Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

The synthesis and transition temperatures of some *trans*-4-alkylcyclohexylethyl-substituted 2,3-difluorobiphenyls

Michael Hird[a]; George W. Gray[ab]; Kenneth J. Toyne[a]
[a] School of Chemistry, The University, Hull, England [b] Merck Ltd, Poole, Dorset, England

To cite this Article Hird, Michael , Gray, George W. and Toyne, Kenneth J.(1992) 'The synthesis and transition temperatures of some *trans*-4-alkylcyclohexylethyl-substituted 2,3-difluorobiphenyls', Liquid Crystals, 11: 4, 531 — 546
To link to this Article: DOI: 10.1080/02678299208029008
URL: http://dx.doi.org/10.1080/02678299208029008

LIQUID CRYSTALS, 1992, VOL. 11, NO. 4, 531–546

The synthesis and transition temperatures of some *trans*-4-alkylcyclohexylethyl-substituted 2,3-difluorobiphenyls

by MICHAEL HIRD, GEORGE W. GRAY†
and KENNETH J. TOYNE*
School of Chemistry, The University, Hull HU6 7RX, England

(*Received 19 July 1991; accepted 1 December 1991*)

Terphenyls with two lateral *ortho*-fluoro-substituents have proved to be excellent host materials for ferroelectric (S_C^*) mixtures. The compounds reported here are biphenyls with the same arrangement of lateral substituents but with a *trans*-4-alkylcyclohexylethyl moiety as one of the terminal substituents. Such three ring systems retain the ability to generate the S_C mesophase and have low melting points. Low temperature lithiation procedures were used to prepare phenylboronic acids, which were then used in palladium catalysed cross-coupling procedures to prepare the desired compounds. The effect of molecular structure on the mesophase types and thermal stabilities is discussed and comparisons are made with analogous terphenyls and biphenyls with open chain terminal substituents.

1. Introduction

The ferroelectric display device has received much research attention in recent years because of its great potential as a fast switching device which has a high multiplexability [1–9]. There are several physical properties and requirements which are important in formulating S_C^* mixtures for use in ferroelectric cells, and these include the following:

(*a*) low viscosity, which is a most important factor for fast switching speeds [10];
(*b*) high negative dielectric anisotropy, which is also important for fast switching speeds [11],
(*c*) a phase sequence of S_C–S_A–N–I, for good alignment [12];
(*d*) a tilt angle of 22·5°, for an optimum compromise of fast switching and good contrast ratio [2, 13];
(*e*) an optical path difference ($d\Delta n$), ideally 0·28 μm, for maximum contrast [2, 13];
(*f*) a chiral dopant with a high P_S value and a long pitch length [11, 14].

The only realistic method of formulating such a ferroelectric (S_C^*) mixture is to prepare an achiral host mixture which has the best possible compromise of the desirable properties and to add between 5 to 10 per cent of a chiral dopant (which need not be mesogenic) to induce chirality within the whole system [7–9, 11, 12, 14].

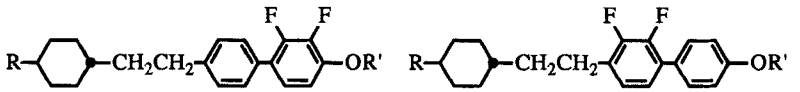
To achieve a very low viscosity and also to obtain a high negative dielectric anisotropy is difficult, since the functional groups usually required to provide a negative dielectric anisotropy protrude from the side of the molecule and so increase the viscosity. The use of two lateral fluoro substituents arranged *ortho* to each other in terphenyl systems [7–9, 15] helps to minimize the viscosity whilst providing a negative dielectric anisotropy. These compounds also show a strong tendency to generate the S_C

* Author for correspondence.
† Present address: Merck Ltd, Broom Road, Poole, Dorset BH12 4NN, England.

0267–8292/92 $3·00

mesophase, to have low melting points and to have the correct phase sequence for good alignment; it is this combination of physical properties which makes these compounds excellent host materials for ferroelectric (S_C^*) mixtures [7–9, 11]. However, their birefringence is relatively high (0·19), and in order to maintain the optimum optical path difference of 0·28 μm, the cell spacing must be kept very small (1·5 μm). High birefringence is, however, advantageous when these materials are considered for use in electrically controlled birefringence devices since these devices utilize nematic materials of negative dielectric anisotropy ($-\Delta\varepsilon$) and require a large optical path difference to give steep electro-optic characteristics [6, 9, 16–18].

The preparation of *ortho*-difluoro-substituted biphenyls which incorporate a cyclohexyl substituent as one of the terminal substituents (compounds **a** and **b**) were expected to provide materials which have similar attributes to their non-cyclohexyl-substituted terphenyl analogues but with a lower birefringence. In order to avoid the presence of undesirable underlying (more ordered) orthogonal smectic mesophases which are often associated with cyclohexyl-substituted compounds [19–22], the dimethylene linking group was used. It was expected that this arrangement would also provide more of a true alkyl-substituted terminal chain than a directly linked cyclohexane ring and that the increased flexibility this creates would give low melting points.

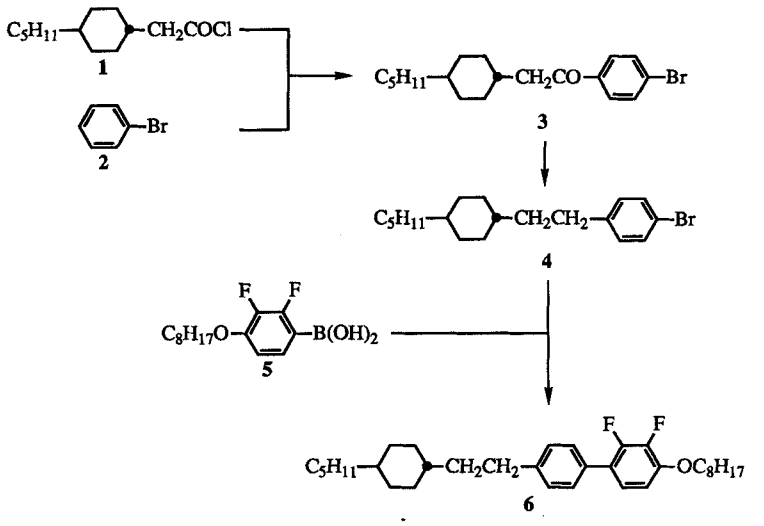


Only alkyloxy-substituted aryl derivatives of the *trans*-4-alkylcyclohexylethylbiphenyls were prepared because it was thought that dialkyl-substituted systems would not exhibit the S_C mesophase. In fact, the related monofluoro-substituted dialkyl compounds (I compounds) [23, 24] are successfully used as low melting nematic materials in commercial mixtures, and therefore, the difluoro-substituted systems would not be likely to show an S_C phase. The compounds reported here are the subject of a patent application which also covers a wide range of other, related, systems [25].

