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Properties of some broad band chiral smectic C materials

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Properties of some broad band chiral smectic C materials

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A comparative study of three related families of ferroelectric liquid crystals and some distinctly different analogues has been made with the aim of clarifying systematic trends in smectic C phase stability and the appearance of macroscopic polarization. The substances are interesting not only because the C phases are broad and occur around ambient temperature, but also because the more highly ordered tilted phases (smectic I, J, . . .) are suppressed. Their collective behaviour also sheds light on the molecular origin of the spontaneous polarization.

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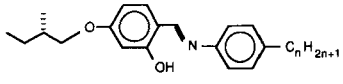
1. Introduction

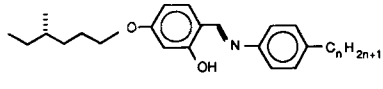
Although the race for high-performance materials for use in ferroelectric liquid crystal devices has certainly started on an international scale, we are still far from understanding the relationships between molecular structure and macroscopic properties. The structures presented in this work are not in themselves convenient building blocks for electro-optical materials but because of the clear trends which their properties display they may serve as logical steps in the design of such materials.

2. Structures

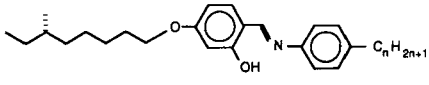
The compounds investigated are members of the three families (*S*)-4′-(2-methylbutyl)-, (*S*)-4′-(4-methylhexyl)- and (*S*)-4′-(6-methyloctyl)resorcylidene 4-alkylanilines or MBRA *n*, MHxRA *n* and MORA *n*, respectively; they are shown below as structures **1**, **2** and **3**, and are characterized by having a hydroxy group in the 2-position of the aldehyde ring. For a conclusive comparison we have also synthesized the corresponding family lacking this hydroxy group, 9 * O . *n*, the formula of which is shown as structure **4**. Tables 1 and 2 show the polymorphism and transition temperatures of the compounds. The synthesis of **1** and **3** has been reported previously [1] and their phases have been identified [2].



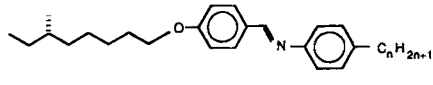
1 MBRA *n*



2 MHxRA *n*



3 MORA *n*



4 9*O.n

Table 1. Phase transitions for series **1**, **2** and **3**. C, crystal; I, isotropic liquid; N*, cholesteric; S_A, smectic A; S_C^*, chiral smectic C; S_I^*, chiral smectic I; S_2 and S_3, unidentified smectic phases.

Compound	*n*	Transition temperatures in °C
1	4	C 51·6 I
1	8	C 35·6 S_C^* 50 S_A 56·8 I
1	9	C 34 (S_3 9) S_C^* 51 S_A 62·7 I
1	12	C 45·4 S_A 63·1 I
2	4	C 42 S_C^* 57·4 N* 61·0 I
2	8	C ? S_2 ≈20 S_C^* 77 I†
2	10	C 26 S_C^* 79·6 I
2	12	C 38 (S_3 24·9 S_2 25·9) S_C^* 79·4 I
3	4	C 38·2 S_C^* 66·1 N* 70·5 I
3	5	C RT S_C^* 81 N* 83 I‡
3	6	C 18·8 C_C^* 80·6 I
3	7	C RT S_C^* 86 I‡
3	8	C 20·4 S_C^* 85·7 I
3	9	C 2 S_C^* 87 I§
3	10	C 25·3 (S_I^* 16·6) S_C^* 87·1 I
3	12	C 36·7 (S_3 24·8 S_I^* 26·6) S_C^* 86·5 I

†The compound did not crystallize above −20°C.
‡No D.S.C. data available.
§Clearing point of *c.* 2°C in spite of extensive purification.

Table 2. Phase transitions for series **4**. S_G^*, chiral smectic G; S_J^*, chiral smectic J; for other abbreviations see table 1.

n	Transition temperatures in °C†
4	C ? S_G^* 60·4 S_C^* I‡
8	C 7 S_J^* 53·6 S_I^* 64·8 S_C^* 69·0 I
10	C 18 S_I^* 64·0 S_C^* 69·3 I
12	C 34 S_I^* 63·0 S_C^* 68·3 I

†The phases are assigned tentatively from texture observations.
‡The compound did not crystallize above −20°C.

