0 (6 H, m, alkyl), 2·8 (2 H, t, Ar<u>CH</u>$_2$CH$_3$–), 4·2 (2 H, t, ArO<u>CH</u>$_2$), 6·9–7·1 (4 H, m, ArH) ppm; ν_{max} (KBr) 2950, 2850, 1540, 1480, 1150, 1050, 880 cm^{-1}.

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