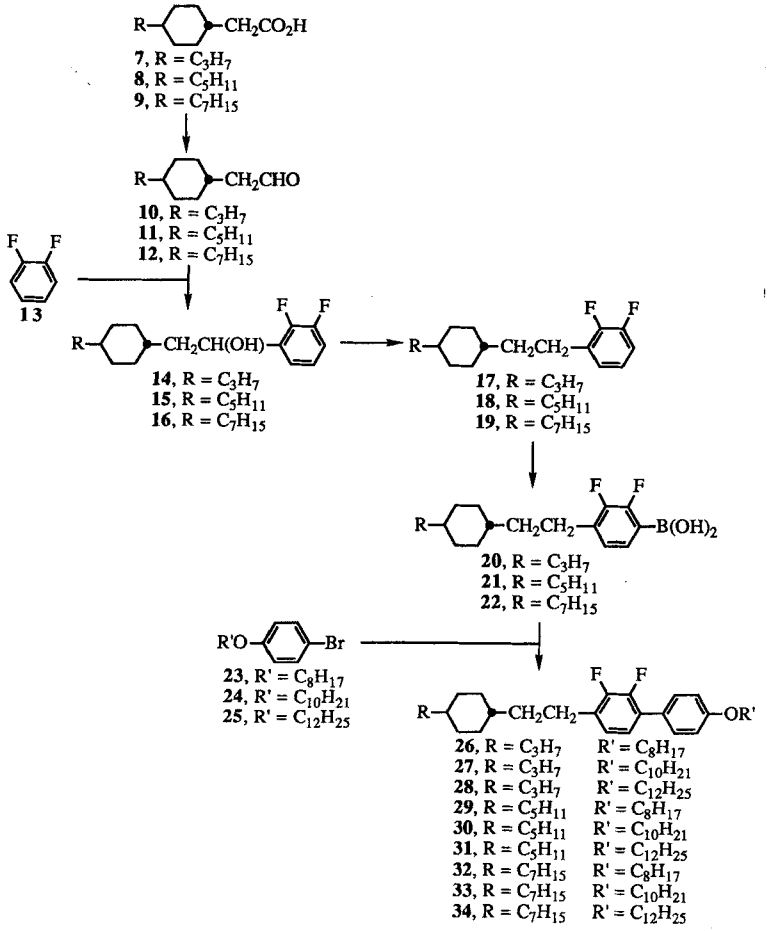
2. Synthesis

The preparation of the required mesogenic compounds was based on a similar methodology to that previously reported [7–9] for the synthesis of the *ortho*-difluoroterphenyls. The final step to all the mesogens was a palladium catalyzed cross-coupling procedure [7–9, 26–30] involving an appropriate arylboronic acid with an appropriate aryl bromide. The syntheses were complicated somewhat by the inclusion of a *trans*-4-alkylcyclohexylethyl moiety as one of the terminal substituents in the biphenyls, rather than the simple open chain terminal substituents used previously, but we were helped by the availability of some *trans*-substituted cyclohexane starting materials from our collaborators at Merck (UK).

The synthesis of compound **6** (see scheme 1) was straightforward, and involved a Friedel–Crafts acylation of bromobenzene (**2**) with the cyclohexyl-substituted acid chloride (compound **1**) to give the ketone **3** which was reduced to the dimethylene linked moiety (compound **4**) by using the mild triethylsilane-trifluoroacetic acid method [31]. The boronic acid **5** was prepared as described previously [7] by the low temperature (−78°C) lithiation of 1,2-difluoro-3-octyloxybenzene and the addition of tri-isopropyl borate followed by hydrolysis; the palladium catalyzed cross-coupling



Scheme 1.



Scheme 2.

procedure involving compounds **4** and **5** gave the desired *ortho*-difluoro-substituted system (compound **6**).

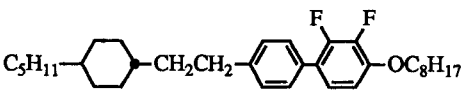
The preparation of mesogenic compounds with the *ortho*-difluoro-substituents in the other benzene ring (compounds **26–34**, see Scheme 2) was more difficult and involved more steps. In order to have the dimethylene linked moiety in the *ortho*-difluoro-substituted benzene ring, an appropriate aldehyde was required. The cyclohexylacetic acid units were available and were reduced to the required aldehyde by a method [32] which involved treating the acid with the complex prepared from oxalyl chloride and *N*,*N*-dimethylformamide (DMF), and then reducing the product with lithium tri-*tert*-butoxyaluminohydride. 1,2-Difluorobenzene (**13**) was mono-lithiated at −78°C by using 1 mol equivalent of *n*-butyllithium; addition of the aldehyde yielded an alcohol which was easily dehydrated (phosphorus(V) oxide) and hydrogenated (5 per cent Pd/C) to yield the desired *trans*-4-alkylcyclohexylethyl-substituted *ortho*-difluorophenyl moiety. The proton site *ortho* to the fluoro-substituent was lithiated at low temperature and treated with tri-isopropyl borate followed by hydrolysis to give the arylboronic acid. The usual palladium catalyzed cross-coupling reactions with the appropriate 1-bromo-4-alkyloxybenzene unit gave good yields of the desired mesogens (**26–34**).

3. Transition temperatures

The two *ortho*-difluoro-substituents in the parent system can be placed either in the alkyloxy-substituted phenyl ring or in the *trans*-alkylcyclohexylethyl-substituted phenyl ring. Both of these types of compound were prepared initially for one homologue combination (compounds **6** and **29** respectively, see table 1) in order to provide guidance for the preparation of further homologues. Compound **6** has the fluoro-substituents in the alkyloxy-substituted phenyl ring and shows pronounced S_A character (the compound was supercooled to 48·0°C and was still in the S_A phase) with a small nematic range above, but without an S_C phase. Compound **29**, however, does show an S_C phase and this is probably because the arrangement with the fluoro-substituents in the phenyl ring carrying the *trans*-alkylcyclohexylethyl-substituent leaves an unfluorinated alkyloxy-substituted phenyl ring which has promoted the S_C phase thermal stability. This situation, combined with a very low melting point, has given a reasonable S_C range. Compound **29** is less smectogenic in character (as measured by the T_{S_AN} value) than compound **6** and has a similar T_{NI} value which has therefore given the compound a wider nematic range. It appears that the *trans*-alkylcyclohexylethyl-substituted phenyl moiety is highly conducive to the S_A mesophase (compound **6**) but when this phenyl ring is fluorinated (compound **29**) the S_A phase thermal stability is reduced. This combined with the effect of the unfluorinated alkyloxy-substituted phenyl ring increases the phase thermal stability of the S_C mesophase [33].

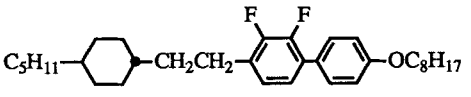
The question as to whether the difluoro-substituents in compound **29** are in an end ring or a middle ring of the mesogenic core is worth considering. For the *ortho*-difluoro-substituted terphenyls [7–9] there are two distinct end rings and a middle ring and there are markedly different effects on transition temperatures and mesophase types caused by substitution in these rings. Compounds **6** and **29** are biphenyl systems and, although both the phenyl rings are end rings, the situation is not as simple as for similar open chain substituted biphenyls [7–9] because of the nature of the cyclohexyl moiety. Compound **6** has the two fluoro-substituents in what is a true end ring position, whereas compound **29** has the two fluoro-substituents in what could be considered a

Table 1. Transition temperatures for 2,3-Difluoro-4-(or -4'-)octyloxy-4'-(or -4-)(*trans*-4-pentylcyclohexylethyl)biphenyls (**6** and **29**).



6

C 59·0°C S_A 113·5°C N 124·0°C I



29

C 32·5°C S_C 55·0°C S_A 83·0°C N 122·0°C I

middle ring. The justification for regarding compound **29** as having difluoro-substituents in a middle ring is provided by the comparison of the melting points and the smectic phase thermal stabilities of compounds **6** and **29**. The characteristic effects of a fluoro-substituent at a position on the edge of the core are higher melting points, higher smectic phase thermal stabilities and often slightly higher nematic phase thermal stabilities than a fluoro-substituent elsewhere in the core. These effects are explained by reduced inter annular twisting and by the space filling effect of the fluoro-substituent *ortho* to the terminal group which provides a larger surface area of contact between neighbouring molecules [7–9, 24, 29, 33]. Compound **6** has a higher melting point (by 26·5°C), a higher smectic phase thermal stability (by 30·5°C) and a slightly higher nematic phase thermal stability (by 2·0°C) and so appears to confirm compound **29** as a middle ring compound. It appears, therefore, that the space filling effect of the outer edge fluoro-substituent in an open-chain terminal substituent is greater than that for the dimethylene-linked cyclohexyl-substituted terminal moiety. However, the differences noted here are much less than for comparable *ortho*-difluoro-substituted terphenyl systems which have definite end and centre rings (for example, see compounds **35–37** in table 3) [7]. It is perhaps fortuitous that the structural features which promote the S_C phase relative to the S_A phase in compound **29** are also conducive to low melting points.