3. Synthesis

The chiral starting material (*S*)-2-methylbutanol was converted to (*S*)-2-methylbutyl tosylate, (*S*)-4-methylhexyl tosylate and (*S*)-6-methyloctyl bromide, respectively. Subsequent alkylation of 2,4-dihydroxybenzaldehyde afforded the chiral 4-alkyloxy-2-hydroxybenzaldehydes in 15–40 per cent overall yields after column chromatography on silica gel. Condensation of the aldehydes with the appropriate anilines in boiling benzene furnished target imines **1**–**3** in good yields. The corresponding compounds 9∗O.*n* (**4**) were prepared in a similar manner. The full synthetic route is outlined in the scheme and details are given in § 7.

4. Smectic thermal stability

Most members of the three series investigated exhibit an unusually high propensity to show chiral smectic C phases; the S_C^* range is in some instances well over 100°C including supercooling; this is certainly remarkable for single two-ring substances.

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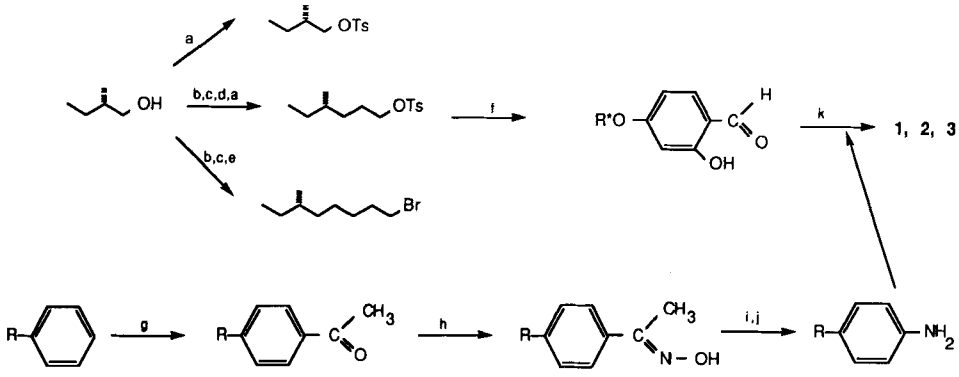


(*a*) *p*-TsCl, py; (*b*) $SOCl_2$, py; (*c*) Mg, Et_2O; (*d*) ethylene oxide, Et_2O; (*e*) 1,4-dibromobutane, Li_2CuCl_4, THF; (*f*) 2,4-dihydroxybenzaldehyde, K_2CO_3, DMF; (*g*) AcCl, $AlCl_3$, CH_2Cl_2; (*h*) NH_2OH HCl, K_2CO_3, EtOH : H_2O; (*i*) PCl_5, Et_2O; (*j*) conc. HCl, EtOH; (*k*) benzene, 4 Å molecular sieves.

Additionally, most members have the less common chiral smectic C to isotropic liquid phase transition. The smectic C interval increases with increasing chain length from **1** to **3** and almost vanishes if the hydroxy group is removed (**4**). In addition to **4** it is convenient to have some more standard reference substances, and as such we have chosen the well-known DOBAMBC and HOBACPC, **5** and **6**. In figure 1 the smectic C phase range as well as its position on the temperature scale is emphasized for all compounds.

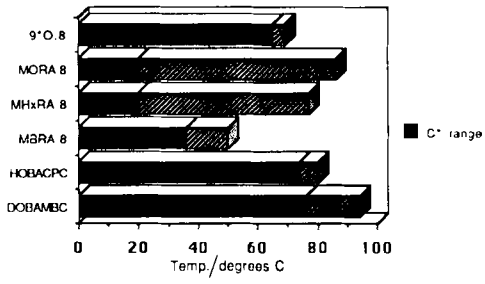
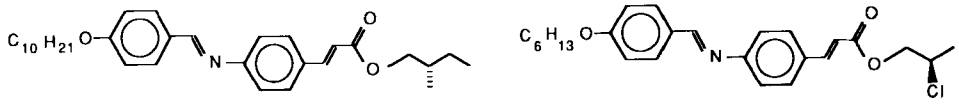


Figure 1. The chiral smectic C range and its relative position on the temperature scale for some selected compounds of this work together with the reference substances HOBACPC and DOBAMBC.



