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Russell A. Lewthwaite[a]; John W. Goodby[a]; Kenneth J. Toyne[a]
[a] School of Chemistry, The University, Hull, Yorkshire, England

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The effect of a lateral hydroxy substituent on the thermal stability of the chiral smectic C phase

by RUSSELL A. LEWTHWAITE, JOHN W. GOODBY
and KENNETH J. TOYNE*
School of Chemistry, The University, Hull, Yorkshire HU6 7RX, England

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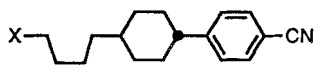
This article describes how the inclusion and positioning of a lateral hydroxy group influences the thermal stability of a chiral smectic C phase. An off-central position of the hydroxy group in the aromatic core has the effect of enhancing the thermal stability of the chiral smectic C phase, whereas a central position of the hydroxy group destabilizes it to the extent that there is no evidence for the phase being present. The results indicate that a hydroxy group *ortho-* to an ester function gives intra- rather than inter-molecular hydrogen bonding. The effects seen with lateral and terminal hydroxy groups are compared with those for analogous fluoro-substituted systems.

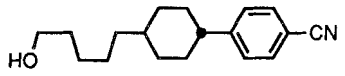
1. Introduction

Some of our recent work on the effects produced by incorporating laterally attached mesogenic moieties in polymers has required the preparation of core units bearing a lateral hydroxy substituent so that a spacer group could be attached to give acrylate, methacrylate and siloxane polymers [1, 2]. Normally, the presence of a lateral group in a core gives a compound with lower transition temperatures than those of the parent compound, but a lateral hydroxy substituent is unusual in that it can lead to increased transition temperatures with the observed effect being dependent on the position of the group in the core of the molecule. The characteristics of the hydroxy group that are responsible for its effects are a combination of small size, polarity, and an ability to hydrogen bond either intramolecularly with a suitable neighbouring unit such as the carbonyl group of an ester or intermolecularly with a polar function in a neighbouring molecule.

An example of how intermolecular association affects transition temperatures is provided by considering substitution by a hydroxy group in the terminal chain of cyanophenylcyclohexane (PCH) systems. Compounds **I** and **III**, compared to the parent C_4H_9 and C_5H_{11} compounds respectively, show a large increase in the thermal



I X = OH C 79·1 N 89·6 I (°C)
II X = F C 42·6 (N 33·7) I
(parent C 41 N 41 I)



III C 91·1 N 103·9 I (°C)
(parent C 31 N 55 I)

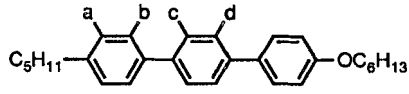
* Author for correspondence.

stability of the nematic phase [3], and this could be attributed to intermolecular hydrogen bonding helping to extend the effective molecular length; the terminal fluoro substituent (compound **II**) has a much smaller effect on transition temperatures. Many other papers have considered the effects of intra- and inter-molecular hydrogen bonding on mesomorphic properties; a recent report compares the effects of terminal OH, Cl and OCH_3 groups [4] and another deals with a lateral OH group *ortho* to a ketonic carbonyl group [5]. Lateral hydroxy substitution is also important for ferroelectric liquid crystals in that a lateral hydroxy group at a central position in the molecular core of a Schiff base was used to generate the first room temperature ferroelectric liquid crystal [6] and lateral hydroxy substituents which hydrogen bond to a terminal carbonyl group can give ferroelectric liquid crystals with large spontaneous polarizations [7–9].

Several theories have been proposed to explain the formation of a smectic C phase, most notably those of McMillan [10] van der Meer and Vertogen [11] and Goodby *et al.* [12], and polar effects are recognized as being important in enhancing molecular tilt. McMillan suggests that large terminal dipoles are needed (for example, from alkoxy groups) for the formation of the smectic C phase, and these dipoles align and stop the rotation of the molecules, and so create a torque parallel to the layer planes, which results in the molecules being tilted within the layer. van der Meer and Vertogen suggest that a permanent dipole in one molecule induces a dipole in a neighbouring mesogen; the positioning of the permanent dipole in the mesogen is important in determining the contribution of the anisotropic part of the induction forces, and they conclude that an acentral dipole is superior in this respect. The permanent and induced dipoles create the forces needed for tilting the mesogens within the layers, and no restriction of the rotation of the mesogens is required. Goodby *et al.*, showed that the terminal dipoles were not essential for the formation of the smectic C phase but their inclusion within a mesogen which exhibits a smectic C phase favourably affects the thermal stability of the phase.

Compound **IV**, shown in table 1, with only one strongly dipolar region arising from the oxygen of the hexyloxy group, exhibits smectic A and B phases, but the effects on the thermal stabilities of these mesophases are extremely varied when one or two dipolar fluoro substituents are introduced [13]. The fluoro substituent at position *a* (compound **V**) depresses the clearing point of the smectic A phase by only 18·5°C; at position (*b*) (compound **VI**) the clearing temperature is depressed by 62·0°C and the

Table 1. The effect of fluoro-substituents on a mesomorphic terphenyl.

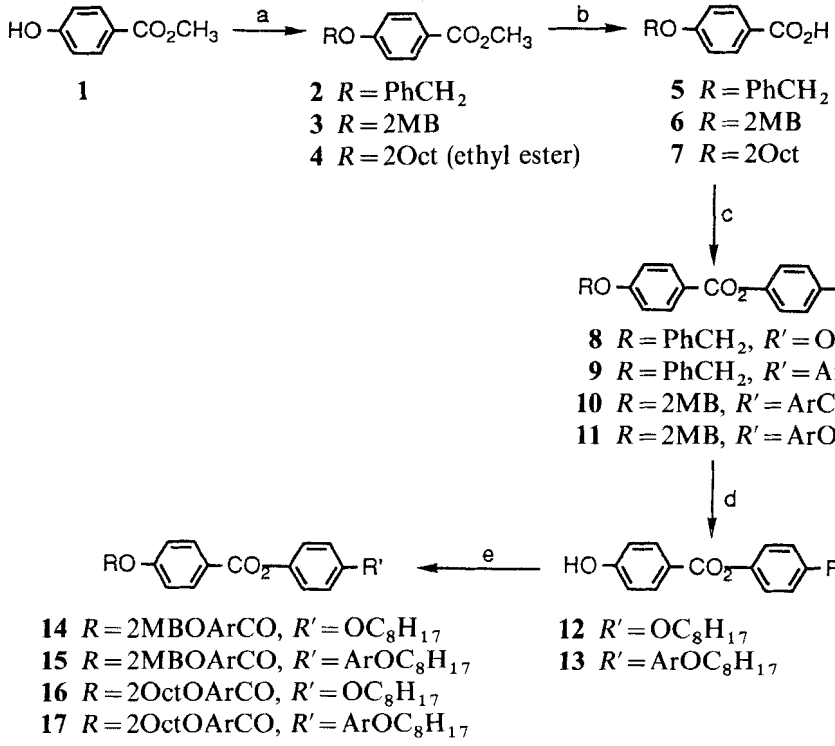


Compound	*a*	*b*	*c*	*d*	Transition temperatures/(°C) [13]
IV	H	H	H	H	C 205·0 S_B 216·0 S_A 228·5 I
V	F	H	H	H	G 176·0 S_A 210·0 I
VI	H	F	H	H	C 115·0 S_C 131·5 N 166·5 I
VII	H	H	F	H	C 70·0 G 78·0 S_B 92·0 S_I 93·0 S_C 118·0 S_A 155·0 N 166·5 I
VIII	F	F	H	H	C 101·5 S_C 156·5 S_A 167·0 N 171·5 I
IX	H	H	F	F	C 54·0 S_C 67·0 N 149·0 I

