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

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To cite this Article Hird, Michael , Toyne, Kenneth J. and Gray, George W.(1994) 'The synthesis and transition temperatures of some ferroelectric host materials based on 4- and 4'-(*trans*-4-alkylcyclohexylmethoxy)-2,3-difluorobiphenyls', Liquid Crystals, 16: 4, 625 — 641

To link to this Article: DOI: 10.1080/02678299408036535

URL: http://dx.doi.org/10.1080/02678299408036535

LIQUID CRYSTALS, 1994, VOL. 16, NO. 4, 625–641

The synthesis and transition temperatures of some ferroelectric host materials based on 4- and 4′-(*trans*-4-alkylcyclohexylmethoxy)-2,3-difluorobiphenyls

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(*Received 21 June 1993; accepted 10 August 1993*)

A range of 2,3-difluoro-substituted biphenyls incorporating a cyclohexylmethoxy unit as one terminal chain has been prepared and these materials are compared to the analogous compounds already reported with a dimethylene linking group. Related, directly-linked cyclohexylbiphenyls and some open-chain analogues have also been prepared which add to the diversity of the compounds reported. These were prepared as host materials of low birefringence for ferroelectric (S_C^*) mixtures and in general, the compounds have quite high S_C phase stability. Metallation procedures have been used to prepare arylboronic acids which were employed in palladium-catalysed cross-coupling reactions to provide good yields of liquid crystal materials. The synthesis and transition temperatures of these compounds are discussed and compared with each other and with other selected *ortho*-difluoro-substituted systems.

1. Introduction

Ferroelectric liquid crystals has been an extremely active field of research over the past several years because of the potential such materials have for low-powered, fast-switching, bistable devices that can provide high resolution over large display areas which is unmatched by any other technology. The recent introduction of prototype ferroelectric displays by both Canon [1] and Thorn–EMI [2] has established the viability of this type of display. However, there are still many problems that need to be overcome before commercial exploitation is possible. In particular, it is desirable to improve the ferroelectric materials that are used in such devices in order to provide faster switching speeds at lower voltage. The materials also need to produce a good alignment that is less susceptible to shock damage and they need to operate successfully over a wider temperature range.

In recent years, one important aspect of our work has been the preparation and evaluation of materials based on the 2,3-difluorophenyl moiety for use as host materials in ferroelectric (S_C^*) mixtures [3–5]. This structural unit confers negative dielectric anisotropy upon its compounds whilst minimizing viscosity and supporting the tilted S_C mesophase. The types of mesophase exhibited and their transition temperatures depend upon the other moieties present and their structural arrangement. Terphenyl systems [3, 4] with 2,3-difluoro-substituents (structure **I**) have very high S_C phase stabilities and wide S_C ranges even if both terminal substituents are alkyl, whereas isomeric 2′,3′-difluoro-substituted compounds (structure **II**) have very low melting points and reduced, but still quite high, S_C phase stabilities. Terphenyl materials (**I** and

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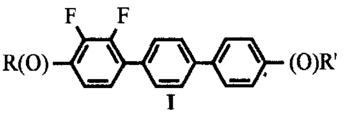
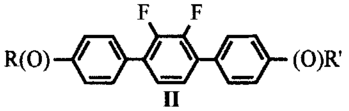


I



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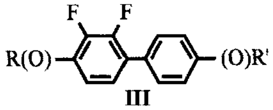

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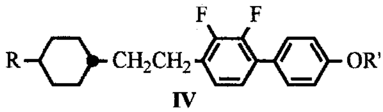

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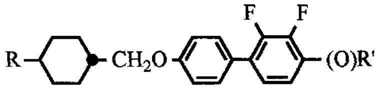

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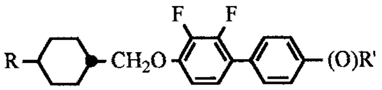

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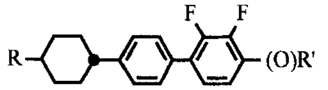


VII

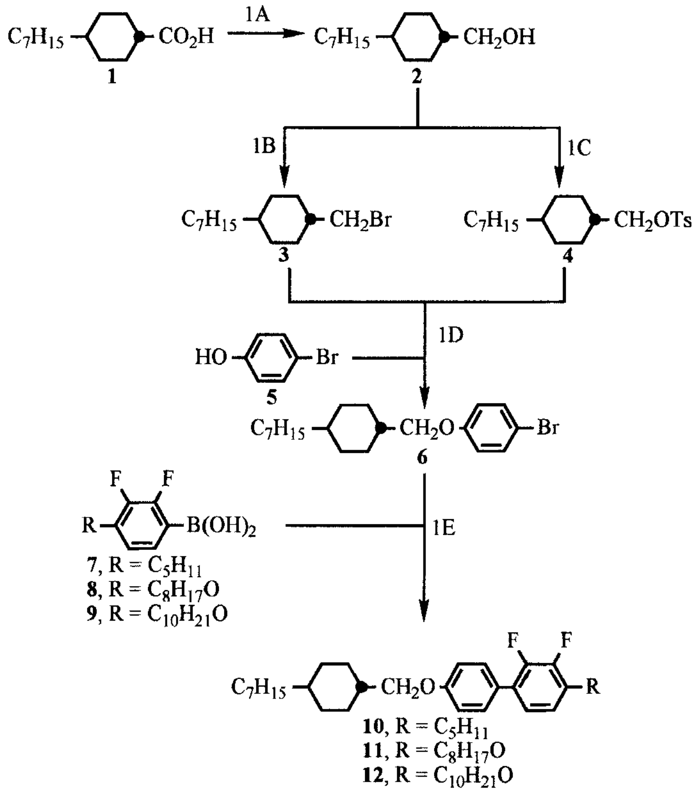
II) have produced excellent host materials and ferroelectric mixtures based on these compounds give excellent alignment and have very fast switching times (3 μs at 30°C and 10 V μm^{-1} [6]). Analogous biphenyl systems [3, 4] (structure **III**) have low melting points and very low S_C phase stabilities, but they do have a lower viscosity than the terphenyls. However, as will be seen later, the incorporation of two terminal alkyloxy-substituents in the biphenyls can provide reasonably high S_C phase stability, but this also leads to higher melting points. Terphenyls of structures **I** and **II** have relatively high birefringence (Δn) values (0·19), but the trend towards thinner cells (1·5 μm) allows such values to be tolerated. The birefringence of the lower viscosity biphenyl systems is much lower than for the terphenyls, but their mesophase behaviour is not so conducive to providing ferroelectric host materials.