5 DOBAMBC **6** HOBACPC

For the basic imine structure the presence of the OH group seems to increase the clearing point and the overall smectic range, quite the opposite effect to other lateral substituents such as halogens, nitro groups or cyano groups [3]. The hydroxyl group also strongly promotes the occurrence of a smectic C phase and seems to suppress rather effectively the appearance of high order smectics which were found, like nematic and smectic A phases, only in some rare cases (cf. table 1 and [2]). The corresponding compounds lacking the hydroxyl group (9 * O . *n*) have considerably

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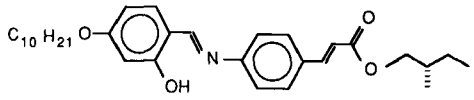
lower clearing points (S_C^*–I transitions) and have much smaller S_C^* ranges. Supercooling is quite pronounced for all liquid-crystalline compounds described in this paper, in fact compounds 9*O.4 and 9*O.8 do not crystallize above −20°C.

The unique C-stabilizing influence of the OH group is found in a few other examples, for instance in the homologous series **7** [4] and **8** [5]. Moreover, no high order tilted phases were reported for these two series.



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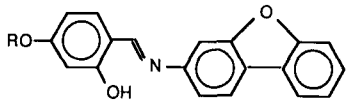

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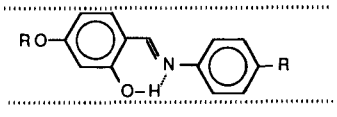
4.1. *Discussion*

The higher smectic thermal stability in the OH-substituted compounds indicates an increased interaction between adjacent molecules in the smectic layers. Gray and Jones [6] pointed out that polar groups, substituted in such a way that they do not significantly increase the molecular breadth, have a stabilizing effect. This may well be the case here since, if the hydroxy hydrogen is intramolecularly hydrogen bonded, the OH group is well accommodated within the rotational volume of the molecule, cf. figure 2. This also leads to an increased coplanarity in the central part of the molecule. All in all, at least three factors can be considered to affect the smecticity, and these are related. They are

(i) coplanarity of the aromatic rings, which favours smectic ordering in general;
(ii) intramolecular hydrogen bonding leading to a *pseudo* three-ring system, and by this related to i;
(iii) intermolecular hydrogen bonding, which out of several tilted smectics may favour the smectic C phase.

We comment on these in order.



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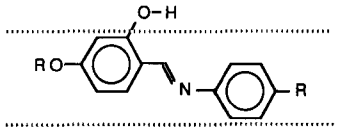

b

Figure 2. (*a*) Intramolecular hydrogen bond giving a *cis* conformation in which the molecular breadth is not increased. (*b*) *Trans* conformation in which the molecular breadth is considerably increased.

(i) An important factor regarding the smectic thermal stability is the coplanarity of the two aromatic rings. The angle between the planes of the two aromatic rings of benzylideneaniline [7] (the core unit of **4**) is approximately 17° larger (66° and 49°, respectively, deduced from X-ray data) than the corresponding angle of salicylideneaniline [8] (the core unit of **1**, **2** and **3**). The angle by which the aniline ring of benzylideneaniline is twisted away from the plane of the imine bond has been calculated from U.V. data and was found to be in agreement with the X-ray data [9]. The increased coplanarity should, in turn, lead to an increased polarizability of the

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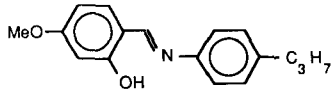
central core, because of more extended conjugation, and thus to an enhanced smectic stability [10]. This will also lead to more favourable packing conditions. It should be noted that phenyl benzoates, in which the aromatic rings are nearly orthogonal [11, 12], usually show lower smectic stability than imines [13].

(ii) The second aspect is that because of intramolecular hydrogen bonding the molecules may adopt a *pseudo* three-ring system, in which the imine bond and the aldehyde ring approach coplanarity, cf. figure 2(*a*). By the previous arguments this then leads to a higher smectic stability. It is known that in chloroform solution a strong intramolecular hydrogen bond exists between the hydroxyl proton and the nitrogen of the imine link, as evidenced by a down-field shift of the N.M.R. signal to approximately $\delta = 14$, independent of concentration. The tendency for this type of bonding will probably remain in the liquid-crystalline states.