mesophase of highest thermal stability is the nematic phase, with an underlying smectic C phase. Compound **VII** shows that positioning the fluoro substituent at position (*c*) has a similar effect on the clearing point to that with fluoro at position (*b*), but many additional changes occur in the smectic behaviour and the smectic C phase is less thermally stable. Of the three mono-fluoro compounds, compound **VI** shows the highest smectic C character but when two fluoro substituents are used in positions (*a*) and (*b*) to give compound **VIII**, then the resultant dipole moment is increased and the stability of the smectic C phase is increased to 156·5°C, which is 25·0°C higher than the value for mono fluoro substitution at position (*b*) alone. Such examples show that the nature and stability of smectic phases are extremely sensitive to the position of dipolar substituents within a molecular core. The purpose of this report is to demonstrate how the mesogenicity of a parent system, and particularly the tendency for chiral smectic C and cholesteric phases, is affected by introducing a lateral hydroxy substituent at different points in the core.

2. Synthesis

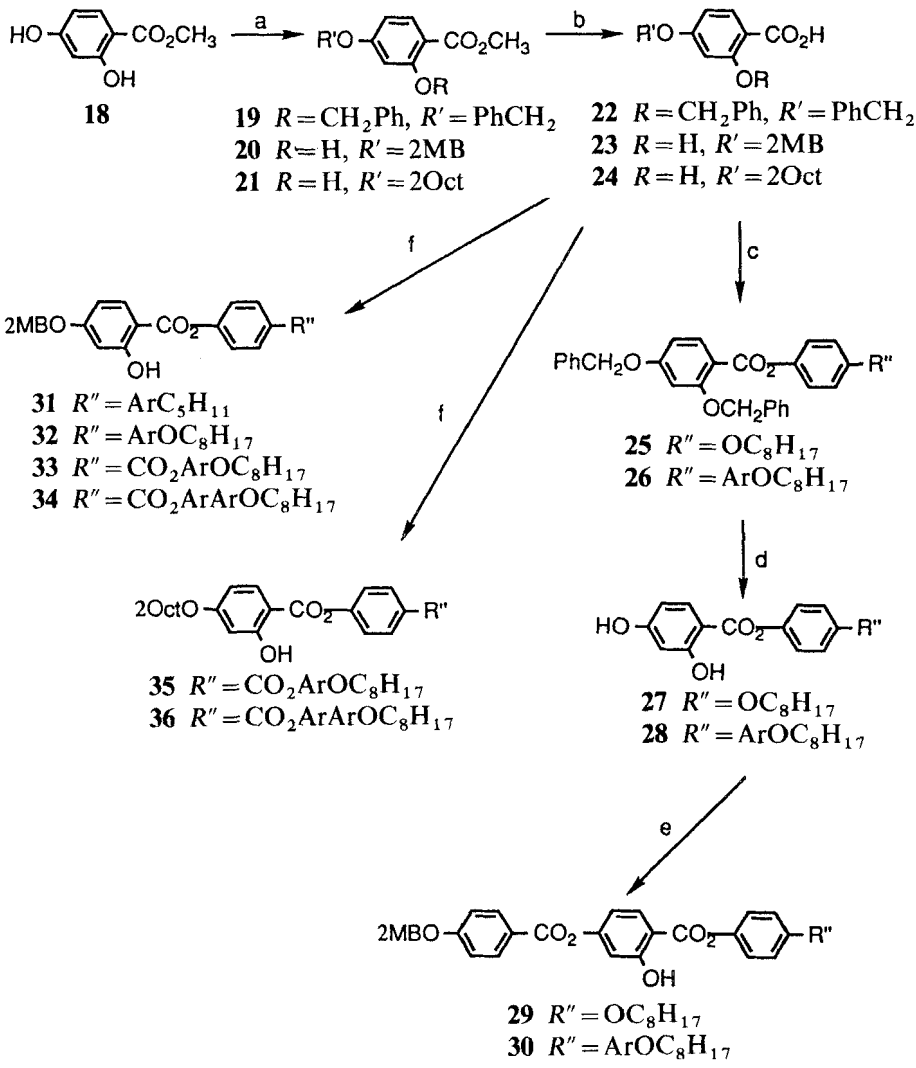
The synthesis of the parent system is shown in scheme 1 and the reactions used are conventional etherification and esterification reactions. The routes to the lateral



a, *R*Br or *R*OTs, K_2CO_3, $C_2H_5COCH_3$
b, (*i*) NaOH, CH_3OH/H_2O, (*ii*) H^+
c, *R'*ArOH, DCC, 4PP, CH_2Cl_2 or THF
d, H_2, Pd-C, $CH_3CO_2C_2H_5$ or 1,4-dioxan
e, *R*OArCO$_2$H, DCC, 4PP, CH_2Cl_2 or THF

Scheme 1.

hydroxy compounds, given in scheme 2, are less straightforward and some of the synthetic problems have been discussed previously [1, 2]. Etherification and esterification of 2,4-dihydroxybenzoates (**18**, **27** and **28**) occurred mainly at the 4-hydroxy group and esterification of the 2-hydroxybenzoic acid derivatives (**23** and **24**) with phenols using *N*,*N*′-dicyclohexylcarbodiimide (DCC) gave variable yields of esters (**31**–**36**), possibly because of reduced reactivity of the acid group caused by the presence of the 2-hydroxy substituent.



a, *R*′Br or *R*′OTs, K_2CO_3, $C_2H_5COCH_3$
b, (*i*) NaOH, CH_3OH/H_2O, (*ii*) H^+
c, *R*″ArOH, DCC, 4PP, CH_2Cl_2 or THF
d, H_2, Pd-C, $CH_3CO_2C_2H_5$ or 1,4-dioxan
e, 2MBOArCO$_2$H, DCC, 4PP, CH_2Cl_2 or THF
f, *R*″ArOH, DCC, 4PP, CH_2Cl_2 or THF

Scheme 2.