High birefringence can be avoided by minimizing the number of aromatic rings and instead using, for example, the *trans*-1,4-disubstituted cyclohexane moiety. However, a suitable compromise has to be found because compounds based on cyclohexane are not normally conducive to S_C phase formation and are more disposed to give orthogonal smectic phases [7–10]. The incorporation of a cyclohexane ring as part of the terminal chain in the biphenyl systems was expected to provide materials with the low birefringence of biphenyls and go some way towards producing the high S_C phase stability of the terphenyl systems, with probably little change in viscosity. We have already reported our work on dimethylene linked cyclohexylbiphenyl systems with 2,3-difluoro-substituents [5] (structure **IV**) and these materials have low melting points and moderately high S_C phase stabilities (for example, compounds **32** and **33**). Here we report some cyclohexylbiphenyl materials with a methyleneoxy linking group (structures **V** and **VI**). In addition to alkyl–alkyloxy-substituted systems, the methyleneoxy linking group allows for the preparation of dialkyloxy-substituted biphenyl systems which ought to have enhanced S_C phase stability, although higher melting points and higher viscosity would also be expected. The linking group separating the cyclohexane ring from the biphenyl unit should also provide more flexibility than a directly linked cyclohexane ring. This arrangement also allows a closer structural similarity with the open chain biphenyls [3, 4] and therefore allows comparison with the excellent terphenyl systems [3, 4]. Compounds with the difluoro-substituents in the end ring (structure **V**) and in the centre ring (structure **VI**) have been prepared, some with an alkyl-substituent and some with a second alkyloxy-substituent.

The effect of a directly linked cyclohexane ring on the mesogenic behaviour of 2,3-difluorobiphenyls was also examined (structure **VII**). The attachment of a directly linked cyclohexane unit to the biphenyl core confers a more rigid and compact structure than when separated by a linking group. Therefore, a higher smectic character was expected, and this was confirmed as will be discussed later. Two cyclohexylbiphenyl compounds have been prepared: an alkyl-substituted system (compound **29**), for comparison with the corresponding S_C-exhibiting dialkyl-substituted terphenyl system, to determine such a compound's mesogenicity and to confirm the expected lack of an S_C phase and also an alkyloxy-substituted homologue (compared **30**), as the most likely generator of S_C character in this class of compound.

2. Synthesis

The development of palladium-catalysed cross-coupling reactions [11–13] has revolutionized the synthesis of liquid crystal materials [3–5, 14, 15] and has facilitated the efficient preparation of a range of interesting materials. The preparation of all of the materials reported here involved a palladium-catalysed cross-coupling reaction in the final stage of synthesis.

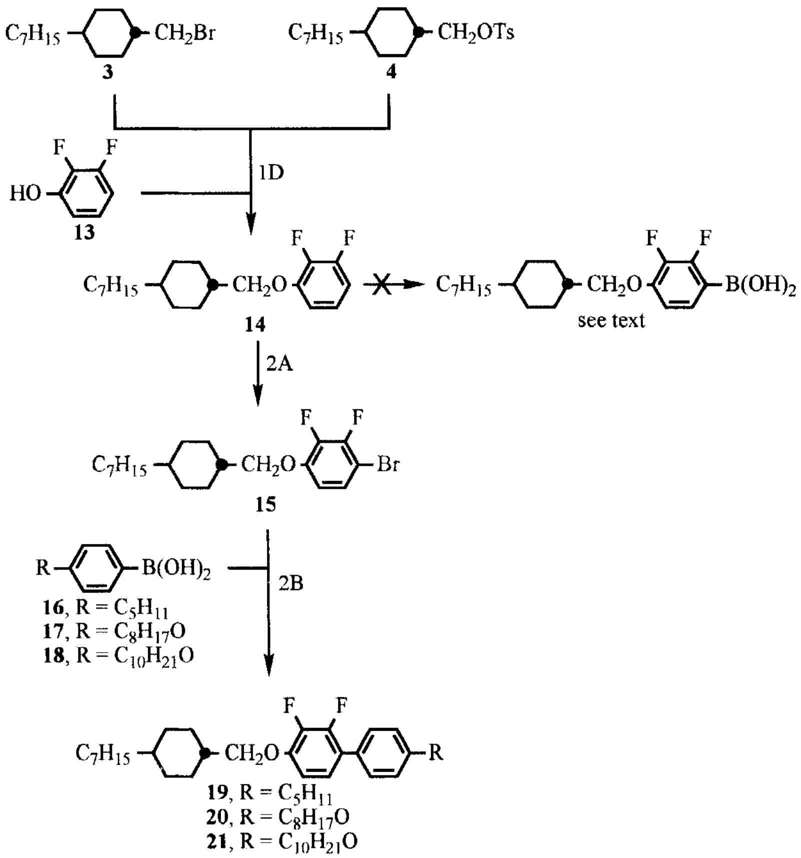


1*A*, $LiAlH_4$, THF.
1*B*, HBr, H_2SO_4.
1*C*, TsCl, pyridine, $CHCl_3$.
1*D*, K_2CO_3, cyclohexanone.
1*E*, $Pd(PPh_3)_4$, benzene, ethanol, 2 M-Na_2CO_3.

Scheme 1.

The first sections of schemes 1 and 2 illustrate the synthetic routes used to obtain the vital intermediates (compounds **6** and **15**) that were then used in palladium-catalysed cross-coupling reactions to provide the final mesomorphic materials (**10**–**12** and **19**–**21**) (see tables 1 and 2). The carboxylic acid **1** was directly reduced in excellent yield using lithium aluminium hydride to give the cyclohexylmethanol derivative (**2**). Two approaches were then used for introducing a good leaving group into the system to facilitate the preparation of the desired ethers (**6** and **14**, schemes 1 and 2 respectively). Firstly, the bromide **3** was prepared with partial success (80 per cent conversion) using a hydrobromic acid and sulphuric acid mixture. Ethers **6** and **14** were prepared using the crude bromide (**3**) and 4-bromophenol (**5**) in an *O*-alkylation procedure that required the use of a high boiling solvent (cyclohexanone). The unreacted methanol derivative (**2**) from the previous step was easily removed. Alternatively, the tosylate derivative of the methanol was prepared in excellent yield which makes for more efficient use of intermediate materials. The tosylate (**4**) was used in the *O*-alkylations under identical conditions to the bromide to give ethers **6** and **14**.

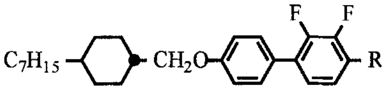
Ether **6** (scheme 1) was then used in palladium-catalysed cross-coupling reactions with the appropriate arylboronic acids (**7**–**9**) [3] in a benzene/ethanol/water solvent to provide the mesomorphic materials **10**–**12** in usually poor yields. Arylboronic acids



2*A*, Br_2, $CHCl_3$.
2*B*. $Pd(PPh_3)_4$, 1,2-dimethoxyethane, 2 M-Na_2CO_3.

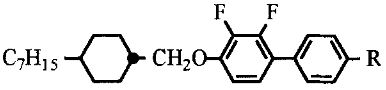
Scheme 2.

Table 1. Transition temperatures (°C) for 4-alkyl- and 4-alkyloxy-2,3-difluoro-4′-(*trans*-4-heptylcyclohexylmethoxy)biphenyls (**10**–**12**).