(iii) In the solid or liquid-crystalline state, where the distance between the neighbouring molecules is considerably smaller, intermolecular hydrogen bonding should also be considered, as illustrated in figure 3. This type of interaction is also suggested by Brand *et al.* [14] for the low temperature phase of MORA 12. Furthermore, intermolecular hydrogen bonding has been assumed in related systems, e.g. in OHMBPA (**9**). Sakamoto and co-workers [15] interpret the low frequency absorptions in the Raman spectrum of **9** as resulting from this kind of bonding. However, no other spectral evidence is presently available.



9 OHMBPA

Nethertheless, it is attractive to discuss intermolecular hydrogen bonding to account for the unique preponderance of smectic C phases in the OH-substituted compounds and we suggest the following approach. Intermolecular hydrogen bonding should develop in the tilt direction and thus stabilize the tilt of the smectic C phase. Higher ordered tilted phases should then be suppressed; the intermolecular forces in smectic I phase, for example, must be equivalent in the directions of a hexagonal net which implies a two-dimensional distribution of hydrogen bonds along the layer plane. This would give a non-uniform tilt direction which is not allowed in the lowest energy state. However, in the smectic C phase, which has no two-dimensional structure, intermolecular hydrogen bonds can exist in only one direction, consistent with the tilt.

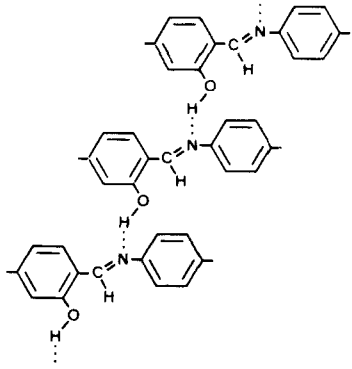


Figure 3. Intermolecular hydrogen bonding favouring smectic C formation.

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Which of these three factors is the most important is not easy to assess. However, the intermolecular hydrogen bonding cannot be dominant as compared to the first two. This can be inferred from values of the rotational viscosities. It has been shown [16] that the rotational viscosity of MBRA 8 is not significantly larger than that of HOBACPC which would probably be the case if intermolecular hydrogen bonding were fully developed.

A comparison between the I.R. spectra, of the crystal, chiral smectic C phase and chloroform solution, does not lend support to the intermolecular hydrogen bond model either. There is a striking similarity in the C=N stretching absorption bands in all three cases. It is expected that the frequencies of absorption are different for intra- and intermolecular hydrogen bonding and therefore, since intramolecular hydrogen bonds prevail in solution (cf. N.M.R. results), the I.R. data [17] do not indicate the presence of intermolecular hydrogen bonds. It is likely, therefore, bearing the results for the benzoates in mind [11] that the coplanarity of the benzene rings is a major factor influencing smectic thermal stability.

Finally we comment upon the enthalpies ($\Delta H_{S_C^*I}$) of the clearing points (S_C^*–I transitions) which reflect the change of intermolecular forces at the transition. If we assume that the attractive forces in the isotropic liquid are equal in the hydroxy and non-hydroxy compounds a higher enthalpy at the phase transition would be found for the former. Table 3 shows that $\Delta H_{S_C^*I}$ for the MORA compounds are indeed higher, though only slightly, than for the 9 * O . *n*s. The unexpectedly small difference implies that the stronger attractive forces, believed to exist for the hydroxy compounds, are to a certain degree retained at the phase transition. The concept of increased attraction forces is also supported by intermolecular energy calculations which indicate a marked stabilization of the molecular orientations [18] for OH-substituted compounds as compared to unsubstituted ones.

Table 3. Clearing point enthalpies ($\Delta H_{S_C^*I}$) for some compounds of series **3** and **4**.

Compound	$\Delta H_{S_C^*I}$/kJ mol^{-1}
9 * O·8	7·8
9 * O·10	7·8
9 * O·12	7·8
MORA 8	9·3
MORA 10	8·7
MORA 12	9·1

5. Spontaneous polarization

The physical characterization of the compounds investigated is difficult because of several factors such as their sometimes low resistivity and poor alignability, especially for members of series **2** and **3**. The polarization is in itself quite low for **2** and **3** and this, in combination with other factors, makes measurement difficult. Pitch and tilt angle measurements may also suffer from large scattering of data. However, the compounds of series **1** and **3** with *S* absolute molecular configuration have been found to have a left-handed S_C^* helix [2], and it is probable that all compounds are of the type [19] –/– for the z/**P** sign combination. (The sign of **P** has been confirmed for some members of **1**, **2** and **3**.) The polarization was measured by the field reversal