3. Results and discussion

3.1. *Non-laterally substituted mesogens (parent compounds, see table 2)*

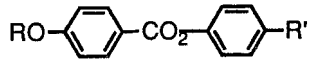
Modifying the structure of compound **10** to give compound **11** by changing from an alkyl to an alkoxy terminal group has the effect of increasing the thermal stability of the cholesteric phase by about 13°C. This small effect is typical of the increase in clearing points caused by such a structural change in a three-ring system and is attributed to the extra polarizability allowed by the alkoxy group. The structural change also causes two other effects; compound **11** has an increased melting point and a monotropic chiral smectic C phase is created, which confirms that the incorporation of terminal, outboard lateral dipoles, as provided by the two alkoxy groups, is an important way of promoting smectic C character [10].

The splitting of the biphenyl moiety of compound **11** by including another ester linking group in the structure to give compound **14** has given a compound with similar phases; the clearing point from the cholesteric phase is only changed slightly, but the thermal stability of the monotropic chiral smectic C phase is depressed by almost 50°C and this is compatible with the additional polar ester group in the middle of the core being a disadvantage for smectic C stability but having little effect on nematic (cholesteric) stability. Comparison of the values for compounds **14** and **15** shows once again that increasing the length of the molecular core increases transition temperatures quite substantially and comparison of values for compound **16** with those for **14** provides a further case showing that with the branching point in the terminal chain closer to the molecular core (as with the 2-octyloxy group in **16**), a compound of reduced mesogenicity is obtained. The comparison of **17** with **15** leads to similar observation for the Ch–I transition values, but the closeness of the values for the S_C^*–Ch transitions in these compounds is surprising since smectic C tendencies in compound **17** might have been expected to be lower because of the chiral centre being closer to the core and the alkyl group of the terminal ester being longer [14].

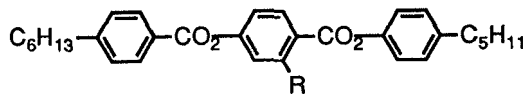
3.2. *Compounds with a centrally positioned, lateral hydroxy group (see table 3)*

Several investigations have been made of the effect on mesophase type and their transition temperatures of lateral substitution in systems with various types of core unit [15–21]. The effect of a lateral substituent near the centre of a core, similar to that shown in table 3, is illustrated by the transition temperatures shown for compounds **X** to **XII**. The methyl and chloro lateral groups have the effect of decreasing the clearing temperature (i.e. the stability of the nematic phase) of the 'parent' compound **X**, by about 55–60°C and this reduction, which is independent of the polarity of the

Table 2. Transition temperatures for the 'parent' mesogens.



Compound	*R*	*R'*	Transition temperatures/(°C)
10	2MB	ArC_5H_{11}	C 95·8 Ch 161·3 I
11	2MB	$ArOC_8H_{17}$	C 136·5 (S_C^* 128·8) Ch 174·0 I
14	2MB	$CO_2ArOC_8H_{17}$	C 95·0 (S_C^* 79·6) Ch 171·8 I
15	2MB	$CO_2ArArOC_8H_{17}$	C 144·0 S_C^* 156·3 Ch 285·6 I
16	2Oct	$CO_2ArOC_8H_{17}$	C 80·3 Ch 90·7 I
17	2Oct	$CO_2ArArOC_8H_{17}$	C 100·6 S_C^* 146·9 Ch 222·7 I



X, R=H, C 74 S 78 N 169 I (°C) [22, 23]
XI, R=CH_3, C 49 N 111 I (°C) [22]
XII, R=Cl, C 40 N 113 I (°C) [23]

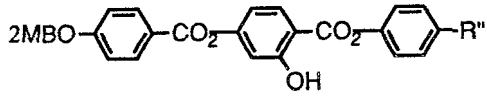
substituent, is attributed primarily to the substituent's steric effect. Although nematic stability is reduced quite substantially by lateral substitution, the stability of the smectic phase is usually affected to an even greater extent.

The transition temperatures for compounds **29** and **30** show the effect of lateral hydroxy groups at a central position in a dialkoxy core analogous to the dialkyl core of compounds **X**–**XII** and these values are related to those for parent compounds **14** and **15** respectively. Only a cholesteric phase is seen for compounds **29** and **30**, although they both have relatively low melting points, and there is a complete lack of smectic character, even in the case of the four-ring system **30**, whose parent compound **15** showed a chiral smectic C phase. For compound **30** there has been a remarkable suppression of smectic C character on introducing the lateral hydroxy substituent; the cholesteric character of the parent compound, **15**, has been decreased by 45°C, but the smectic character has been depressed by more than 150°C (compound **30** supercools as a cholesteric phase to 53·9°C before crystallizing). Similar effects are seen with monofluorination in the centre ring of a terphenyl (for example, compare **XIII** and **XIV**), where the small substituent has a huge effect on melting point and smectic phase stabilities and yet has a less pronounced effect on the nematic clearing temperature [24].

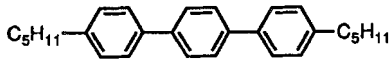
The comparison between diester systems such as **X**–**XII** and terphenyls obviously involves very different core units with dipolar groups in one case (diesters) and in the other (terphenyls) non-polar cores with positions at which substitution leads to twisting of phenyl to biphenyl links and a consequential diminution of conjugation and polarizability. The situation is also reminiscent of the effects seen for *ortho*-difluoro substituents in the centre ring of terphenyls where twisting about both inter-annular bonds occurs. An example is given in table 1 which shows how difluoro substitution in an end ring (compound **VIII**) gives a smectic C phase, but the same type of difluoro substitution in the middle of a core (**IX**) is not so conducive to smectic C character. Comparison of compounds **XV** and **XVI** shows similar effects in dialkylterphenyls.

For all three cases of fluoro, difluoro and hydroxy substituents, it appears that any steric or dipolar influence at the centre of a core does not help to induce molecular tilt or encourage a smectic C phase, but severely disrupts the smectic packing without

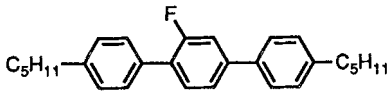
Table 3. The transition temperatures for compounds with a centrally positioned, lateral hydroxy group.