		Transition temperatures/°C								
Compound	R	C		S_C		S_A		N		I
10	C_5H_{11}	●	54·0	—		●	111·5	●	116·0	●
11	$C_8H_{17}O$	●	65·5	(●	65·0)	●	132·0	●	133·0	●
12	$C_{10}H_{21}O$	●	66·0	●	77·0	●	129·0	—		●

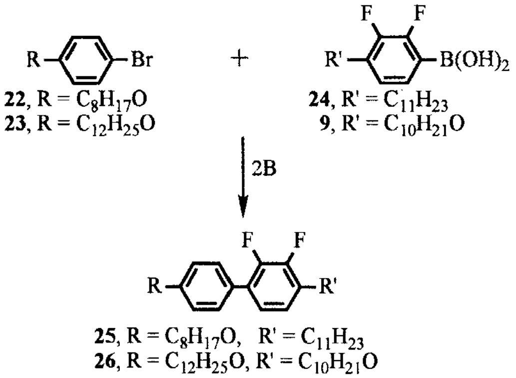
Table 2. Transition temperatures (°C) for 4′-alkyl- and 4′alkyloxy-2,3-difluro-4-(*trans*-4-heptylcyclohexylmethoxy)biphenyls (**19**–**21**).



		Transition temperatures/°C								
Compound	R	C		S_C		S_A		N		I
19	C_5H_{11}	●	51·0	—		●	91·0	●	110·0	●
20	$C_8H_{17}O$	●	78·0	●	86·5	●	118·0	●	128·0	●
21	$C_{10}H_{21}O$	●	76·0	●	83·0	●	116·5	●	122·5	●

such as compounds **7**–**9** are prone to hydrodeboronation (protonolysis) which competes with the coupling reaction. This was not a problem in the synthesis of the original difluoroterphenyl materials [3] because the coupling reactions were not sterically restricted and were therefore very fast. However, the added bulk from the cyclohexane-containing terminal chains (compound **6** and similar compounds in a previous publication [5]) appears to slow the coupling and the relatively more significant hydrodeboronation process causes lower product yields. The use of 1,2-dimethoxyethane in place of the benzene and ethanol considerably improves yields with these particular systems [5, 13] and the use of anhydrous conditions can eliminate the hydrodeboronation problem completely [13, 16, 17]. The strategy of synthesis for the isomeric mesogenic materials with the fluoro-substituents in the centre ring was different because of the absence of a bromo-substituent with which coupling could occur. However, the difluoro-substituted ether (**14**) has an acidic proton *ortho* to a fluoro-substituent. In such cases, it is usual [3–5] to remove the proton with butyllithium at −78°C and quench the lithium salt with trimethyl borate to give the appropriate arylboronic acid (this can then be coupled to an appropriate aryl bromide). This was attempted, but solubility problems at the required low temperature prevented lithiation (a problem that has since been overcome by simply using large amounts of solvent). The alternative approach involved bromination of compound **14** and this gave a quantitative yield of compound **15**. Bromination occurred entirely in the 4-position because steric hindrance from the bulky cyclohexyl moiety prevented any bromination in the 2-position. The efficiency of the steric hindrance, despite the use of an excess of bromine, was pleasantly surprising and is synthetically significant. The bromo-substituted compound (**15**) was then coupled with boronic acids **16**–**18** to provide three mesomorphic materials (**19**–**21**) in very good yields. For these coupling reactions, the superior solvent system (for this type of compound) of 1,2-dimethoxyethand and water was employed even though the boronic acids were not, in this case, prone to hydrodeboronation.

The preparation of the simple *ortho*-difluorobiphenyls with two long terminal chains was more straightforward (scheme 3). Appropriate arylboronic acids and aryl bromides (prepared by existing methods [3]) were coupled together to provide the desired materials (**25** and **26**) (see table 3). The yields of these materials are believed to show the role of the very long terminal alkyl chains in reducing the rate of the coupling reaction. Even though 1,2-dimethoxyethane was used as the solvent, the yield of compound **25** was only moderate and for the even longer alkyl chain compound (**26**), the yield was very low. In these cases the coupling rate is probably reduced by the long alkyl chains sterically protecting the reaction site or by the greater aliphatic nature of the molecule altering the local solvent environment; the competing hydrodeboronation can therefore lead to low yields of coupled product. If high yields are required then anhydrous coupling conditions [13, 16, 17] would be particularly advisable in such cases.



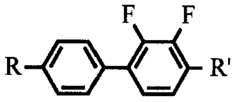
22, R = $C_8H_{17}O$
23, R = $C_{12}H_{25}O$

24, R' = $C_{11}H_{23}$
9, R' = $C_{10}H_{21}O$

25, R = $C_8H_{17}O$, R' = $C_{11}H_{23}$
26, R = $C_{12}H_{25}O$, R' = $C_{10}H_{21}O$

Scheme 3.

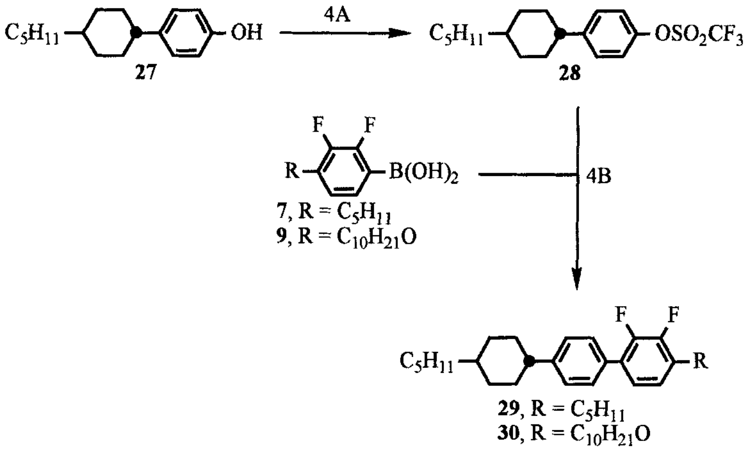
Table 3. Transition temperature (°C) for 4-alkyl-4'-alkyloxy- and 4,4'-dialkyloxy-2,3-difluorobiphenyls (**25** and **26**).



			Transition temperatures/°C						
Compound	*R*	*R'*	C		S_C		S_A		I
25	$C_8H_{17}O$	$C_{11}H_{23}$	●	30·5	—		●	37·0	●
26	$C_{12}H_{25}O$	$C_{10}H_{21}O$	●	70·5	(●	68·0	●	68·0)	●

Scheme 4 shows how a trifluoromethanesulphonate (triflate) leaving group has been used in a palladium-catalysed cross-coupling with an arylboronic acid in essentially the same manner as for bromide leaving groups. The use of the lithium chloride is reported [18] to facilitate the oxidative addition step of the mechanism which produces the arylpalladium species, but there are reports that lithium chloride has little effect in some coupling reactions [19]. Phenol **27** was easily converted into its triflate (compound **28**) using trifluoromethanesulphonic anhydride in pyridine [18]. Arylboronic acids **7** and **8** were prepared as usual and then coupled to triflate **28** to provide mesomorphic materials **29** and **30** (see table 4).

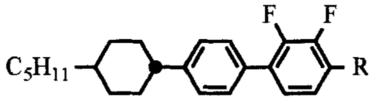
The ability of the triflate group to undergo palladium-catalysed cross-coupling reactions is particularly valuable because phenols are sometimes available when the corresponding halogen materials are not. The use of a combination of the triflate leaving group and the traditional bromo leaving group enables useful selective couplings to be achieved [14, 15].