The types of mesophase exhibited and the transition temperatures of the compounds reported here, and of the other lateral fluoro-substituted compounds previously reported, can be explained quite satisfactorily by using an argument based on steric effects which involves an end ring/middle ring issue. However, the same conclusions can be reached by discussing the mesogenic behaviour of compounds **6** and **29** (and other lateral fluoro-substituted systems) in terms of the electric dipoles generated by the appropriate moieties (for example lateral fluoro-substituents and terminal alkyloxy-substituents); see [34]. Compound **6** exhibits an S_C phase because the dipole generated by the two fluoro-substituents is acting independently of the dipole moment generated by the terminal alkyloxy-substituent; this situation provides the required environment for the molecules to tilt. Compound **29**, on the other hand, has interacting dipoles producing a lowered tendency for a tilted arrangement and hence a lowered S_C phase thermal stability; in this case no S_C phase is exhibited. We are

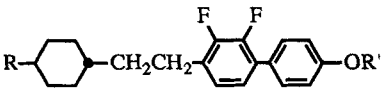
currently using molecular modelling to provide further information on how these, and other related, compounds may be expected to pack in smectic phases.

In view of the very high S_C tendency of the *ortho*-difluoro-substituted terphenyls (for example, compounds **35–37**) [7–9] it was surprising that compound **6** did not show an S_C phase, and therefore no further homologues of this type were prepared. However, the transition temperatures of compound **29** were encouraging because of the presence of an S_C phase combined with a low melting point. This prompted the preparation of further homologues giving a total of nine compounds whose transition temperatures are shown in table 2.

It was felt that in order to promote the thermal stability of the S_C phase or at least to retain it at the level shown for compound **29**, the terminal alkyloxy-substituent (*R'*) would need to have eight carbon atoms or more. Therefore, octyloxy, decyloxy and dodecyloxy groups were chosen and these were combined with propyl, pentyl and heptyl terminal chains (*R*) in the cyclohexyl moiety. Such a series obviously provides two methods of comparison; one for fixed length of the alkyl chain (*R*) and the other for fixed length of the alkyloxy chain (*R'*). Generally, the melting points increase as the alkyloxy chain length (*R'*) increases but they decrease as the alkyl chain length (*R*) increases. There are some exceptions to this generalization but the lowest melting points are seen for the octyloxy compounds (**26**, **29** and **32**) and compounds **27** and **33** (decyloxy compounds). All of the compounds (**26–34**) are very smectogenic and, combined with the low melting points, they give wide smectic ranges, but the relative distributions of the S_C and S_A phases varies considerably with structure, although all of the compounds show an enantiotropic S_C phase.

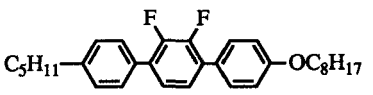
Compound **26** is the shortest compound and is exceptional in that it does not exhibit an S_A phase; its S_C phase thermal stability is much lower (46·0°C) than would be expected based on the trends of the pentyl and heptyl homologues and its S_A phase thermal stability is similarly very much depressed. Its nematic phase thermal stability is, however, somewhat higher than for any other compound. The S_A phase thermal stability shows regular trends throughout for compounds **27–34** and always increases

Table 2. Transition temperatures for 2,3-difluoro-4'-alkyloxy-4-(*trans*-4-alkylcyclohexylethyl)biphenyls (**26–34**).



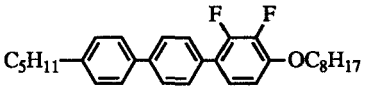
	Compound		Transition temperatures/°C								
No.	*R*	*R'*	C		S_C		S_A		N		I
26	C_3H_7	C_8H_{17}	•	35·5	•	46·0	—		•	125·0	•
27	C_3H_7	$C_{10}H_{21}$	•	38·5	•	68·5	•	88·0	•	119·0	•
28	C_3H_7	$C_{12}H_{25}$	•	49·5	•	63·5	•	100·5	•	116·5	•
29	C_5H_{11}	C_8H_{17}	•	32·5	•	55·0	•	83·0	•	122·0	•
30	C_5H_{11}	$C_{10}H_{21}$	•	49·5	•	57·5	•	105·0	•	121·0	•
31	C_5H_{11}	$C_{12}H_{25}$	•	47·0	•	60·5	•	112·0	•	119·0	•
32	C_7H_{15}	C_8H_{17}	•	23·0	•	49·5	•	106·5	•	120·5	•
33	C_7H_{15}	$C_{10}H_{21}$	•	36·5	•	55·0	•	116·0	•	121·0	•
34	C_7H_{15}	$C_{12}H_{25}$	•	45·0	•	57·0	•	117·5	•	118·5	•

Table 3. Transition temperatures for some *ortho*-difluoro-substituted terphenyls (**35–37**) for comparison with compound **29**.†



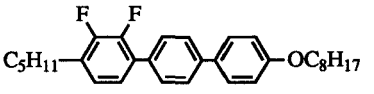
35

C 48·5°C S_C 95·0°C N 141·5°C I
{+16·0°C} {+40·0°C} {+19·5°C}



36

C 93·5°C S_C 144·0°C S_A 148·0°C N 159·0°C I
{+61·0°C} {+89·0°C} {+65·0°C} {+37·0°C}



37

C 89·0°C S_C 155·5°C S_A 165·0°C N 166·0°C I
{+56·5°C} {+100·5°C} {+82·0°C} {+44·0°C}

† The values in { } show the extent to which the melting points and phase thermal stabilities are higher (+) or lower (−) than those for compound **29**.

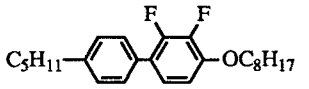
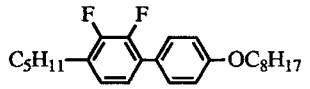
with increasing alkyloxy or alkyl chain length. The increases in S_A phase thermal stability are slightly greater with increasing alkyl chain length (*R*) than for increasing alkyloxy chain length (*R'*); for example, from compound **27** the S_A phase thermal stability increases by 17·0°C on increasing the alkyl chain length (compound **30**) but by only 12·5°C on increasing the alkyloxy chain length by the same amount (compound **28**); T_{S_AN} values range from 83·0 to 117·5°C.

The S_C phase thermal stability also generally increases with increasing alkyloxy chain length (*R'*) but falls with increasing alkyl chain length (*R*), except on going from the exceptional compound **26** (low S_C phase thermal stability) to compound **29**. For example, from compound **29** the S_C phase thermal stability is increased by 2·5°C on increasing the alkyloxy chain length (compound **30**) but it is reduced by 5·5°C on increasing the alkyl chain length by the same amount (compound **32**). The highest S_C phase thermal stabilities are seen for those compounds (**27**, **28** and **31**) with shorter alkyl chain length (*R*) and longer alkyloxy chain length (*R'*). This trend arises because the increasing S_A character begins to push out the S_C phase when the alkyl chain length becomes longer.

The nematic phase thermal stability is remarkably similar (~120°C) for all of the compounds and even the exceptional compound **26** is close to this value and appears to be reduced more by increasing the alkyloxy chain length (*R'*) than by increasing the alkyl chain length (*R*) so that compound **28** has the lowest T_{NI} value.