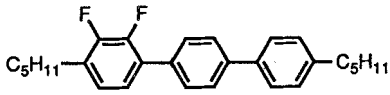
Compound	R''	Transition temperatures/(°C)
29	OC_8H_{17}	C 71·5 Ch 122·5 I
30	$ArOC_8H_{17}$	C_1 65·2 C_2 86·5 Ch 240·6 I



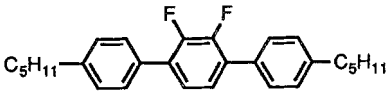
XIII C 192·0 S_A 213·0 I (°C)



XIV C 51·5 S_B 62·0 S_A 109·5 N 136·5 I (°C)



XV C 81·0 S_C 115·5 S_A 131·5 N 142·0 I (°C)



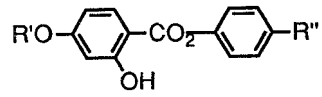
XVI C 60·0 N 120 I (°C)

having such a serious effect on the nematic phase. In contrast the terminal phenolic hydroxy compounds **12** and **13**, with intermolecular hydrogen bonding and non-linear associations, have raised melting points with respect to their 4-substituted 'parent' compounds **8** and **9** (see experimental section) and the terminal alcoholic hydroxy substituent also raises melting points (see compounds **I** and **III** [3]). The lateral hydroxy substituent in compounds **29** and **30** obviously has a different effect on the molecular associations within the mesophase from that of the terminal hydroxy substituent. The effect does not appear to be compatible with intermolecular hydrogen bonding, which one would expect to increase smectic stability, but is much more likely to arise from intramolecular hydrogen bonding of the hydroxy group with the carbonyl oxygen of the adjacent ester group (for example, see figure 1 (*b*) and related comments below).

3.3. *Compounds with an off-centre, lateral hydroxy group (see table 4)*

The effect on transition temperatures caused by the introduction of an off-centre, lateral hydroxy group into the 'parent' mesogens is illustrated by the values given in table 4 where the substituent is in the end ring of each of the various core systems. For all of the compounds in table 4, the lateral hydroxy group has led to reduced melting points (compounds **31**–**36** in table 4 are related respectively to the parent compounds **10**, **11** and **14**–**17** in table 2) and reduced clearing temperatures, but in all cases the smectic C and cholesteric phases in the parent compounds are still present. Compound **31** is particularly interesting because without the hydroxy substituent, (compound **10**) only a cholesteric phase is seen, but with the lateral hydroxy substituent present, depression of the melting point has revealed some interesting underlying mesophases. On cooling compound **31** from the isotropic liquid, a cholesteric phase is produced which undergoes a transition to a helical smectic A phase, before becoming a non-helical smectic A phase. The helical smectic A phase is a TGB smectic A* phase and has spiral ordering of the molecules within the molecular layers, and gives a texture with filaments when viewed by polarizing microscopy. This texture indicates that the phase has long range order, and not the short range order shown by a cholesteric phase [25]. The smectic A phase then gives a disordered crystal E* phase which has another crystal phase (unidentified) below it. For all of the compounds shown in table 4 the hydroxy substituent has caused a greater depression of the cholesteric clearing point than of the smectic C stability, i.e. relative to the cholesteric phase, the stability of the smectic C phase has been enhanced. This is a very different situation to that observed for hydroxy substitution in the centre of a core [see § 3.2.], where smectic character is much more

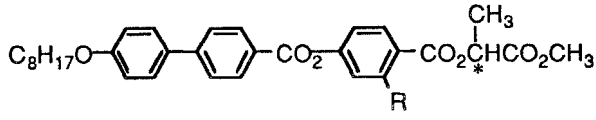
Table 4. The transition temperatures for compounds with an off-centre, lateral hydroxy group. S_1 denotes an unidentified smectic crystal phase.



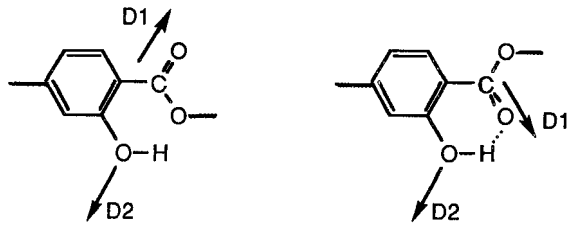
Compound	*R'*	*R''*	Transition temperatures/(°C)
31	2MB	ArC_5H_{11}	S_1 ~ 12 E* 36·0 S_A^* 49·8 TGB A* 50·2 Ch 134·5 I
32	2MB	$ArOC_8H_{17}$	C 72·9 S_C^* 96·2 Ch 129·2 I
33	2MB	$CO_2ArOC_8H_{17}$	C 62·0 S_C^* 68·8 Ch 141·8 I
34	2MB	$CO_2ArArOC_8H_{17}$	C 109·1 S_C^* 157·3 Ch 243·6 I
35	2Oct	$CO_2ArOC_8H_{17}$	C 63·1 Ch 89·6 I
36	2Oct	$CO_2ArArOC_8H_{17}$	C 73·3 S_C^* 141·7 Ch 187·3 I

severely affected than is the nematic. Once again, this result is in keeping with the effects seen for difluoro substitution in the end ring of a terphenyl (see compound **XV**, and compound **VIII** in table 1). The effect of the hydroxy substituent on the smectic C stability in the three-ring compounds **11** and **14** is to lower the transitions by 32·6 and 10·8°C, respectively, but for the four-ring compounds **15** and **17** the effect is an *increase* of 1·0 and a decrease of only 5·2°C, respectively. With the four-ring systems, there is the approximate 100°C rise associated with the introduction of an extra aromatic ring, but the lateral hydroxy group in the end ring, placed more towards one side of the molecule, has a more favourable effect on smectic C character and this is compatible with the creation of a tendency for a tilt in a longer molecule to give a relative enhancement of smectic C behaviour.

The effects of lateral hydroxy groups have been noticed previously in materials prepared for ferroelectric applications in which hydrogen bonding from the hydroxy substituent was being considered as a way of restricting rotation about the chiral centre [26]. Both compounds **XVII** and **XVIII** show chiral smectic C phases, but the incorporation of the lateral hydroxy group near the terminal ester function has caused the stability of the chiral smectic C phase to be depressed significantly (34°C); this is similar to the situation revealed for compound **32**, although the compounds differ in that the hydroxy group in **32** points inwards to an ester group, whereas that in **XVIII** points towards an ester group in a terminal chain. However, an important effect noted [26] is that the lateral hydroxy group in **XVIII** has the effect of increasing the spontaneous polarization of the material quite considerably. This is because the β-hydroxy ester unit has two dipoles ($D1$ and $D2$) associated with it; one arises from the hydroxy function itself and the other from the carbonyl group of the ester. In figure 1 (*a*) the two dipoles are opposed and give only a small resultant dipole. In figure 1 (*b*) the carbonyl and the hydroxy groups are shown forming a six-membered, hydrogen-bonded ring, and this has the effect of suppressing the intra-molecular rotation of the



XVII, *R* = H, C 68 S_C^* 120 S_A 172 I (°C)
XVIII, *R* = OH, C 28 S_C^* 86 S_A 141 I (°C)



(*a*) (*b*)

Figure 1. The two dipoles of the β-hydroxy carbonyl group.