4*A*, $(CF_3SO_2)_2O$, pyridine.
4*B*, $Pd(PPh_3)_4$, 1,2-dimethoxyethane, 2 M-Na_2CO_3, LiCl.

Scheme 4.

Table 4. Transition temperatures (°C) for 4-alkyl- and 4-alkyloxy-2,3-difluoro-4′-(*trans*-4-pentylcyclohexyl)biphenyls (**29** and **30**).



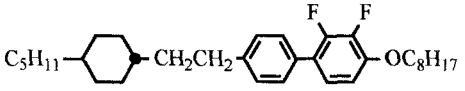
		Transition temperatures/°C								
Compound	*R*	C		S_C		S_A		N		I
29	C_5H_{11}	●	33·0	—		●	96·5	●	123·0	●
30	$C_{10}H_{21}O$	●	52·0	●	58·5	●	126·5	●	137·0	●

3. Transition temperatures

The preparation of the *ortho*-difluoroterphenyl materials [3, 4] showed the exceptional ability of the 2,3-difluorophenyl moiety to confer high S_C character on a material and examples of these excellent ferroelectric host materials are shown in table 6.

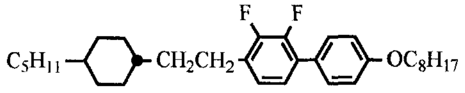
The corresponding dimethylene-linked cyclohexyl-difluorobiphenyls [5] (see table 5) showed that it was necessary for the difluoro unit to be placed in the non-alkyloxy-substituted ring (for example, compound **32**) for the S_C phase to be exhibited. However, the fluoro-substituents in the centre ring also cause a reduction in melting point and a reduction in the thermal stability of the S_A and nematic phases (compare compounds **31**

Table 5. Transition temperature (°C) for selected dimethylene-linked cyclohexyldifluorobiphenyls [5].



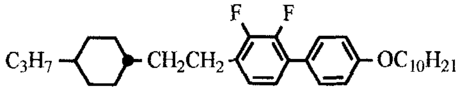
31

C 59·0 S_A 113·5 N 124·0 I



32

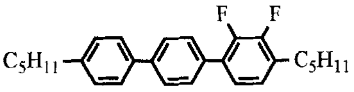
C 32·5 S_C 55·0 S_A 83·0 N 122·0 I



33

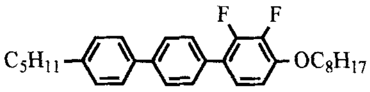
C 38·5 S_C 68·5 S_A 88·0 N 119·0 I

Table 6. Transition temperatures (°C) for selected 2,3-difluoroterphenyls [3].



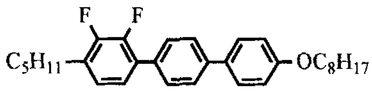
34

C 83·0 S_C 115·5 S_A 131·5 N 142·0 I



35

C 93·5 S_C 144·0 S_A 148·0 N 159·0 I



36

C 89·0 S_C 155·5 S_A 165·0 N 166·0 I with compound **32**, shown in table 5). There are several other examples of terminal alkyl–alkyloxy-substituted systems that show enhanced S_C character when a non-fluoro-substituted phenyl moiety contains the terminal alkyloxy-substituent (monofluoro-substituted terphenyls, difluoro-substituted biphenyls and terphenyls [3, 20–22] but in these cases the thermal stability of the other mesophases exhibited is also enhanced.

A rationalization of the S_C phase formation in difluorobiphenyls is best started by comparing the dimethylene-linked difluorobiphenyls (compounds **31** and **32**, table 5). A high smectic stability is favoured by having the cyclohexyldimethylene-containing phenyl moiety unfluorinated (compound **31**), because this unit possesses an additional ring (a cyclohexane ring which from the way these pack tends to support the S_A phase rather than the S_C phase) [5, 7–10]. When this unit is fluoro-substituted (compound **32**), the sub-structure becomes broader and therefore the ability to promote an S_A phase is reduced However, the phenyl unit with the polar ether oxygen is now less broad (unfluorinated) and this allows an enhancement of the S_C phase stability. There appear to be two competing factors affecting the mesogenic behaviour of cyclohexyl-containing difluorobiphenyls. Firstly, the non-fluoro-substituted phenyl unit with the open chain terminal substituent is the feature that is controlling the stability of the S_C phase, and if an alkyloxy terminal substituent is present, then the S_C phase stability is particularly enhanced. Secondly, there is the phenyl unit with the cyclohexyldimethylene terminal group which tends to control the degree of S_A phase stability. If this phenyl unit is fluoro-substituted then the S_A phase stability is reduced, and because the other phenyl moiety will be unfluorinated (less broad), and in the case of compound **32** also contain an alkyloxy terminal substituent, the S_C phase stability will be enhanced. Compound **31** has the reverse situation, with a non-fluoro-substituted cyclohexyldimethylene-substituted phenyl moiety that will ensure enhanced S_A phase stability and, to make things worse, the alkyloxy-substituted phenyl unit is fluorinated, and so the S_C phase stability is depressed. The reduced melting point of compound **32** when compared with compound **31** (which enhances the S_C range) probably results from the reduced dipole in the molecules when the fluoro-substituents are no longer acting in a 'push–pull' manner with the ether oxygen [3, 5].

Compounds **10** and **19** are structurally analogous to compounds **31** and **32**, but have their ether oxygen in the linking group (methyleneoxy). This is an interesting situation because, in combination with the results for compounds **31** and **32**, the effect on the mesogenic behaviour (especially the phase stability of the S_C phase) can be studied in relation to the position of the polar ether oxygen and the difluoro unit. In fact, neither compound **10** nor compound **19** (see tables 1 and 2) exhibits the S_C phase, which is surprising, given the previously recognized ability of the 2,3-difluorophenyl moiety for generating the S_C phase. However, for these compounds (**10** and **19**), the ether oxygen has been removed from the S_C enhancing open chain position and placed at the S_A enhancing cyclohexyl-containing moiety; the lack of an S_C phase can be explained by considering the above discussion of the dimethylene linked analogues. The alkyloxy-substituted phenyl unit is desirable for enhanced S_C phase stability and for these compounds (**10** and **19**) this happens to be part of the cyclohexyl moiety that is detrimental to S_C phase formation. In compound **10**, the unfluorinated phenyl unit is alkyloxy-substituted, which may be expected to produce an S_C phase, but this alkyloxy unit is cyclohexyl based, which promotes the S_A phase and suppresses S_C phase formation. Compounds **19** might also be thought conducive to S_C phase formation, but the unfluorinated phenyl unit simply contains a terminal alkyl-substituent; the alkyloxy-substituent is rendered ineffective in generating the S_C phase by being part of the cyclohexyl moiety and the phenyl unit to which it is attached is fluorinated. The pattern of S_A and nematic phase thermal stabilities for compounds **10** and **19** is the same as that seen for the dimethylene-linked materials (compounds **31** and **32**, respectively). The fact that compound **10** has the higher melting point, the higher S_A phase stability and the higher nematic phase stability does show that the cyclohexyl moiety, ether linked to an unfluorinated phenyl unit is conducive to high mesogenicity but not, unfortunately, to the generation of an S_C phase.