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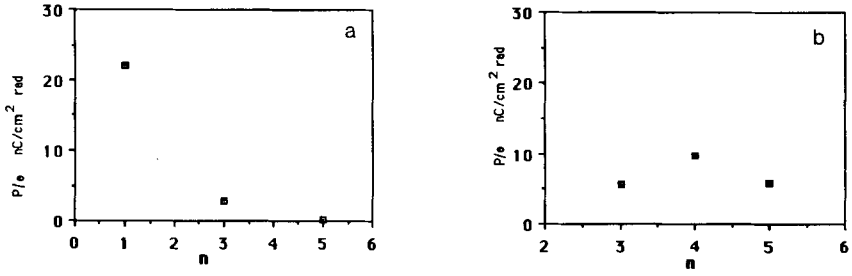
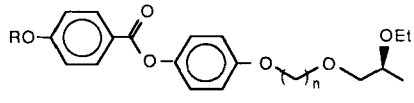


Figure 4. (*a*) Polarization/tilt angle for MBRA 8, MHxRA 8 and MORA 8; n = number of carbons between the asymmetric centre and the core. (*b*) Polarization/tilt angle for **10**, $R = C_{14}$, n = 3–5 (from [22]).

Table 4. P and θ values for MBRA 8, MHxRA 8 and MORA 8. n, number of carbons between the asymmetric centre and the core.

n	P/nC cm^{-2}	θ/°	P/θ/nC cm^{-2} rad^{-1}	
1	3	8	22	(MBRA 8)
3	2	40†	2·9	(MHxRA 8)
5	0·1†	35†	0·16	(MORA 8)

† Approximate values.



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(square wave) current method, [20]. By contrast, the compensated bridge method [21] proved to be inadequate for delineating different perturbing current contributions for the cases of very low polarization. The data for MBRA 8, MHxRA 8 and MORA 8 are compared in table 4. The ratio polarization/tilt angle is shown in figure 4 (*a*). As a comparison, the corresponding data [22] for the compounds **10** are shown in figure 4 (*b*). As can be seen from these figures, it is possible to move a chiral group out from the core without essentially changing the polarization properties of the substance, if the chiral group is polar, which means that the polar group retains its rotational bias (cf. figure 4 (*b*). On the other hand (cf. figure 4 (*a*)), if the chiral group moves away from the dipoles contributing to the polarization, the latter will decrease markedly as a function of distance. As the non-polar chiral groups still affect the helicity, independent manipulation with the separate side chains is an obvious though luxurious tool in a later stage of delicate optimization (infinite chiral nematic pitch, infinite chiral smectic C pitch materials).

5.1. *Discussion*

The polar character of the hydroxy-substituted molecules described in this paper is marked, the lateral dipole moment being predicted to be as high as 2·85 D (CNDO/2 value [23]; 1 D $\equiv$ 3·338 $\times$ 10^{-30} C m). The total calculated dipole moment is 2·90 D which should be compared with the corresponding value for salicylidene-aniline: 2·91 D [24]. These values agree fairly well with the experimentally measured

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dipole moments; 2·20 D (4′-nonyloxyresorcylidene-4-oktylaniline [23]) and 2·39 D (salicylideneaniline [24]), respectively. Since the spontaneous polarization can be considered as the dipole moment density, the molecular dipole moment divided by the molecular volume (van der Waals volume, V) gives an estimate of the maximum attainable value of the ferroelectric polarization in the absence of rotational averaging, according to

$$P_{\max} = \mu_{\perp}/V.$$

Insertion of $\mu_{\perp} = 2{\cdot}85\,\mathrm{D}$ ($0{\cdot}95 \times 10^{-27}\,\mathrm{C\,cm}$) and $V = 230\,\text{Å}^3$ ($2{\cdot}3 \times 10^{-22}\,\mathrm{cm}^3$) gives $P_{\max} \approx 4100\,\mathrm{nC/cm^2}$ (V is obtained from a molecular mechanics calculation). This large lateral dipole moment is, however, not reflected in the experimentally measured polarization which amounts to only $3\,\mathrm{nC/cm^2}$ (MBRA 8) [20], i.e. less than 0·1 per cent of the value corresponding to complete dipolar order. Because the alkyl chains of MBRA are non-polar the molecular dipole moments are confined to the aromatic core. It can therefore be concluded that non-chiral molecular dipole moments in the central part of the molecule are not a major advantage since such dipoles of the central core are not easily oriented in a constructive way, the only orientation-biasing interaction being with a distant chiral end group, with which the core is only weakly sterically related. In comparison, the calculated $P_{\max}$ of HOBACPC is approximately $1800\,\mathrm{nC/cm^2}$, *c.* 100 times the experimental value ($\mu_{\perp} = 1{\cdot}50\,\mathrm{D}$, CNDO/2 value [23]).