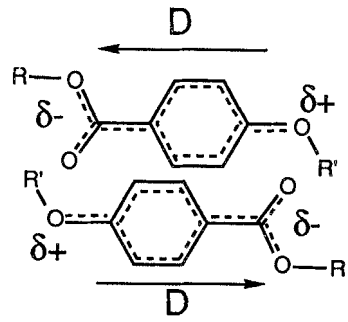


Figure 2. The dipole–dipole, anti-parallel interactive packing.

carbonyl group which carries the neighbouring chiral centre. The hydrogen bonded form gives a greater resultant dipole moment and also the formation of the ring promotes a compact molecular arrangement in the smectic layer. This molecular arrangement hinders a dipole–dipole, anti-parallel interactive packing of molecules shown in figure 2, and so suppresses the ordered phases often seen in such compounds and gives less ordered smectic phases [27]. The closely-packed six-membered, hydrogen-bonded ring compounds are broader than the non-hydroxy substituted compounds, even though the hydroxy group is small, and so they give rise to less ordered phases because of their decreased lateral molecular associations.

3.4. *Laterally attached alkoxy compounds*

For all of the lateral hydroxy compounds reported here, conversion of the hydroxy group into an alkoxy group (for example, the pent-5-enyloxy [1, 2]) gives compounds without any chiral smectic C character. Whether the hydroxy group is in a central or off-centre position, the isotropisation temperatures of the cholesteric phases are dramatically reduced by about 100°C, and in some cases the alkoxy compounds are not mesomorphic.

4. Conclusions

The temperature of the chiral smectic C to cholesteric transition in compounds **34** and **36** is much less influenced by the hydroxy substituent than is the cholesteric to isotropic transition. The lateral hydroxy group decreases the clearing temperature by broadening the molecules (and hence reduces the ordering within the mesophase), but the smectic phase appears to be more dependent for its stability on the major part of the mesogenic core and the two terminal alkoxy groups, than on the lateral hydroxy group which is positioned to one side of the core unit.

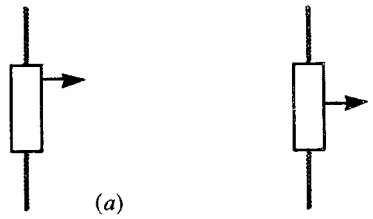


Figure 3. The dipoles associated with the positioning of the lateral hydroxy group.

The discussion given previously has largely drawn a comparison between the values for the hydroxy substituted compounds and those for their parent systems. An alternative approach is to highlight the effect of moving the hydroxy group to a new position within the same core. In this comparison the compounds with the hydroxy substituent at one side of the molecule, compounds **33** and **34**, should be compared with those with the hydroxy group in the middle of the same core, compounds **29** and **30**, respectively. Neither of the latter compounds shows a smectic phase but the former compounds both show chiral smectic C phases with the phase in compound **34** being enhanced by more than 100°C relative to that in compound **30**, which supercools to 53·9°C as a cholesteric phase. It is therefore clear that the positioning of the lateral hydroxy group has a pronounced effect on the thermal stability of the chiral smectic C phase; this observation can be rationalised partly on the basis of the steric effect of the lateral group being more acceptable towards one end of the molecule, and partly on the basis of the dipoles associated with the lateral hydroxy groups having different effects on the mesogens when molecules are aligned within this phase. The off-central positioning of the lateral hydroxy group, see figure 3 (*a*), and the associated dipole which arises as shown in figure 1 (*b*), are more favourable for the formation of a tilted chiral smectic C phase than is the central positioning of the hydroxy group (see figure 3 (*b*)).

5. Experimental

Infrared spectra were produced using a Perkin–Elmer 783 spectrometer, ^{1}H NMR spectra using a JEOL JNM-GX270 FT NMR with $CDCl_3$ as solvent and TMS as an internal reference, and mass spectra using a Finnigan 1020 Automated GC/MS. Optical rotations were measured using a ETL-NPL automatic polarimeter control unit Type 143A, differential scanning calorimetry was carried out using a Perkin–Elmer DSC 7, with TAC 7/PC instrument cooler and controlled cooling accessory, and optical microscopy was carried out using an Olympus BH-2 polarizing microscope in conjunction with a Mettler FP 52 hot stage and Mettler FP 5 temperature control unit. Compounds were purified, where specified, by flash chromatography using silica gel (200–400 mesh) and their purities were checked by HPLC analysis (Microsorb C18 80-215-C5 RP column); all compounds were >99 per cent pure. The following are abbreviations used in this paper; petrol fraction, bp 40–60°C (petrol); tetrahydrofuran (THF); *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-(*N*-pyrrolidino)pyridine (4PP); 2-methylbutyl (2MB); 2-octyl (2Oct); 1,4-disubstituted-benzene (Ar).

4-Octyloxyphenol, 4-hydroxy-4′-octyloxybiphenyl, compounds **3**, **6**, **19**, **22** and **25**–**30** were prepared as described in [1]. Compounds **2**, **5**, **9**, **13** and **20** were prepared as described in [2]; (*S*)-2-methylbutyl toluene-4-sulphonate and (*R*)-2-octyl toluene-4-sulphonate were prepared using the procedure given in reference [28].

5.1. *(R)-Ethyl 4-(2-octyloxy)benzoate* (**4**)

The reaction was carried out using ethyl 4-hydroxybenzoate and (*R*)-2-octyl toluene-4-sulphonate by following the procedure described for the preparation of compounds **2**. Yield 0·51 g (98 per cent). MS (*m/z*) 278 (M^+), 233, 166, 138, 121, 43 (100 per cent); IR ν_{max}/cm^{-1} 2930, 2860, 1710, 1605, 1575, 1505, 1460, 1250, 1170, 1100, 1020, 850; ^1H NMR δ 0·87 (3 H, t, CH_3), 1·30–1·75 (16 H, m, 2x CH_3, 5x CH_2), 3·90 (2 H, q, CH_2O), 4·45 (1 H, m, CHO), 6·90 (2 H, d, arom), 8·00 (2 H, d, arom).

5.2. *(R)-4-(2-Octyloxy)benzoic acid* (**7**)

The reaction was carried out using compound **3** by following the procedure described for the preparation of compound **5**. Yield 0·24 g (52 per cent). mp 64·5–66°C. MS (*m/z*) 250 (M^+), 138, 120, 42 (100 per cent); IR ν_{max}/cm^{-1} 3400–2400, 2920, 2860, 1675, 1600, 1570, 1510, 1465, 1255, 1015, 845; ^1H NMR δ 0·87 (3 H, t, CH_3), 1·30–1·75 (13 H, m, CH_3, 5x CH_2), 4·45 (1 H, m, CHO), 6·87 (2 H, d, arom), 8·05 (2 H, d, arom).