In order to provide some measure of the S_C phase stability of compounds **10** and **19**, these materials were mixed with compound **36** [3] (a difluoroterphenyl material with a high S_C phase stability) in various proportions across the phase diagram. Extrapolated values of S_C phase stability for both compound **10** and compound **19** were identical (within experimental error) at ~30°C. The S_C phase was then generated in this type of compound by using an open chain alkyloxy-substituent (compounds **11**, **12** and **20**, **21**; see tables 1 and 2). This makes these materials dialkyloxy-substituted which is usually undesirable because of high melting points. However, in the case of these materials, the increase in melting points is nowhere near as great as the increase in S_C phase stability. Both terminal substituents now contain polar oxygen substituents, but the same arguments as used previously still hold for these compounds (**11**, **12** and **20**, **21**). Where the potentially S_C enhancing open-chain phenyl moiety is fluorinated (compounds **11** and **12**) then the S_C phase stability is not very great (~15°C less than compounds **20** and **21**), but because the other phenyl ring is unfluorinated, then the S_A and nematic phase stabilities are greater than for compounds **20** and **21** (by ~15°C for the S_A phase and by ~5°C for the nematic phase). The use of the second alkyloxy-substituent in compounds **11**, **12** and **20**, **21**) emphasizes the desirability of a terminal open-chain alkyloxy-substituent in generating the S_C phase in these types of materials.

Difluorobiphenyls with open-chain terminal substituents have a very low length to breadth ratio and so would not be expected to be mesomorphic. However, some of those materials already reported [1] show enantiotropic liquid crystal phases because of their very low melting points. The polarity from the two *ortho*-fluoro-substituents also allows the generation of the S_C phase, albeit monotropic and of low thermal stability. Compound **25** (see table 3) reveals that the use of long terminal chains (alkyl–alkyloxy-substituents) confers greater crystallinity and only an S_A phase is produced. The use of two long open-chain alkyloxy-substituents in difluorobiphenyls has been investigated with the preparation of compound **26**. As expected, the use of two ether oxygens has led to a high melting point (70°C) and increased the thermal stability of the smectic phases. Most importantly, the S_C phase has been generated with a similarly high thermal stability to that of the S_A phase (68°C). In the cyclohexyl-substituted compounds, the S_A phase stability is always considerably greater than that of the S_C phase (if it is generated at all). This does illustrate that the absence of a cyclohexane moiety causes considerably depressed mesogenicity, but a greater ability to generate the S_C mesophase within that mesogenic range. The big advantage of the cyclohexyl-substituent is its ability to confer a relatively low melting point upon its compounds compared with their mesophase thermal stabilities. If the correct blend of structural features is included in the materials (for example, compounds **32** and **33**), then compounds with low melting points and S_C phases of quite high stabilities and reasonable ranges can be obtained, which is not possible for open-chain difluorobiphenyls.

Table 4 shows the transition temperatures for two directly-linked cyclohexyl-difluorobiphenyls (compounds **29** and **30**). These can be discussed in relation to all of the compound types previously discussed in this section in addition to the difluoroterphenyl materials (for example, compounds **34**–**36**, table 6). As expected, the non-ether substituted material (compound **29**) does not show the S_C phase, but the melting point is low (33°C) and the polarity from the outer-ring fluoro-substituents ensures a high S_A phase stability.

The alkyloxy-substituted material (compound **30**) does exhibit the S_C phase and, when compared with compound **31** (isomeric and with similar structural combinations), shows that the removal of the linking group has not greatly affected the melting point. However, the added rigidity of the core has enhanced both the S_A and nematic phase stabilities by 13°C. More significantly, the S_C phase stability has been increased by ~30°C (based on the extrapolated value of S_C phase stability for compound **31** discussed above), which suggests that a more rigid molecular core enhances the S_C phase stability more than the S_A and nematic phase stabilities. A comparison with compound **33** shows the effect of removing the linking group and changing the fluoro-substituents to the outer aromatic ring in isomeric materials. The melting point has been increased by 14°C in compound **30**, yet the S_C phase stability has been reduced by 10°C, and these important effects have occurred despite large increases in the S_A and nematic phase stabilities of 39°C and 18°C, respectively. Although the position of the fluoro-substituents has altered, this comparison would suggest that S_C phase stability is increased by a more flexible molecular core. However, it is probable that the linking group makes both aromatic rings act as 'end-rings' and that the space-filling effect of the outer edge fluoro-substituent in compound **33**, in combination with the unfluorinated alkyloxyphenyl moiety (as discussed above), is responsible for the higher S_C lower S_A phase stabilities when compared with compound **30**. The comparison of compound **30** with the compound **33** clearly illustrates the large tendency for a cyclohexane ring to confer S_A character on a compound and the effect of a flexible linking group in reducing the S_A tendency.

Compounds **29** and **30** can be compared with their terphenyl analogues (compounds **34** and **35**, table 6). The increased rigidity of the terphenyl material causes large increases in melting points (40–50°C in each case). The S_C phase thermal stability for compound **35** is a massive 86°C higher than for its cyclohexyl-substituted analogue (compound **30**), whereas the S_A and nematic phase stabilities are both just 23°C higher.

4. Summary

(1) When a single polar oxygen substituent is part of the cyclohexyl terminal chain in the methyleneoxy-linked systems (compounds **10** and **19**), no S_C phase is generated, regardless of where the two polar fluoro-substituents are positioned.

(2) When a single polar oxygen substituent is part of the open terminal chain in the dimethylene-linked systems, then the S_C phase can be generated if the polar-substituents are suitably positioned to provide the necessary tilt (compounds **32** and **33**) [5].

(3) The use of a second polar oxygen substituent in the methyleneoxy-linked systems is necessary to generate an S_C phase when one of the oxygen substituents is part of the cyclohexyl terminal chain (compounds **11**, **12**, **20** and **21**).

(4) The use of two very long alkyloxy chains in difluorobiphenyls can produce materials that exhibit the S_C phase, albeit with a very short range because of the high melting points (compound **26**).

(5) The use of a directly linked cyclohexylbiphenyl core can produce materials which generate the S_C phase (for example, compound **30**), but a very high S_A phase stability is also produced by this structural arrangement.

(6) A cyclohexane ring can be successfully used for enhancing mesophase stabilities, but such a unit is not very good for generating the S_C phase. The generation of the S_C phase from cyclohexane-containing compounds requires a subtle blend of features such as the correct combination of terminal chain lengths, the correct position of the alkyloxy-terminal substituents and the correct position of the difluoro-substituents.

5. Experimental

5.1. *Analyses*

Confirmation of the structures of intermediates and products was obtained by ^1H and ^{13}C NMR spectroscopy (JEOL JNM-GX270 spectrometer), infrared spectroscopy (Perkin–Elmer 457 grating spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 GC/MS spectrometer). The progress of reactions was frequently monitored using a Perkin–Elmer 8320 capillary gas chromatograph fitted with a 12 m QC2/BP1–1·0 SGE column. Transition temperatures were measured using a Mettler FP 5 hot-stage and control unit in conjuction with an Olympus BH 2 polarizing microscope and these were confirmed using differential scanning calorimetry (Perkin–Elmer DSC-7 and IBM data station). The purities of all intermediates were checked by GLC analysis (see above). The purities of each of the final compounds shown in tables 1, 2, 3 and 4 were checked by GLC analysis (see above) and by HPLC analysis (Microsorb C 18 80-215-C5 RP column) and were found to be >99·9 per cent unless stated otherwise.