The transition temperatures of compound **29** can be compared with the three *ortho*-difluoro-substituted terphenyls, compounds **35**, **36** and **37** [7], which have the same

Table 4. Transition temperatures for some *ortho*-difluoro-substituted biphenyls (**38** and **39**) for comparison with compound **29**.†

 **38**	 **39**
C 14·0°C (N 13·5°C) I {−18·5°C} {−108·5°C}	C 8·0°C S_A 12·0°C N 18·0°C I {−24·5°C} {−71·0°C} {−104·0°C}

† The values in { } show the extent to which the melting points and phase thermal stabilities are higher (+) or lower (−) than those for compound **29**.

alkyl (pentyl) and alkyloxy (octyloxy) terminal substituents. The transition temperatures of compounds **35–37** are shown in table 3 and the values given in brackets indicate the extent to which the transition temperatures are higher than those for compound **29**. Even in the most favourable comparison (compound **35**) the S_C phase thermal stability for compound **29** is reduced by 40·0°C, the nematic phase is less affected (reduced by 19·5°C) and compound **35** does not show an S_A phase. Comparisons of compound **29** with the terphenyls with the *ortho*-difluoro-substituents in an end ring (compounds **36** and **37**) reveal huge reductions in S_C phase thermal stability (~90°C), large reductions in S_A phase thermal stability (~70°C) and moderate reductions in nematic phase thermal stability (~40°C). Overall, the dimethylene-linked cyclohexyl-substituted systems have nowhere near the S_C phase thermal stability of the terphenyl systems but the S_C phase thermal stability is still moderately pronounced and there is consolation in the very low melting points of these systems.

The transition temperatures of the straight chain *ortho*-difluoro-substituted biphenyls (compounds **38** and **39**) [7] are shown in table 4 and as for table 3 the figures given in brackets { } are differences in the values from those for compound **29**. In comparison with these systems, the dimethylene-linked cyclohexyl moiety has a significantly boosted mesophase thermal stability whilst the effect on the melting points has been slight.

4. Summary

(*a*) Compounds with the two fluoro-substituents in the cyclohexylethyl-substituted phenyl ring (centre ring, compound **29**) have lower melting points, exhibit an S_C mesophase but have reduced S_A phase thermal stability and have similar T_{NI} values to compound **6** which has the two fluoro-substituents in the end ring.

(*b*) The *trans*-alkylcyclohexylethyl moiety confers S_A character on the compounds, which increases as the alkyl chain length (*R*) increases.

(*c*) S_C phase thermal stability is favoured by a shorter alkyl chain length (*R*) in the cyclohexyl moiety (which suppresses S_A phase thermal stability) and by a longer alkyloxy chain length (*R'*).

(*d*) Compounds **26–34** have low melting points but they also have much reduced S_C phase thermal stability when compared with the appropriate *ortho*-difluoroterphenyls. When compared with the appropriate straight chain *ortho*-difluorobiphenyls the melting points are slightly higher and mesophase thermal stabilities are much increased for compounds **26–34** which therefore show melting points and transition temperatures intermediate between the values for the appropriate open-chain biphenyls and terphenyls.

5. Experimental

Confirmation of the structures of intermediates and products was obtained by ^{1}H 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 FP 5 hot stage and control unit in conjunction with an Olympus BH2 polarizing microscope; these were confirmed using differential scanning calorimetry (Perkin–Elmer DSC-7 and data station). The purity of each of the final liquid-crystalline compounds was checked by GLC analysis (see above) and by HPLC analysis (Microsorb C18 80-215-C5 RP column); all compounds were >99·9 per cent pure.

Compounds **1**, **7**, **8** and **9** were kindly supplied by our collaborators at Merck (UK), Poole. Dorset. Compounds **5** and **23** were prepared as described in [7].

5.1. *1-Bromo-4-*(trans-*4-pentylcyclohexylacetyl)benzene* (**3**)

Quantities: compound **1** (12·00 g, 0·052 mol), compound **2** (35 ml), aluminium chloride (8·00 g, 0·060 mol). The experimental procedure was as described in a previous publication [7]. The crude product was recrystallized from ethanol to yield an off-white powder.

Yield 10·05 g (55 per cent); mp 73–74°C; ^{1}H NMR ($CDCl_3$) δ 0·85 (3 H, t), 0·95 (4 H, m), 1·15–1·35 (9 H, 2xm), 1·75 (4 H, m), 1·90 (1 H, m), 2·80 (2 H, d), 7·60 (2 H, d), 7·80 (2 H, d); IR (KCl) ν_{max} 2960, 2920, 2850, 1690, 1585, 1450, 1400, 1200, 1075, 1010, 990, 815 cm^{-1}; MS *m/z* 352 (M^+), 350 (M^+), 326, 306, 294.

5.2. *1-Bromo-4-*(trans-*4-pentylcyclohexylethyl)benzene* (**4**)

Triethylsilane (7·50 g, 0·065 mol) was added slowly, dropwise to a stirred, ice-cold solution of compound **3** (9·00 g, 0·026 mol) in trifluoroacetic acid (45·0 g, 0·39 mol). The mixture was stirred at room temperature for 3·25 h (GLC analysis revealed a complete reaction) and poured into water. The product was extracted into ether (twice), the combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* and other volatile fractions were removed by distillation (Kugelrohr) to give a brown liquid which was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 3 : 1) to give a pale yellow liquid.

Yield 5·18 g (60 per cent); ^{1}H NMR ($CDCl_3$) δ 0·85 (7 H, m), 1·10–1·30 (10 H, m), 1·50 (2 H, m), 1·75 (4 H, m), 2·55 (2 H, t) 7·00 (2 H, d), 7·35 (2 H, d); IR (film) ν_{max} 2960, 2920, 2850, 1495, 1460, 1075, 1015, 805 cm^{-1}; MS *m/z* 338 (M^+), 336 (M^+), 319, 292, 282, 280.

5.3. *2,3-Difluoro-4-octyloxy-4'-*(trans-*4-pentylcyclohexylethyl)biphenyl* (**6**)

Quantities: compound **4** (1·45 g, 4·30 mmol), compound **5** (1·50 g, 5·24 mmol), tetrakis(triphenylphosphine)palladium(0) (0·29 g, 0·25 mmol). The experimental procedure was as described in a previous publication [7]. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 6 : 1) to give a colourless solid which was recrystallized from ethanol to yield colourless crystals.

Yield 0·48 g (24 per cent); transitions C 59·0°C S_A 113·5°C N 124·0°C I; ^{1}H NMR ($CDCl_3$) δ 0·90 (10 H, m), 1·30 (18 H, m), 1·55 (4 H, m), 1·80 (6 H, m), 2·70 (2 H, t), 4·10 (2 H, t), 6·82 (1 H, sext), 7·12 (1 H, sext), 7·28 (2 H, d), 7·46 (2 H, q); IR (KCl) ν_{max} 2960, 2940, 2860, 1640, 1510, 1470, 1320, 1305, 1205, 1110, 1080, 900, 800 cm^{-1}; MS *m/z* 498 (M^+), 442, 397, 386, 331, 219.

5.4. trans-*4-Propylcyclohexylethanal* (**10**)

Oxalyl chloride (47·00 g, 0·370 mol) was added dropwise to a stirred, cooled (0°C) solution of dry DMF (9·65 g, 0·132 mol) in dry dichloromethane (120 ml) under dry nitrogen. The resulting mixture was stirred at 0°C for 1 h and the solvent was removed *in vacuo* to give a colourless powder. A solution of compound **7** (22·12 g, 0·120 mol) and dry pyridine (10·50 g, 0·133 mol) in dry THF (150 ml) was added dropwise to a stirred, cooled (−30°C) solution of the colourless powder in dry acetonitrile (150 ml) and dry THF (200 ml) under dry nitrogen. The mixture was stirred at −30°C for 1 h and then cooled to −78°C. Copper (I) iodide (2·62 g, 0·014 mol) was added followed by dropwise addition of a solution of lithium tri-*tert*-butyloxyaluminohydride (prepared from 2-methylpropan-2-ol (58·39 g, 0·789 mol) and lithium aluminium hydride (10·00 g, 0·263 mol) in dry THF (200 ml) at −78°C and stirring for 1 h). The reaction mixture was stirred for 1·5 h (no further cooling) and was then quenched by the dropwise addition of 10 per cent hydrochloric acid at −40°C and allowed to warm to room temperature. The product was extracted into ether (twice) and the combined ethereal extracts were washed with aqueous sodium hydrogen carbonate, and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was distilled to yield a colourless liquid.