5.3. *4-Octyloxyphenyl 4-benzyloxybenzoate* (**8**)

A mixture of compound **5** (3·50 g, 15·3 mmol), 4-octyloxyphenol (3·41 g, 15·3 mmol), DCC (3·79 g, 18·0 mmol), and 4PP (0·57 g, 3·8 mmol) was stirred overnight in dry dichloromethane (50 ml) with the exclusion of moisture. The solvent was removed and the residue was purified by chromatography (dichloromethane) and then recrystallised (petrol and a small amount of toluene) to leave white crystals. Yield 5·54 g (84 per cent). Transitions (°C) C 125·6 (N 104·4) I. MS (*m/z*) 432 (M^+), 341, 211, 120, 91 (100 per cent); IR ν_{max}/cm^{-1} 3070, 2930, 2860, 1730, 1610, 1585, 1515, 1460, 1260, 1250, 1080, 860; ^1H NMR δ 0·90 (3 H, t, CH_3), 1·30–155 (10 H, m, 5x CH_2), 1·83 (2 H, m, CH_2), 4·00 (2 H, t, CH_2O), 5·20 (2 H, s, CH_2O), 6·93 (2 H, d, arom), 7·08 (4 H, m, arom), 7·40 (5 H, m, Ph), 8·15 (2 H, d, arom)

5.4. *(S)-4′-Pentylbiphenyl-4-yl 4-(2-methylbutyloxy)benzoate* (**10**)

The reaction was carried out using compound **6** and 4-hydroxy-4′-pentylbiphenyl by following the procedure described for the preparation of compound **8**: Yield 0·14 g (33 per cent). Transitions (°C) C 95·8 Ch 161·3 I. $[\alpha]_D = +6·6°$ at 21°C; MS (*m/z*) 430 (M^+), 359, 239, 191 (100 per cent), 120. IR ν_{max}/cm^{-1} 2980, 2870, 1730, 1605, 1580, 1510, 1495, 1465, 1260, 1165, 1080, 845; ^1H NMR δ 0·95 (9 H, m, 3x CH_3), 1·35–1·65 (8 H, m, 4x, CH_2), 1·90 (1 H, m, CH), 2·63 (2 H, t, CH_2), 3·85 (2 H, octet, CH_2O), 6·98 (2 H, d, arom), 7·28 (4 H, 2x d, arom), 7·50 (2 H, d, arom), 7·63 (2 H, d, arom), 8·18 (4 H, 2x d, arom).

5.5. *(S)-4′-Octyloxybiphenyl-4-yl 4-(2-methylbutyloxy)benzoate* (**11**)

The reaction was carried out using compound **6** and 4-hydroxy-4′-octyloxybiphenyl by following the procedure described for the preparation of compound **8**: Yield 0·30 g (59 per cent). Transitions (°C) C 136·5 (S_C^* 128·8) Ch 174·0 I. $[\alpha]_D = +6·6°$ at 21°C. MS (*m/z*) 488 (M^+), 418, 296, 191 (100 per cent), 120; IR ν_{max}/cm^{-1} 3040, 2980, 2860, 1730, 1605, 1580, 1510, 1495, 1470, 1255, 1215, 1165, 1175, 840, 805; ^1H NMR δ 1·05 (9 H, m, 3x CH_3), 1·33–1·83 (12 H, m, 6x CH_2), 1·93 (3 H, m, CH_2, CH), 3·85 (2 H, octet, CH_2O), 4·00 (2 H, t, CH_2O), 7·00 (4 H, 2x d, arom), 7·25 (2 H, d, arom), 7·53 (4 H, 2x d, arom), 8·18 (2 H, d, arom).

5.6. *4-Octyloxyphenyl 4-hydroxybenzoate* (**12**)

Compound **8** (5·54 g, 12·8 mmol), dissolved in ethyl acetate (75 ml) with 10 per cent palladium-on-carbon catalyst (0·5 g), was stirred under a hydrogen atmosphere until completion of reaction. The mixture was filtered through 'Hyflo Supercel' and the solvent was removed. The product was recrystallized (toluene and a small amount of petrol) to leave fine, white needles. Yield 4·01 g (91 per cent). m.p. 152–155°C. MS (*m/z*) 342 (M^+), 222, 121 (100 per cent), 110; IR ν_{max}/cm^{-1} 3400, 2980, 2860, 1705, 1610, 1590, 1515, 1470, 1280, 1250, 1190, 1160, 1085, 860; ^1H NMR δ 0·90 (3 H, t, CH_3), 1·33–1·48 (10 H, m, 5x CH_2), 1·80 (2 H, m, CH_2), 3·95 (2 H, t, CH_2O), 5·35 (1 H, s, OH), 6·88 (4 H, m, arom), 7·10 (2 H, d, arom), 8·10 (2 H, d, arom).

5.7. *(S)-4-Octyloxyphenyl 4-[4-(2-methylbutyloxy)benzoyloxy]benzoate* (**14**)

The reaction was carried out using compound **6** and compound **12** by following the procedure described for the preparation of compound **8**: Yield 0·39 g (74 per cent). Transitions (°C) C 95·0 (S_C^* 79·6) Ch 171·8 I. $[\alpha]_D = +3·8°$ at 21°C. MS (*m/z*) 532 (M^+), 311, 221, 190 (100 per cent), 120; IR ν_{max}/cm^{-1} 3070, 2960–2860, 1740, 1730, 1605, 1580, 1510, 1470, 1260, 1250, 1190, 1165, 1060, 845; ^1H NMR δ 1·00 (9 H, m, 3x CH_3), 1·33–1·58 (12 H, m, 6x CH_2), 1·80–1·90 (3 H, m, CH_2, CH), 3·88 (2 H, octet, CH_2O), 3·98 (2 H, t, CH_2O), 6·95 (4 H, m, arom), 7·13 (2 H, d, arom), 7·38 (2 H, d, arom), 8·13 (2 H, d, arom), 8·25 (2 H, d, arom).

5.8. *(S)-4'-Octyloxybiphenyl-4-yl 4-[4-(2-methylbutyloxy)benzoyloxy]benzoate* (**15**)

The reaction was carried out using compound **6** and compound **13** by following the procedure described for the preparation of compound **8**: Yield 0·17 g (28 per cent). Transition (°C) C 144·0 S_C^* 156·3 Ch 285·6 I. $[\alpha]_D = +4·2°$ at 21°C. MS (*m/z*) 608 (M^+), 417, 311, 297, 191, 121 (100 per cent); IR ν_{max}/cm^{-1} 3080, 2980–2860, 1740, 1600, 1580, 1500, 1465, 1265, 1165, 1065, 840; ^1H NMR δ 0·95 (9 H, m, 3x CH_3), 1·33–1·58 (12 H, m, 6x CH_2), 1·83 (3 H, m, CH_2, CH), 3·85 (2 H, octet, CH_2O), 4·00 (2 H, t, CH_2O), 6·95 (4 H, 2x d, arom), 7·25 (2 H, d, arom), 7·38 (2 H, d, arom), 7·50 (2 H, d, arom), 7·60 (2 H, d, arom), 8·15 (2 H, d, arom), 8·30 (2 H, d, arom).