Compounds **1** and **27** were kindly supplied by our collaborators at Merck (U.K.) Ltd, Poole, Dorset. The preparations of intermediates **7–9** [3], **13** [3], **16–18** [14], and **22–24** [3] have been previously reported. Tetrakis(triphenylphosphine)palladium(0) [23] was prepared according to the literature procedure and compound **5** was purchased from the Aldrich Chemical Co.

5.2. *Synthesis of trans-4-heptylcyclohexylmethanol* (**2**)

A solution of compound **1** (103·0 g, 0·456 mol) in dry THF (160 ml) was added dropwise to a stirred mixture of lithium aluminium hydride (20·0 g, 0·526 mol) in dry THF (330 ml) at room temperature under dry nitrogen. The mixture was heated under reflux for 1 h and stirred at room temperature overnight. The mixture was cooled, a mixture of THF and 10 per cent hydrochloric acid was added dropwise and the product was extracted into ether (×2). The combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was distilled to give a colourless oil.

Yield 91·8 g (95 per cent); b.p. 135–140°C at 0·5 mmHg; ^1H NMR ($CDCl_3$) δ 0·85 (7 H, m), 1·25 (13 H, m), 1·45 (1 H, s), 1·75 (4 H, d), 2·00 (1 H, s), 3·45 (2 H, d); IR (film) ν_{max} 3600–3050, 2940, 2860, 1450, 1380, 1040 cm^{-1}; MS *m/z* 212(M^+), 211, 194, 179.

5.3. *Synthesis of trans-4-heptylcyclohexylbromomethane* (**3**)

Compound **2** (25·0 g, 0·118 mol) was added to a mixture of 48 per cent hydrobromic acid (38 ml) and concentrated sulphuric acid (5 ml); the mixture was heated under reflux for 6 h (GLC analysis revealed ~80 per cent conversion). The cooled mixture was poured on to ice and the product was extracted into ether (twice). The combined ethereal extract were washed with water, aqueous sodium hydrogen carbonate, water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was distilled to yield a colourless oil (80 per cent product, 20 per cent starting material). Yield 26·9 g (83 per cent); purity (GLC) 80 per cent; b.p. 106–108°C at 0·1 mmHg; no spectroscopic data were obtained.

5.4. *Synthesis of trans-4-heptylcyclohexylmethyl tosylate* (**4**)

Toluene-4-sulphonyl chloride (117·0 g, 0·614 mol) was added in small portions to a stirred, cooled (0°C) solution of compound **2** (86·0 g, 0·406 mol) and pyridine (65·0 g, 0·823 mol) in chloroform (250 ml). The stirred mixture was allowed to warm to room temperature over 2·5 h (GLC analysis revealed a complete reaction) and ether and water added. The separated aqueous layer was washed with ether and the combined ethereal extract were washed with 10 per cent HCI, water, aqueous sodium hydrogen carbonate and water and dried ($MgSO_4$). The solvent was removed *in vacuo* to give a colourless solid which was recrystallized from ethanol to yield colourless crystals.

Yield 132·0 g (89 per cent); m.p. 40–41°C; ^1H NMR ($CDCl_3$) δ 0·85 (7 H, m), 1·20–1·40 (13 H, m), 1·60 (1 H, m), 1·70 (4 H, m), 2·45 (3 H, s), 3·80 (2 H, d), 7·35 (2 H, d), 7·80 (2 H, d); IR (KBr) γ_{max} 2960, 2860, 1600, 1450, 1360, 1275, 955, 820, 670, 560 cm^{-1}; MS *m/z* 366 (M^+), 194.

5.5. *Synthesis of 1-bromo-4-(trans-4-heptylcyclohexylmethoxy)benzene* (**6**)

A stirred mixture of compound **3** (10·0 g, 0·036 mol; 86 per cent pure), compound **5** (8·72 g, 0·050 mol) and potassium carbonate 15·0 g, 0·109 mol) in cyclohexanone (100 ml) was heated under reflux for 24 h (GLC analysis revealed a complete reaction). The mixture was cooled and the potassium carbonate was filtered off. The solvent and the *trans*-4-heptylcyclohexylmethanol (impurity) were distilled off (0·1 mmHg) and the residue was dissolved in ether and washed with aqueous 10 per cent sodium hydroxide. The aqueous layer was washed with ether and the combined organic extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C)-dichloromethane, 5 : 1) to yield a colourless solid.

Yield 7·75 g (59 per cent); m.p. 60–61°C; ^1H NMR ($CDCl_3$) δ 0·85–0·95 (3 H, t), 0·95–1·05 (4 H, m), 1·10–1·20 (4 H, m), 1·20–1·35 (9 H, m), 1·65–1·80 (5 H, m), 3·70 (2 H, d), 6·75 (2 H, d), 7·35 (2 H, d); IR (KCl) ν_{max} 2960, 2940, 2860, 1590, 1580, 1490, 1470, 1290, 1290, 1245, 1175, 1030, 1005, 825, 805 cm^{-1}; MS *m/z* 368 (M^+), 366 (M^+), 194, 174, 172.

5.6. *Synthesis of 2,3-difluoro-4′-(trans-4-heptylcyclohexylmethoxy)-4-pentylbiphenyl* (**10**)

Quantities: compound **6** (1·75 g, 4·77 mmol), compound **7** (1·45 g, 6·36 mmol). The experimental procedure was as described in a previous publication [1]. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C)-dichloromethane, 10 : 1) to give a colourless solid which was recrystallized from ethanol to yield colourless crystals.

Yield 0·65 g (29 per cent); transitions (°C) C 54·0 S_A 111·5 N 116·0 I; ^1H NMR ($CDCl_2$) δ 0·85 (6 H, 2xt), 0·95–1·10 (4 H, m), 1·15–1·25 (4 H, m), 1·25–1·40 (13 H, m), 1·65 (2 H, quint), 1·80–1·90 (5 H, m), 2·70 (2 H, t), 3·80 (2 H, d), 6·94 (1 H, sext), 6·79 (2 H, d), 7·07 (1 H, sext), 7·45 (2 H, q); IR (KCl) ν_{max} 2960, 2940, 2860, 1615, 1530, 1500, 1475, 1415, 1320, 1280, 1185, 1120, 1045, 900, 810 cm^{-1}; MS *m/z* 470 (M^+), 276, 219.

5.7. *Synthesis of 2.3-difluoro-4′-(trans-4-heptylcyclohexylmethoxy)-4-octyloxybiphenyl* (**11**)

Quantities: compound **6** (1·40 g, 3·81 mmol), compound **8** (1·45 g, 5·07 mmol). The experimental procedure was as described for the preparation of compound **10**. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C)-dichloromethane, 5 : 1) to give a colourless solid which was recrystallized from ethanol–ethyl acetate (50 : 1) to yield colourless crystals.