Yield 14·50 g (72 per cent); bp 65–70°C at 0·5 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·87 (3 H, t), 0·90–1·00 (4 H, m), 1·15 (3 H, m), 1·30 (2 H, quint), 1·70–1·80 (5 H, m), 2·30 (2 H, q), 9·77 (1 H, t); IR (film) ν_{max} 2960, 2940, 2860, 1730, 1450 cm^{-1}; MS *m/z* 168 (M^+), 149, 143, 124, 109.

5.5. trans-*4-Pentylcyclohexylethanal* (**11**)

Quantities: compound **8** (17·81 g, 0·084 mol). The experimental procedure was as described for the preparation of compound **10**.

Yield 11·91 g (72 per cent); bp 92–94°C at 0·5 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·85–0·90 (3 H, t). 0·90–1·05 (4 H, m), 1·10–1·20 (4 H, m), 1·20–1·35 (5 H, m), 1·75 (4 H, d), 1·75–1·85 (1 H, m), 2·30 (2 H, q), 9·75 (1 H, t); IR (film) ν_{max} 2960, 2940, 2860, 1730, 1450 cm^{-1}; MS *m/z* 196 (M^+), 152, 123, 109, 96, 81.

5.6. trans-*4-Heptylcyclohexylethanal* (**12**)

Quantities: compound **9** (17·00 g, 0·071 mol). The experimental procedure was as described for the preparation of compound **10**.

Yield 9·56 g (60 per cent); bp 110–112°C at 0·1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·85–0·90 (3 H, t), 0·90–1·05 (4 H, m), 1·10–1·20 (4 H, m), 1·20–1·35 (9 H, m), 1·75 (4 H, d), 1·75–1·85 (1 H, m), 2·30 (2 H, q), 9·75 (1 H, t); IR (film) ν_{max} 2960, 2940, 2860, 1730, 1450 cm^{-1}; MS *m/z* 224 (M^+), 206, 180.

5.7. *1-(2,3-Difluorophenyl)-2-*(trans-*4-propylcyclohexyl)ethanol* (**14**)

Quantities: compound **13** (10·50 g, 0·092 mol), *n*-butyllithium (9·20 ml, 10·0 M in hexane, 0·092 mol), compound **10** (14·00 g, 0·083 mol). The experimental procedure was as described in a previous publication [7]. The crude product was distilled to yield a colourless oil.

Yield 9·20 g (85 per cent); bp 130–134°C at 0·1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (7 H, m), 1·10–1·40 (6 H, m), 1·55 (1 H, m), 1·70 (4 H, m), 1·85 (1 H, m), 1·95 (1 H, s), 5·15 (1 H, q), 7·00–7·12 (2 H, m), 7·17–7·24 (1 H, m); IR (film) ν_{max} 3700–3100, 2960, 2940, 2860, 1490, 1280, 1205, 790, 730 cm^{-1}; MS *m/z* 282 (M^+), 264, 218.

5.8. *1-(2,3-Difluorophenyl)-2-*(trans-*4-pentylcyclohexyl)ethanol* (**15**)

Quantities: compound **13** (4·10 g, 0·036 mol), *n*-butyllithium (3·60 ml, 10·0 M in hexane, 0·036 mol), compound **11** (6·80 g, 0·035 mol). The experimental procedure was as described for the preparation of compound **14**. The crude product was purified by column chromatography (silica gel/dichloromethane) to yield a colourless solid.

Yield 9·20 g (85 per cent); mp 42–43°C; ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (7 H, m), 1·10–1·40 (10 H, m), 1·55 (1 H, m), 1·70 (4 H, m), 1·85 (1 H, m), 2·05 (1 H, s), 5·15 (1 H, q), 7·00–7·12 (2 H, m), 7·17–7·24 (1 H, m); IR (film) ν_{max} 3700–3100, 2960, 2940, 2860, 1490, 1280, 1205, 790, 730 cm^{-1}; MS *m/z* 310 (M^+), 292, 143.

5.9. *1-(2,3-Difluorophenyl)-2-*(trans-*4-heptylcyclohexyl)ethanol* (**16**)

Quantities: compound **13** (5·00 g, 0·044 mol), *n*-butyllithium (4·50 ml, 10·0 M in hexane, 0·045 mol), compound **12** (9·00 g, 0·040 mol). The experimental procedure was as described for the preparation of compound **14**. The crude product was purified by column chromatography (silica gel/dichloromethane) to yield a light brown oil.

Yield 10·61 g (71 per cent); ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (7 H, m), 1·10–1·40 (14 H, m), 1·55 (1 H, m), 1·70 (4 H, m), 1·85 (1 H, m), 1·85 (1 H, s), 5·15 (1 H, q), 7·00–7·12 (2 H, m), 7·17–7·24 (1 H, m); IR (film) ν_{max} 3700–3100, 2960, 2940, 2860, 1490, 1280, 1205, 790, 730 cm^{-1}; MS *m/z* 338 (M^+), 320, 143.

5.10. *1,2-Difluoro-3-*(trans-*4-propylcyclohexylethyl)benzene* (**17**)

Quantities: compound **14** (19·00 g, 0·067 mol), phosphorus(V) oxide (29·00 g, 0·204 mol), 5 per cent palladium-on-carbon (2·00 g). The experimental procedure was as described in a previous publication [7]. The crude product was distilled to yield a colourless oil.

Yield 14·82 g (83 per cent); bp 116–118°C at 0·1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·85–1·00 (7 H, m), 1·10–1·20 (4 H, m), 1·30 (2 H, quint), 1·50 (2 H, m), 1·80 (4 H, m), 2·65 (2 H, t), 6·90–7·00 (3 H, m); IR (film) ν_{max} 2980, 2940, 2860, 1630, 1600, 1490, 1285, 1210, 780, 730 cm^{-1}; MS *m/z* 266 (M^+), 246, 128.

5.11. *1,2-Difluoro-3-*(trans-*4-pentylcyclohexylethyl)benzene* (**18**)

Quantities: compound **15** (8·95 g, 0·029 mol), triethylsilane (8·42 g, 0·073 mol), trifluoroacetic acid (49·6 g, 0·44 mol). The experimental procedure was as described for the preparation of compound **4**. Analysis by GLC revealed the disappearance of compound **15**. The crude mixture was distilled (Kugelrohr, 175°C (maximum) at 0·1 mmHg) in an attempted fractionation but the whole mixture distilled. Analysis of the distillate by GLC now revealed the presence of starting material in addition to the components present previously. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)) to yield a colourless oil (the desired product (compound **18**); 2·20 g, 26 per cent) and the eluent was changed to dichloromethane to yield a colourless solid (the starting alcohol (compound **15**); 4·60 g). Phosphorus(V) oxide (6·75 g, 0·048 mol) was added to a solution of this solid (4·60 g,

0·015 mol) in pentane (80 ml) and this mixture was stirred at room temperature overnight (GLC analysis revealed a complete reaction). The mixture was filtered and the filtrate was hydrogenated at room temperature and atmospheric pressure over 5 per cent palladium-on-carbon (0·50 g) for 4 h (GLC analysis revealed a complete reaction). The catalyst was removed by filtration and the pentane was removed *in vacuo* to yield a colourless oil (4·25 g, 96 per cent).