5.9. *(R)-4-Octyloxyphenyl 4-[4-(2-octyloxy)benzoyloxy]benzoate* (**16**)

The reaction was carried out using compound **7** and compound **12** by following the procedure described for the preparation of compound **8**: Yield 0·90 g (39 per cent). Transitions (°C) C 80·3 Ch 90·7 I. MS (*m/z*) 574 (M^+), 353, 233, 221, 121 (100 per cent); IR ν_{max}/cm^{-1} 2930, 2850, 1735, 1600, 1505, 1465, 1245, 1195, 1160, 1000, 850; ^1H NMR δ 0·90 (6 H, 2x t, 2x CH_3), 1·35–1·60 (21 H, m, CH_3, 9x CH_2), 1·80 (4 H, m, 2x CH_2), 3·95 (2 H, t, CH_2O), 4·45 (1 H, m, CHO), 6·95 (4 H, 2x d, arom), 7·13 (2 H, d, arom), 7·35 (2 H, d, arom), 8·13 (2 H, d, arom), 8·28 (2 H, d, arom).

5.10. *(R)-4'-Octyloxybiphenyl-4-yl 4-[4-(2-octyloxy)benzoyloxy]benzoate* (**17**)

The reaction was carried out using compound **7** and compound **13** by following the procedure described for the preparation of compound **8**: Yield 0·11 g (31 per cent). Transitions (°C) C 100·6 S_C^* 146·9 Ch 222·7 I. MS (*m/z*) 650 (M^+), 353, 298, 233, 121 (100 per cent); IR ν_{max}/cm^{-1} 2940, 2850, 1740, 1605, 1500, 1465, 1270, 1250, 1205, 1165, 1170, 830; ^1H NMR δ 0·87 (6 H, 2x t, 2x CH_3), 1·30–1·60 (21 H, m, CH_3, 9x CH_2), 1·80 (4 H, m, 2x CH_2), 4·00 (2 H, t, CH_2O), 4·50 (1 H, m, CHO), 6·95 (4 H, 2x d, arom), 7·23 (2 H, d, arom), 7·38 (2 H, d, arom), 7·50 (2 H, d, arom), 7·60 (2 H, d, arom), 8·15 (2 H, d, arom), 8·30 (2 H, d, arom).

5.11. *(S)-Methyl 2-hydroxy-4-(2-methylbutyloxy)benzoate* (**20**)

The reaction was carried out using compound **18** and (*S*)-2-methylbutyl toluene-4-sulphonate by following the procedure described for the preparation of compound **2**: Yield (80 per cent)—oil. MS (*m/z*) 238 (M^+), 224, 168, 136 (100 per cent); IR ν_{max}/cm^{-1} 3180, 3040, 2960, 2880, 1740, 1650, 1570, 1510, 1440, 1350, 1260, 1225, 1190, 1140, 1100, 1030, 855, 840; ^1H NMR δ 1·00 (6 H, d, t, 2x CH_3), 1·25 (1 H, m, CH), 1·55–1·85 (2 H, m, 2x CH), 3·78 (2 H, octet, CH_2O), 3·90 (3 H, s, CH_3O), 6·40 (2 H, m, arom), 7·70 (1 H, d, arom), 10·95 (1 H, s, OH).

5.12. *(R)-Methyl 2-hydroxy-4-(2-octyloxy)benzoate* (**21**)

The reaction was carried out using compound **18** and (*R*)-2-octyl toluene-4-sulphonate by following the procedure described for the preparation of compound **2**: Yield 6·58 g (64 per cent)—oil. MS (*m/z*) 280 (M^+), 249, 168 (100 per cent), 136, 43; IR ν_{max}/cm^{-1} 3260, 2930, 2860, 1670, 1620, 1500, 1440, 1255, 1195, 1090, 890, 830; ^1H NMR δ 0·87 (3 H, t, CH_3), 1·25–1·75 (13 H, m, CH_3, 5x CH_2), 3·87 (3 H, s, CH_3O), 4·40 (1 H, m, CHO), 6·43 (2 H, m, arom), 7·70 (1 H, m, arom), 10·95 (1 H, s, OH).

5.13. *(S)-2-Hydroxy-4-(2-methylbutyloxy)benzoic acid* (**23**)

The reaction was carried out using compound **20** by following the procedure described for the preparation of compound **5**: Yield 2·16 g (57 per cent). m.p. 123–124·5°C. MS (*m/z*) 224 (M^+), 136, 69 (100 per cent); IR ν_{max}/cm^{-1} 3300–2300, 3090, 2980, 2880, 1660, 1630, 1580, 1505, 1460, 1440, 1390, 1250, 1200, 1150, 1030, 930, 880, 860, 800; ^1H NMR δ 1·00 (6 H, d, t, 2x CH_3), 1·30 (1 H, m, CH), 1·55 (1 H, m, CH), 1·85 (1 H, m, CH), 3·80 (2 H, octet, CH_2O), 6·45 (2 H, m, arom), 7·80 (2 H, d, arom), 10·58 (1 H, s, OH).

5.14. *(R)-2-Hydroxy-4-(2-octyloxy)benzoic acid* (**24**)

The reaction was carried out using compound **21** by following the procedure described for the preparation of compound **5**: Yield 0·25 g (86 per cent)—waxy solid. MS (*m/z*) 266 (M^+), 154, 136, 43 (100 per cent); ^1H NMR δ 0·87 (3 H, t, CH_3), 1·28–1·75 (13 H, m, CH_3, 5x CH_2), 4·40 (1 H, m, CHO), 6·43 (2 H, m, arom), 8·78 (1 H, d, arom).