Yield 0·67 g (33 per cent); transitions (°C) C 65·5 (S_C 65·0) S_A 132·0 N 133·0 I; ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (6 H, m), 0·95–1·10 (4 H, m), 1·10–1·20 (4 H, m), 1·20–1·35 (17 H, m), 1·45 (2 H, quint), 1·70–1·90 (7 H, m), 3·75 (2 H, d), 4·10 (2 H, t), 6·77 (1 H, sext), 6·95 (2 H, d), 7·04 (1 H, sext), 7·41 (2 H, q); IR (KCl) ν_{max} 2960, 2940, 2860, 1510, 1465, 1255, 1075, 800 cm^{-1}; MS *m/z* 528 (M^+), 416, 334.

5.8. *Synthesis of 2,3-difluoro-4′-(trans-4-heptylcyclohexylmethoxy)-4-decyloxybiphenyl* (**12**)

Quantities: compound **6** (1·46 g, 3·98 mmol), compound **9** (1·40 g, 4·46 mmol). The experimental procedure was as described for the preparation of compound **10**. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C)-dichloromethane, 10 : 1) to give a colourless solid which was recrystallized from hexane to yield colourless crystals.

Yield 0·20 g (9 per cent); transitions (°C) C 66·0 S_C 77·0 S_A 129·0 I; ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (6 H, m), 0·95–1·10 (4 H, m), 1·10–1·20 (4 H, m), 1·20–1·35 (21 H, m), 1·45 (2 H, quint), 1·70–1·90 (7 H, m), 3·75 (2 H, d), 4·10 (2 H, t), 6·77 (1 H, sext), 6·95 (2 H, d), 7·04 (1 H, sext), 7·41 (2 H, q); IR (KCl) ν_{max} 2960, 2940, 2860, 1510, 1465, 1255, 1075, 800 cm^{-1}; MS *m/z* 556 (M^+), 498, 471.

5.9. *Synthesis of 1,2-difluoro-3-(trans-4-heptylcyclohexylmethoxy)benzene* (**14**)

Quantities: compound **3** (10·5 g, 0·038 mol; 80 per cent pure), compound **13** (6·00 g, 0·046 mol), potassium carbonate (15·0 g, 0·110 mol), cyclohexanone (100 ml). The experimental procedure was as described for the preparation of compound **6** except that the crude product was distilled to yield a colourless solid.

Yield 8·00 g (65 per cent); m.p. 46–47°C; b.p. 160–162°C at 0·1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (3 H, t), 0·95–1·05 (4 H, m), 1·10–1·20 (4 H, m), 1·20–1·35 (9 H, m), 1·65–1·80 (5 H, m), 3·80 (2 H, d), 6·67–6·77 (2 H, m), 6·89–6·98 (1 H, m); IR (KCl) ν_{max} 2960, 2940, 2860, 1635, 1620, 1515, 1490, 1470, 1310, 1295, 1260, 1220, 1080, 770, 730, 705 cm^{-1}; MS *m/z* 324 (M^+).

5.10. *Synthesis of 1-bromo-2,3-difluoro-4-(trans-4-heptylcyclohexylmethoxy)benzene* (**15**)

A solution of bromine (14·7 g, 0·092 mol) in chloroform (20 ml) was added dropwise to a stirred solution of compound **14** (14·7 g, 0·046 mol) in chloroform (250 ml) at room temperature. The mixture was heated under reflux for 24 h (GLC analysis revealed a complete reaction and only one product peak), cooled and washed with aqueous sodium metabisulphite. The separated aqueous layer was washed with chloroform and the combined organic extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to give a off-white solid (GLC analysis revealed 99 per cent pure).

Yield 18·5 g (100 per cent); m.p. 62–64°C; ^{1}H NMR ($CDCl_3$) δ 0·85–0·95 (3 H, t), 0·95–1·05 (4 H, m), 1·15–1·25 (4 H, m), 1·25–1·35 (9 H, m), 1·70–1·90 (5 H, m), 3·80 (2 H, d), 6·64 (1 H, sext), 7·18 (1 H, sext); IR (KCl) ν_{max} 2960, 2920, 2860, 2860, 1625, 1510, 1470, 1310, 1220, 1075, 885, 800, 740 cm^{-1}; MS *m/z* 404 (M^+), 402 (M^+).

5.11. *Synthesis of 2,3-difluoro-4-(trans-4-heptylcyclohexylmethoxy)-4′-pentylbiphenyl* (**19**)

Quantities: compound **15** (2·35 g, 5·83 mmol), compound **16** (1·45 g, 7·55 mmol). The experimental procedure was as described for the preparation of compound **10**. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C)-dichloromethane, 10: 1 (followed by 20: 1)) to give a colourless solid which was recrystallized from ethanol to yield colourless crystals (98 per cent pure by HPLC).

Yield 1·10 g (40 per cent); transitions (°C) C 51·0 S$_A$ 91·0 N 110·1; ^{1}H NMR (CDCl$_3$) δ 0·85–095 (6 H, 2xt), 0·95–1·10 (4 H, m), 1·15–1·25 (4 H, m), 1·25–1·40 (13 H, m), 1·65 (2 H, quint), 1·80–1·90 (5 H, m), 2·70 (2 H, t), 3·80 (2 H, d), 6·77 (1 H, sext), 7·08 (1 H, sext), 7·24 (2 H, d), 7·41 (2 H, q); IR (CI) ν_{max} 2980, 2940, 2860, 1640, 1510, 1470, 1305, 1205, 1110, 1075, 895, 855, 800 cm^{-1}; MS *m*/*z* 470 (M$^+$), 413, 276.

5.12. *Synthesis of 2,3-difluoro-4-(trans-4-heptylcyclohexylmothoxy)-4′-octyloxy-biphenyl* (**20**)

Quantities: compound **15** (1·70 g, 4·22 mmol), compound **17** (1·37 g, 5·48 mmol). The experimental procedure was as described for the preparation of compound **10** 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 (b.p. 40–60°C)-dichloromethane, 10: 1) to give a colourless solid which was recrystallized from ethanol–ethyl acetate (20: 1) to yield colourless crystals.

Yield 1·75 g (79 per cent); transitions (°C) C 78·0 S$_C$ 86·5 S$_A$ 118·0 N 128·0 I; ^{1}H NMR (CDCl$_3$) δ 0·85–0·95 (6 H, m), 0·95–1·15 (4 H, m), 1·15–1·40 (21 H, m), 1·45 (2 H, quint), 1·75–1·95 (7 H, m), 3·85 (2 H, d), 4·00 (2 H, t), 6·75 (1 H, sext), 6·95 (2 H, d), 7·04 (1 H, sext), 7·41 (2 H, q); IR (KBr) ν_{max} 2960, 2940, 2860, 1605, 1500, 1465, 1295, 1250, 1100, 1070, 1040, 890, 840, 800 cm^{-1}; MS *m*/*z* 528 (M$^+$), 304, 289.