Total yield 6·45 g (76 per cent); ^{1}H NMR ($CDCl_3$) δ 0·85–1·00 (7 H, m), 1·10–1·35 (10 H, m), 1·50 (2 H, m), 1·80 (4 H, m), 2·65 (2 H, t), 6·90–7·00 (3 H, m); IR (film) ν_{max} 2980, 2940, 2860, 1630, 1600, 1490, 1285, 1210, 780, 730 cm^{-1}; MS *m/z* 294 (M^+), 274, 128.

5.12. *1,2-Difluoro-3-*(trans-*4-heptylcyclohexylethyl)benzene* (**19**)

Quantities: compound **16** (10·00 g, 0·030 mol), phosphorus (V) oxide (13·00 g, 0·092 mol), 5 per cent palladium-on-carbon (1·00 g). The experimental procedure was as described for the preparation of compound **17**. The crude product was distilled to yield a colourless oil.

Yield 6·69 g (69 per cent); bp 155–158°C at 0·5 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·85–1·00 (7 H, m), 1·10–1·35 (14 H, m), 1·50 (2 H, m), 1·80 (4 H, m), 2·65 (2 H, t), 6·90–7·00 (3 H, m); IR (film) ν_{max} 2980, 2940, 2860, 1630, 1600, 1490, 1285, 1210, 780, 730 cm^{-1}; MS *m/z* 322 (M^+), 302.

5.13. *2,3-Difluoro-4-*(trans-*4-propylcyclohexylethyl)phenylboronic acid* (**20**)

Quantities: compound **17** (13·50 g, 0·051 mol), *n*-butyllithium (5·50 ml, 10·0 M in hexane, 0·055 mol), trimethyl borate (10·61 g, 0·102 mol). The experimental procedure was as described in a previous publication [7].

Yield 15·10 g (96 per cent); ^{1}H NMR (DMSO) δ 0·85–0·95 (7 H, m), 1·10–1·20 (4 H, m), 1·28 (2 H, quint), 1·43 (2 H, m), 1·65–1·80 (4 H, m), 2·65 (2 H, t), 7·03 (1 H, sext), 7·25 (1 H, sext), 8·25 (2 H, s); IR (film) ν_{max} 3600–3100, 2960, 2920, 2860, 1635, 1460, 1420–1300, 1220, 1140, 1060, 1010, 905, 815, 675 cm^{-1}; MS *m/z* 310 (M^+), 246, 218, 183, 170, 127.

5.14. *2,3-Difluoro-4-*(trans-*4-pentylcyclohexylethyl)phenylboronic acid* (**21**)

Quantities: compound **18** (5·98 g, 0·020 mol), *n*-butyllithium (8·10 ml, 2·5 M in hexane, 0·020 mol), tri-isopropyl borate (7·60 g, 0·040 mol). The experimental procedure was as described for the preparation of compound **20**.

Yield 6·80 g (100 per cent); ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (7 H, m), 1·10–1·35 (10 H, m), 1·50 (2 H, quint), 1·80 (4 H, m), 2·70 (2 H, t), 7·00 (1 H, sext), 7·45 (1 H, sext), no obvious OH absorption; IR (film) ν_{max} 3600–3100, 2960, 2920, 2860, 1635, 1460, 1420–1300, 1220, 1140, 1060, 1010, 905, 815, 675 cm^{-1}; MS *m/z* 338 (M^+), 318, 294, 274, 266, 256.

5.15. *2,3-Difluoro-4-*(trans-*4-heptylcyclohexylethyl)phenylboronic acid* (**22**)

Quantities: compound **19** (6·20 g, 0·019 mol), *n*-butyllithium (8·40 ml, 2·5 M in hexane, 0·021 mol), tri-isopropyl borate (7·60 g, 0·040 mol). The experimental procedure was as described for the preparation of compound **20**.

Yield 6·90 g (99 per cent); ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (7 H, m), 1·10–1·30 (14 H, m), 1·41 (2 H, quint), 1·78 (4 H, m), 2·65 (2 H, t), 7·02 (1 H, sext), 7·25 (1 H, sext), no obvious OH absorption; IR (film) ν_{max} 3700–3100, 2960, 2920, 2860, 1630, 1460, 1420–1300, 1220, 1140, 1060, 1010, 905, 815, 675 cm^{-1}; MS *m/z* 366 (M^+), 127.

5.16. *1-Bromo-4-decyloxybenzene* (**24**)

Quantities: 4-bromophenol (18·00 g, 0·104 mol), 1-bromodecane (30·00 g, 0·136 mol), potassium carbonate (43·00 g, 0·312 mol), butanone (200 ml). The experimental procedure was as described in a previous publication [7]. The crude product was distilled to yield a colourless solid.

Yield 32·51 g (99 per cent); bp 160°C at 0·1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·90 (3 H, t), 1·25 (12 H, m), 1·45 (2 H, quint), 1·80 (2 H, quint), 3·95 (2 H, t), 6·75 (2 H, d), 7·35 (2 H, d); IR (film) ν_{max} 2940, 2860, 1595, 1490, 1245, 1170, 825 cm^{-1}; MS *m/z* 314 (M^+), 312 (M^+), 173, 171.

5.17. *1-Bromo-4-dodecyloxybenzene* (**25**)

Quantities: 4-bromophenol (18·00 g, 0·104 mol), 1-bromododecane (32·00 g, 0·130 mol), potassium carbonate (54·00 g, 0·390 mol), butanone (200 ml). The experimental procedure was as described for the preparation of compound **24**. The crude product was distilled to yield a colourless solid.

Yield 33·00 g (97 per cent); bp 180°C at 0·5 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·90 (3 H, t), 1·25 (16 H, m), 1·45 (2 H, quint), 1·75 (2 H, quint), 3·90 (2 H, t), 6·75 (2 H, d), 7·35 (2 H, d); IR (film) ν_{max} 2940, 2860, 1595, 1490, 1245, 1170, 825 cm^{-1}; MS *m/z* 342 (M^+), 340 (M^+), 174, 172.

5.18. *2,3-Difluoro-4'-octyloxy-4-*(trans-*4-propylcyclohexylethyl)biphenyl* (**26**)

Quantities: compound **23** (1·30 g, 4·56 mmol), compound **20** (1·70 g, 5·48 mmol), tetrakis(triphenylphosphine)palladium(0) (0·16 g, 0·14 mmol). The experimental procedure was as described for the preparation of compound **6** except that 1,2-dimethoxyethane was used in place of benzene and ethanol. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C) with the gradual introduction of dichloromethane) to give a colourless solid which was recrystallized from ethanol/ethyl acetate (20 : 1) to yield colourless crystals.

Yield 2·08 g (97 per cent); transitions C 35·5°C S_C 46·0°C N 125·0°C I; ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (10 H, m), 1·10–1·20 (4 H, m), 1·20–1·40 (10 H, m), 1·45–1·55 (4 H, m), 1·75–1·85 (6 H, m), 2·65 (2H, t), 4·00 (2 H, t), 6·94 (1 H, sext), 6·96 (2 H, d), 7·05 (1 H, sext), 7·45 (2 H, q); IR (KBr) ν_{max} 2960, 2940, 2860, 1610, 1520, 1490, 1465, 1250, 1175, 895, 840, 815 cm^{-1}; MS *m/z* 470 (M^+), 383, 358.