5.15. *(S)-4'-Pentylbiphenyl-4-yl 2-hydroxy-4-(2-methylbutyloxy)benzoate* (**31**)

The reaction was carried out using compound **23** and a 200 per cent excess of 4-hydroxy-4'-pentylbiphenyl by following the procedure described for the preparation of compound **29**: Yield 2·40 g (87 per cent). Transitions (°C) $S_1 \sim 12$ E* 36·0 S_A^* 49·8 TGB A* 50·2 Ch 134·5 I. MS (*m/z*) 446 (M^+), 240, 207, 183, 137 (100 per cent); IR ν_{max}/cm^{-1} 3420, 2960, 2860, 1685, 1625, 1585, 1500, 1470, 1400, 1355, 1250, 1190, 1130, 1070, 885, 860, 800; ^1H NMR δ 0·95–1·90 (18 H, m, 3x CH_3, 4x CH_2, CH), 2·65 (2 H, t, CH_2), 3·85 (2 H, m, CH_2O), 7·25 (6 H, m, arom), 7·50 (2 H, d, arom), 7·65 (2 H, d, arom), 8·00 (1 H, d, arom), 10·70 (1 H, s, OH).

5.16. *(S)-4'-Octyloxybiphenyl-4-yl 2-hydroxy-4-(2-methylbutyloxy)benzoate* (**32**)

The reaction was carried out using compound **23** and 4-hydroxy-4'-octyloxybiphenyl by following the procedure described for the preparation of compound **31**: Yield 60 mg (43 per cent). Transitions (°C) C 72·9 S_C^* 96·2 Ch 129·2 I. MS (*m/z*) 504 (M^+), 410 (100 per cent), 298, 207, 185, 137; IR ν_{max}/cm^{-1} 3420, 2970, 2860, 1680, 1630, 1610, 1585, 1505, 1470, 1255, 1170, 1030, 805; ^1H NMR δ 0·95 (9 H, m, 3x

CH_3), 1·30–1·80 (15 H, m, 7x CH_2, CH), 3·83 (2 H, octet, CH_2O), 4·00 (2 H, t, CH_2O), 6·50, (2 H, m, arom), 6·95 (2 H, d, arom), 7·25 (2 H, d, arom), 7·50 (2 H, d, arom), 7·60 (2 H, d, arom), 7·98 (1 H, d, arom).

5.17. *(S)-4-Octyloxyphenyl 4-[2-hydroxy-4-(2-methylbutyloxy)benzoyloxy]benzoate* (**33**)

The reaction was carried out using compounds **12** and **23** by following the procedure described for the preparation of compound **31**: Yield 70 mg (47 per cent). Transitions (°C) C 62·0 S_C^* 68·8 Ch 141·8 I. MS (*m/z*) 548 (M^+), 327, 222, 209, 137, 121 (100 per cent); IR ν_{max}/cm^{-1} 3440, 3070, 2980–2860, 1735, 1690, 1625, 1600, 1580, 1510, 1470, 1250, 1195, 1020, 840; ^1H NMR δ 0·95 (9 H, m, 3x CH_3), 1·30–1·55 (12 H, m, 6x CH_2), 1·80 (3 H, m, CH_2, CH), 3·85 (2 H, octet, CH_2O), 4·00 (2 H, t, CH_2O), 6·55 (2 H, m, arom), 6·95 (2 H, d, arom), 7·15 (2 H, d, arom), 7·38 (2 H, d, arom), 7·95 (1 H, d, arom), 8·28 (2 H, d, arom), 10·55 (1 H, s, OH).

5.18. *(S)-4'-Octyloxybiphenyl-4-yl 4-[2-hydroxy-4-(2-methylbutyloxy)benzoyloxy]benzoate* (**34**)

The reaction was carried out using compounds **13** and **23** by following the procedure described for the preparation of compound **31**: Yield 40 mg (24 per cent). Transitions (°C) C 109·1 S_C^* 157·3 Ch 243·6 I. MS (*m/z*) 418, 298 (100 per cent), 207, 186, 137, 121; IR ν_{max}/cm^{-1} 3200, 2970–2860, 1730, 1685, 1630, 1600, 1580, 1500, 1470, 1250, 1100, 1020, 885, 855, 835; ^1H NMR δ 0·95 (9 H, m, 3x CH_3), 1·30–1·50 (12 H, m, 6x CH_2), 1·80 (3 H, m, CH_2, CH), 3·83 (2 H, octet, CH_2O), 4·00 (2 H, t, CH_2O), 6·53 (2 H, m, arom), 6·95 (2 H, d, arom), 7·25 (2 H, d, arom), 7·38 (2 H, d, arom), 7·53 (2 H, d, arom), 7·60 (2 H, d, arom), 7·95 (2 H, d, arom), 8·35 (2 H, d, arom).

5.19. *(R)-4-Octyloxyphenyl 4-[2-hydroxy-4-(2-octyloxy)benzoyloxy]benzoate* (**35**)

The reaction was carried out using compounds **12** and **24** by following the procedure described for the preparation of compound **31**: Yield 30 mg (10 per cent). Transitions (°C) C 63·1 Ch 89·6 I. MS (*m/z*) 590 (M^+), 343, 249, 222, 137, 121 (100 per cent); IR ν_{max}/cm^{-1} 3480, 2920, 2860, 1730, 1670, 1620, 1600, 1575, 1505, 1465, 1340, 1255, 1195, 1165, 1025, 870, 830, 800; ^1H NMR δ 0·87 (6 H, 2x t, 2x CH_3), 1·45–1·63 (23 H, m, CH_3, 10x CH_2), 1·78 (2 H, m, CH_2), 3·95 (2 H, t, CH_2O), 4·43 (1 H, m, CHO), 6·48 (2 H, m, arom), 6·93 (2 H, d, arom), 7·13 (2 H, d, arom), 7·35 (2 H, d, arom), 7·95 (1 H, d, arom), 8·30 (2 H, d, arom), 10·55 (1 H, s, OH).

5.20. *(R)-4'-Octyloxybiphenyl-4-yl 4-[2-hydroxy-4-(2-octyloxy]benzoate* (**36**)

The reaction was carried out using compounds **13** and **24** by following the procedure described for the preparation of compound **31**: Yield 70 mg (19 per cent). Transitions (°C) C 73·3 S_C^* 141·7 Ch 187·3 I. MS (*m/z*) 666 (M^+), 418, 369, 298, 248, 186, 137, 121, 43 (100 per cent): IR ν_{max}/cm^{-1} 3420, 2920, 2860, 1735, 1675, 1620, 1600, 1570, 1500, 1465, 1340, 1265, 1205, 1160, 1015, 880, 840, 800; ^1H NMR δ 0·87 (6 H, 2x t, 2x CH_3), 1·33–1·53 (23 H, m, CH_3, 10x CH_2), 1·80 (2 H, m, CH_2), 4·00 (2 H, t, CH_2O), 4·45 (1 H, m, CH), 6·50 (2 H, m, arom), 6·98 (2 H, d, arom), 7·13 (2 H, d, arom), 7·35 (2 H, d, arom), 7·50 (2 H, d, arom), 7·60 (2 H, d, arom), 7·98 (1 H, d, arom), 8·33 (2 H, d, arom), 10·53 (1 H, s, OH).

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