5.13. *Synthesis of 2,3-difluoro-4-(trans-4-heptylcyclohexylmethoxy)-4′-decyloxy-biphenyl* (**21**)

Quantities: compound **15** (1·60 g, 3·97 mmol), compound **18** (1·43 g, 5·14 mmol). The experimental procedure was as described for the preparation of compound **20**. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 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 1·51 g (68 per cent); transitions (°C) C 76·0 S$_C$ 83·0 S$_A$ 116·5 N 122·5 I; ^{1}H NMR (CDCl$_3$) δ 0·85–0·95 (6 H, m), 0·95–1·15 (4 H, m), 1·15–1·40 (25 H, quint), 1·45 (2 H, quint), 1·75–1·95 (7 H, m), 3·85 (2 H, d), 4·00 (2 H, t), 6·75 (1 H, sext), 6·95 (2 H, d), 7·04 (1 H, sext), 7·41 (2 H, q); IR (KCl) ν_{max} 2960, 2940, 2860, 1605, 1500, 1465, 1295, 1250, 1100, 1070, 1040, 890, 840, 800 cm^{-1}; MS *m*/*z* 556 (M$^+$), 531, 491.

5.14. *Synthesis of 2,3-difluoro-4′-octyloxy-4-undecylbiphenyl* (**25**)

Quantities: compound **22** (1·90 g, 6·67 mmol), compound **24** (2·30 g, 7·73 mmol). The experimental procedure was as described for the preparation of compound **20**. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C)-dichloromethane, 10: 1) to give a colourless solid which was recrystallized from ethanol to yield colourless crystals.

Yield 1·42 g (45 per cent); transitions (°C) C 30·5 S_A 37·0 I; ^{1}H NMR ($CDCl_3$) δ 0·90 (6 H, 2xt), 1·30 (24 H, m), 1·45 (2 H, quint), 1·65 (2 H, quint), 1·80 (2 H, quint), 2·65 (2 H, t), 4·00 (2 H, t), 6·94 (1 H, sext), 6·96 (2 H, d), 7·06 (1 H, sext), 7·45 (2 H, q); IR (KBr) ν_{max} 2960, 2940, 2860, 1495, 1465, 1250, 1170, 895, 840, 815 cm^{-1}; MS *m*/*z* 472 (M^+), 360.

5.15. *Synthesis of 4-decyloxy-4′-dodecyloxy-2,3-difluorobiphenyl* (**26**)

Quantities: compound **23** (1·60 g, 4·69 mmol), compound **9** (1·77 g, 5·64 mmol). The experimental procedure was as described for the preparation of compound **25** and produced colourless crystals.

Yield 0·31 g (12 per cent); transitions (°C) C 70·5 (S_C 68·0 S_A 68·0) I; ^{1}H NMR ($CDCl_3$) δ 0·90 (6 H, t), 1·25 (28 H, m), 1·45 (4 H, m), 1·80 (4 H, m), 3·95 (2 H, t), 4·05 (2 H, t), 6·77 (1 H, sext), 6·96 (2 H, d), 7·05 (1 H, sext), 7·42 (2 H, q); IR (KBr) ν_{max} 2960, 2940, 2860, 1510, 1470, 1255, 1080, 895, 840, 805 cm^{-1}; MS *m*/*z* 530 (M^+), 502, 390, 222.

5.16. *Synthesis of 4-(trans-4-pentylcyclohexyl)phenyl triflate* (**28**)

Triflic anhydride (6·50 g, 0·023 mol) was added dropwise to a stirred, cooled (0°C) solution of compound **27** (5·00 g, 0·020 mol) in dry pyridine (80 ml) under dry nitrogen. The mixture was stirred at room temperature overnight and poured into water. The product was extracted into ether (× 2) and the combined ethereal extracts were washed successively with water, 10 per cent hydrochloric acid (× 2), water and brine, and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C)-dichloromethane, 5 : 1) to give a colourless oil.

Yield 7·20 g (95 per cent); ^{1}H NMR ($CDCl_3$) δ 0·90 (3 H, t), 0·90–1·12 (2 H, m), 1·20–1·50 (11 H, m), 1·88 (4 H, d), 2·50 (1 H, t), 7·16 (2 H, d), 7·26 (2 H, d); IR (film) ν_{max} 2960, 2940, 2860, 1510, 1435, 1260, 1220, 1150, 895, 845, 615 cm^{-1}; MS *m*/*z* 378 (M^+), 350, 322, 252.

5.17. *Synthesis of 2,3-difluoro-4-pentyl-4′-(trans-4-pentylcyclohexyl)biphenyl* (**29**)

Quantities: compound **28** (1·20 g, 3·17 mmol), compound **7** (0·94 g, 4·12 mmol), lithium chloride (0·42 g, 9·91 mmol). The experimental procedure was as described for the preparation of compound **20** except that lithium chloride was added with the catalyst. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C)) to give a colourless solid which was recrystallized from ethanol to yield colourless crystals.

Yield 0·82 g (63 per cent); transitions (°C) C 33·0 S_A 96·5 N 123·0 I; ^{1}H NMR ($CDCl_3$) δ 0·90 (6 H, m), 1·00–1·15 (2 H, m), 1·20–1·40 (13 H, m), 1·45–1·55 (2 H, m), 1·65 (2 H, quint), 1·85–2·00 (4 H, m), 2·50 (1 H, m), 2·65 (2 H, t), 6·96 (1 H, sext), 7·08 (1 H, sext), 7·28 (2 H, d), 7·45 (2 H, q); IR (KBr), ν_{max} 2960, 2940, 1460, 890, 810 cm^{-1}; MS *m*/*z* 412 (M^+), 398, 369, 355.

5.18. *Synthesis of 2,3-difluoro-4-decyloxy-4′-(trans-4-pentylcyclohexyl)biphenyl* (**30**)

Quantities: compound **28** (1·50 g, 3·01 mmol), compound **9** (1·15 g, 3·66 mmol), lithium chloride (0·40 g, 9·43 mmol). The experimental procedure was as described for the preparation of compound **29**. The crude product was purified by column chromatography (silica gel/petroleum fraction (b.p. 40–60°C-dichloromethane, 10 : 1) to give a colourless solid which was recrystallized from ethanol–ethyl acetate (5 : 1) to yield colourless crystals.

Yield 0·92 g (61 per cent); transitions (°C) C 52·0 S_C 58·5 S_A 126·5 N 137·0 I; ^{1}H NMR ($CDCl_3$) δ 0·90 (6 H, m), 1·00–1·15 (2 H, m), 1·20–1·40 (21 H, m), 1·45–1·55 (4 H, m), 1·80–2·00 (6 H, m), 2·50 (1 H, m), 4·05 (2 H, t), 6·77 (1 H, sext), 7·07 (1 H, d), 7·43 (2 H, q); IR (KBr) ν_{max} 2960, 2940, 2860, 1640, 1505, 1470, 1300, 1075, 895, 80 cm^{-1}; MS *m/z* 498 (M^+), 358.

The work reported here has been carried out with the support of the Ministry of Defence and is published by permission of the director, HMSO. We express our thanks to our collaborators at DRA (Malvern) and Merck Limited (Poole) and to Dr D. F. Ewing, Mrs B. Worthington, Mr R. Knight, and Mr A. D. Roberts for various spectroscopic measurements.

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