5.19. *2,3-Difluoro-4'-decyloxy-4-*(trans-*4-propylcyclohexylethyl)biphenyl* (**27**)

Quantities: compound **24** (1·35 g, 4·31 mmol), compound **20** (1·60 g, 5·16 mmol), tetrakis(triphenylphosphine)palladium(0) (0·15 g, 0·13 mmol). The experimental procedure was as described for the preparation of compound **26**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C) with the gradual introduction of dichloromethane) to give a colourless solid which was recrystallized from ethanol/ethyl acetate (20 : 1) to yield colourless crystals.

Yield 2·10 g (98 per cent); transitions C 38·5°C S_C 68·5°C S_A 88·0°C N 119·5°C I; ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (10 H, m), 1·10–1·20 (4 H, m), 1·20–1·40 (14 H, m), 1·45–1·55 (4 H, m), 1·75–1·85 (6 H, m), 2·65 (2 H, t), 4·00 (2 H, t), 6·94 (1 H, sext), 6·96 (2 H, d), 7·05 (1 H, sext), 7·45 (2 H, q); IR (KBr) ν_{max} 2960, 2940, 2860, 1610, 1520, 1490, 1465, 1250, 1175, 895, 840, 815 cm^{-1}; MS *m/z* 498 (M^+), 470, 358.

5.20. *2,3-Difluoro-4'-dodecyloxy-4-*(trans-*4-propylcyclohexylethyl)biphenyl* (**28**)

Quantities: compound **25** (1·43 g, 4·19 mmol), compound **20** (1·56 g, 5·03 mmol), tetrakis(triphenylphosphine)palladium(0) (0·15 g, 0·13 mmol). The experimental procedure was as described for the preparation of compound **26**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C) with the gradual introduction of dichloromethane) to give a colourless solid which was recrystallized from ethanol/ethyl acetate (5 : 1) to yield colourless crystals.

Yield 1·90 g (86 per cent); transitions C 49·5°C S_C 63·5°C S_A 100·5°C N 116·5°C I; ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (10 H, m), 1·10–1·20 (4 H, m), 1·20–1·40 (18 H, m), 1·45–1·55 (4 H, m), 1·75–1·85 (6 H, m), 2·65 (2 H, t), 4·00 (2 H, t), 6·94 (1 H, sext), 6·96 (2 H, d), 7·05 (1 H, sext), 7·45 (2 H, q); IR (KBr) ν_{max} 2960, 2940, 2860, 1610, 1520, 1490, 1465, 1250, 1175, 895, 840, 815 cm^{-1}; MS *m/z* 526 (M^+), 499, 358.

5.21. *2,3-Difluoro-4'-octyloxy-4-*(trans-*4-pentylcyclohexylethyl)biphenyl* (**29**)

Quantities: compound **23** (1·35 g, 4·74 mmol), compound **21** (2·10 g, 6·21 mmol), tetrakis(triphenylphosphine)palladium(0) (0·2161 g, 0·19 mmol). The experimental procedure was as described for the preparation of compound **6**. 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 recrystallized from ethanol/ethyl acetate (20 : 1) to yield colourless crystals.

Yield 1·06 g (45 per cent); transitions C 32·5°C S_C 55·0°C S_A 83·0°C N 122·0°C I; ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (10 H, m), 1·10–1·20 (4 H, m), 1·20–1·40 (14 H, m), 1·45–1·55 (4 H, m), 1·75–1·85 (6 H, m), 2·65 (2 H, t), 4·00 (2 H, t), 6·94 (1 H, sext), 6·96 (2 H, d), 7·05 (1 H, sext), 7·45 (2 H, q); IR (KCl) ν_{max} 2960, 2940, 2860, 1610, 1520, 1490, 1465, 1250, 1175, 895, 840, 815 cm^{-1}; MS *m/z* 498 (M^+), 386, 219.

5.22. *2,3-Difluoro-4'-decyloxy-4-*(trans-*4-pentylcyclohexylethyl)biphenyl* (**30**)

Quantities: compound **24** (0·80 g, 2·56 mmol), compound **21** (1·00 g, 2·96 mmol), tetrakis(triphenylphosphine)palladium(0) (0·10 g, 0·087 mmol). The experimental procedure was as described for the preparation of compound **26**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C) with the gradual introduction of dichloromethane) to give a colourless solid which was recrystallized from ethanol/ethyl acetate (20 : 1) to yield colourless crystals.

Yield 0·40 g (30 per cent); transitions C 49·5°C S_C 57·5°C S_A 105·0°C N 121·0°C I; ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (10 H, m), 1·10–1·20 (4 H, m), 1·20–1·40 (18 H, m), 1·45–1·55 (4 H, m), 1·75–1·85 (6 H, m), 2·65 (2 H, t), 4·00 (2 H, t), 6·94 (1 H, sext), 6·96 (2 H, d), 7·05 (1 H, sext), 7·45 (2 H, q); IR (KBr) ν_{max} 2960, 2940, 2860, 1610, 1520, 1490, 1465, 1250, 1175, 895, 840, 815 cm^{-1}; MS *m/z* 526 (M^+), 386.

5.23. *2,3-Difluoro-4'-dodecyloxy-4-*(trans-*4-pentylcyclohexylethyl)biphenyl* (**31**)

Quantities: compound **25** (1·35 g, 3·96 mmol), compound **21** (1·65 g, 4·88 mmol), tetrakis(triphenylphosphine)palladium(0) (0·15 g, 0·13 mmol). The experimental procedure was as described for the preparation of compound **26**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C) with the gradual introduction of dichloromethane) to give a colourless solid which was recrystallized from ethanol/ethyl acetate (10 : 1) to yield colourless crystals.

Yield 2·10 g (98 per cent); transitions C 47·0°C S_C 60·5°C S_A 112·0°C N 119·0°C I; ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (10 H, m), 1·10–1·20 (4 H, m), 1·20–1·40 (22 H, m), 1·45–1·55 (4 H, m), 1·75–1·85 (6 H, m), 2·65 (2 H, t), 4·00 (2 H, t), 6·94 (1 H, sext), 6·96 (2 H, d),

7·05 (1 H, sext), 7·45 (2 H, q); IR (KBr) ν_{max} 2960, 2940, 2860, 1610, 1520, 1490, 1465, 1250, 1175, 895, 840, 815 cm^{-1}; MS *m/z* 554 (M^+), 508, 380.

5.24. *2,3-Difluoro-4'-octyloxy-4-*(trans-*4-heptylcyclohexylethyl*)*biphenyl* (**32**)

Quantities: compound **23** (2·00 g, 7·02 mmol), compound **22** (3·10 g, 8·47 mmol), tetrakis(triphenylphosphine)palladium(0) (0·25 g, 0·22 mmol). The experimental procedure was as described for the preparation of compound **26**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C) with the gradual introduction of dichloromethane) to give a colourless solid which was recrystallized from ethanol/ethyl acetate (20 : 1) to yield colourless crystals.

Yield 3·38 g (92 per cent); transitions C 23·0°C S_C 49·5°C S_A 106·5°C N 120·5°C I; ^1H NMR ($CDCl_3$) δ 0·85–0·95 (10 H, m), 1·10–1·20 (4 H, m), 1·20–1·40 (18 H, m), 1·45–1·55 (4 H, m), 1·75–1·85 (6 H, m), 2·65 (2 H, t), 4·00 (2 H, t), 6·94 (1 H, sext), 6·96 (2 H, d), 7·05 (1 H, sext), 7·45 (2 H, q); IR (KBr) ν_{max} 2960, 2940, 2860, 1610, 1520, 1490, 1465, 1250, 1175, 895, 840, 815 cm^{-1}; MS *m/z* 526 (M^+), 414, 218.

5.25. *2,3-Difluoro-4'-decyloxy-4-*(trans-*4-heptylcyclohexylethyl*)*biphenyl* (**33**)

Quantities: compound **24** (1·42 g, 4·54 mmol), compound **22** (2·00 g, 5·46 mmol), tetrakis(triphenylphosphine)palladium(0) (0·16 g, 0·14 mmol). The experimental procedure was as described for the preparation of compound **26**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)/dichloromethane (20 : 1)) to give a colourless solid which was recrystallized from ethanol/ethyl acetate (20 : 1) to yield colourless crystals.

Yield 2·00 g (80 per cent); transitions C 36·5°C S_C 55·0°C S_A 116·0°C N 121·0°C I; ^1H NMR ($CDCl_3$) δ 0·85–0·95 (10 H, m), 1·10–1·20 (4 H, m), 1·20–1·40 (22 H, m), 1·45–1·55 (4 H, m), 1·75–1·85 (6 H, m), 2·65 (2 H, t), 4·00 (2 H, t), 6·94 (1 H, sext), 6·96 (2 H, d), 7·05 (1 H, sext), 7·45 (2 H, q); IR (KBr) ν_{max} 2960, 2940, 2860, 1610, 1520, 1490, 1465, 1250, 1175, 895, 840, 815 cm^{-1}; MS *m/z* 554 (M^+), 541, 526.

5.26. *2,3-Difluoro-4'-dodecyloxy-4-*(trans-*4-heptylcyclohexylethyl*)*biphenyl* (**34**)

Quantities: compound **25** (1·10 g, 3·23 mmol), compound **22** (1·42 g, 3·88 mmol), tetrakis(triphenylphosphine)palladium(0) (0·12 g, 0·10 mmol). The experimental procedure was as described for the preparation of compound **26**. 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 recrystallized from ethanol/ethyl acetate (10 : 1) to yield colourless crystals.

Yield 1·15 g (61 per cent); transitions C 45·0°C S_C 57·0°C S_A 117·5°C N 118·5°C I; ^1H NMR ($CDCl_3$) δ 0·85–0·95 (10 H, m), 1·10–1·20 (4 H, m), 1·20–1·40 (26 H, m), 1·45–1·55 (4 H, m), 1·75–1·85 (6 H, m), 2·65 (2 H, t), 4·00 (2 H, t), 6·94 (1 H, sext), 6·96 (2 H, d), 7·05 (1 H, sext), 7·45 (2 H, q); IR (KBr) ν_{max} 2960, 2940, 2860, 1610, 1520, 1490, 1465, 1250, 1175, 895, 840, 815 cm^{-1}; MS *m/z* 582 (M^+), 511, 414.

The work reported here is published by permission of the Director, HMSO, and was funded under a Ministry of Defence contract. We express our thanks to our collaborators at RSRE (Malvern) and Merck (UK), Poole, Dorset and to Dr D. F. Ewing, Mrs B. Worthington, Mr R. Knight, and Mr A. D. Roberts for various spectroscopic measurements.

References

[1] MEYER, R. B., LIEBERT, L., STRZELECKI, L., and KELLER, P., 1975, *J. Phys. Lett., Paris*, **36**, 69.
[2] CLARK, N. A., and LAGERWALL, S. T., 1980, *Appl. Phys. Lett.*, **36**, 899.
[3] GOODBY, J. W., 1986, *Science N.Y.*, **231**, 350.
[4] GOODBY, J. W., and PATEL, J. S., 1986, *Proc. SPIE.*, **684**, 52.
[5] ESCHER, C., 1986, *Kontakte (Darmstadt)*, **2**, 3.
[6] SCHEUBLE, B. S., 1989, *Kontakte (Darmstadt)*, **1**, 34.
[7] GRAY, G. W., HIRD, M., LACEY, D., and TOYNE, K. J., 1989, *J. chem. Soc. Perkin Trans. 2*, 2041.
[8] GRAY, G. W., HIRD, M., LACEY, D., and TOYNE, K. J., 1990, *Molec. Crystals liq. Crystals*, **191**, 1.
[9] HIRD, M., 1990, Ph.D. Thesis, University of Hull.
[10] HANDSCKY, M. A., and CLARK, N. A., 1982, *Appl. Phys. Lett.*, **41**, 39.
[11] CONSTANT, J., RAYNES, E. P., and SAMRA, A. K., 1990, Abstract FER-11-O-Fri, *Proceedings 13th International Liquid Crystal Conference*, Vancouver, Canada.
[12] BRADSHAW, M. J., BRIMMELL, V., and RAYNES, E. P., 1987, *Liq. Crystals*, **2**, 107.
[13] BORN, M., 1972, *Optik* (Springer Verlag).
[14] CHAN, L. K. M., GRAY, G. W., LACEY, D., SCROWSTON, R. M., SHENOUDA, I. G., and TOYNE, K. J., 1989, *Molec. Crystals liq. Crystals*, **172**, 125.
[15] REIFFENRATH, V., KRAUSE, J., PLACH, H. J., and WEBER, G., 1989, *Liq. Crystals*, **5**, 159.
[16] SCHIEKEL, M., and FAHRENSCHON, K., 1973, *Appl. Phys. Lett.*, **44**, 4869.
[17] LABRUNIE, G., and ROBERT, J., 1973, *J. appl. Phys.*, **44**, 4869.
[18] MATSUMOTO, S., KAWAMOTO, M., and MIZUNOYA, K., 1976, *J. appl. Phys.*, **47**, 3842.
[19] MARGERUM, J. D., WONG, S.-M., JENSEN, J. E., VAN AST, C. I., and LACKNER, A. M., 1985, *Molec. Crystals liq. Crystals*, **122**, 97.
[20] GRAY, G. W., 1976, *Advances in Liquid Crystals*, Vol. 2, edited by G. H. Brown (Academic Press), p. 16.
[21] TOYNE, K. J., 1987, *Thermotropic Liquid Crystals*, edited by G. W. Gray (Wiley), chap. 2.
[22] KELLY, S. M., 1989, *Liq. Crystals*, **5**, 171.
[23] BISHOP, D. I., BALKWILL, P. H., SAGE, I. C., MCDONNELL, D. G., GRAY, G. W., LACEY, D., and TOYNE, K. J., 1984, U.K. Pat., G.B. 2 134 110B.
[24] BALKWILL, P., BISHOP, D., PEARSON, A., and SAGE, I. C., 1985, *Molec. Crystals liq. Crystals*, **123**, 1.
[25] REIFFENRATH, V., KRAUSE, J., WACHTLER, A., WEBER, G., FINKENZELLER, U., COATES, D., SAGE, I. C., GREENFIELD, S., GRAY, G. W., HIRD, M., LACEY, D., and TOYNE, K. J., 1989, W. O. Pat. 08687.
[26] MIYAURA, N., YANAGI, T., and SUZUKI, A., 1981, *Synth. Commun.*, **11**, 513.
[27] MILLER, R. B., and DUGAR, S., 1984, *Organometallics*, **3**, 1261.
[28] GRAY, G. W., HIRD, M., LACEY, D., and TOYNE, K. J., 1989, *Molec. Crystals liq. Crystals*, **172**, 165.
[29] GRAY, G. W., HIRD, M., and TOYNE, K. J., 1991, *Molec. Crystals liq. Crystals*, **195**, 221.
[30] HIRD, M., GRAY, G. W., and TOYNE, K. J., 1991, *Molec. Crystals liq. Crystals*, **206**, 187.
[31] WEST, C. T., DONNELLY, S. J., KOOISTRA, D. A., and DOYLE, M. P., 1973, *J. Org. Chem.*, **38**, 2675.
[32] FUJISAWA, T., MORI, T., TSUGE, S., and SATO, T., 1983, *Tetrahedron Lett.*, **24**, 1543.
[33] HIRD, M., GRAY, G. W., and TOYNE, K. J., 1991, *Molec. Crystals liq. Crystals*, **204**, 43.
[34] MCMILLAN, W. L., 1973, *Phys. Rev.* A, **8**, 1921.