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6. Conclusions

For electro-optical devices using surface stabilized ferroelectric liquid crystals the chiral smectic C phase is still the prime candidate because of its combination of simplicity and high switching speed. The more highly ordered tilted phases (smectic, J, F, . . .) are also extremely interesting in a longer time perspective. In any case, however, it is fundamental for any practical device mixture to keep the chosen working phase constant and thermodynamically stable within a very broad temperature range (working and storage conditions). It is therefore important to find classes of substances which are not characterized by a whole series of phase changes, even between electro-optically usable phases, but for which one of these phases has a strong predominance, suppressing the others. Such classes of substances can be used as additives in mixtures in order to suppress the appearance of undesired phases. In our discussed case the substances have a very strong tendency to suppress all but the smectic C phase. In some other respects, especially as regards their low polarization, the present compounds are not convenient as electro-optic materials. In spite of this low polarization, the surface interaction seems to be pronouncedly polar, in most cases an undesired property.

Regarding the polarization properties, our results clearly support the assumption that a ferroelectric liquid crystal with a large spontaneous polarization should preferably consist of molecules with chiral, polar side chains. In such substances spacer groups can be inserted (e.g. for optimizing the thermal phase stability properties) without markedly changing the polarization properties. In contrast, a non-polar chiral group cannot be moved away from the molecular dipoles (the rotational motion of which it has to influence) without rapidly losing its biasing, and thus ferroelectricity-inducing, power.

7. Experimental

(*S*)-1-Chloro-2-methylbutane and (*S*)-2-methylbutyl tosylate were obtained from optically active (*S*)-2-methylbutanol according to the methods of Dailey and Yates [25] and Dolphin *et al.* [26], respectively. The Grignard reagent from 1-chloro-2-methylbutane was allowed to react with ethylene oxide furnishing 4-methylhexanol which was converted to the corresponding tosylate using standard procedures. 4-Butyl-, 4-octyl-, 4-decyl- and 4-dodecylaniline were purchased from Aldrich Chemical Company and were distilled immediately before use. Other alkylanilines were obtained as outlined in scheme 1; 4-alkylacetophenones were prepared from alkylbenzene and acetyl chloride under standard Friedel–Crafts conditions using aluminum trichloride as a catalyst. Further experimental details and analytical data are available on application to the authors.

Diethyl ether, tetrahydrofuran (THF) and benzene were distilled from sodium and dimethylformamide (DMF) was distilled from calcium hydride prior to use. ^{1}H N.M.R. spectra were recorded on a Bruker WH 270 instrument at 270 MHz and specific rotations were obtained on a Perkin–Elmer 141 polarimeter I.R. spectra were recorded on a Perkin–Elmer 197 spectrometer and low resolution mass spectra were obtained on a Finnegan Mat 1020B instrument. Phase transitions and melting points were determined on a Perkin-Elmer DSC7 apparatus and texture observations were made using an Olympus BHA polarizing microscope in conjuction with a Mettler FP52 hot stage and FP5 control unit.

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(S)-1-Bromo-6-methyloctane. The Grignard reagent from (*S*)-1-chloro-2-methylbutane (0·28 mol) in dry diethyl ether (100 ml) was added slowly to a solution of 1,4-dibromobutane (60·5 g, 0·28 mol) and dilithium tetrachlorocuprate [27] (3 mmol) (prepared from lithium chloride (6 mmol) and copper(II) chloride (3 mmol) in dry THF (30 ml)) in dry THF (150 ml) at 0°C and under argon. When the addition was complete the reaction mixture was allowed to warm up slowly to room temperature for 4 hours. The reaction mixture was hydrolyzed in hydrochloric acid (2 M) and extracted three times with diethyl ether. The combined organic layers were washed twice with aqueous sodium hydrogen carbonate, twice with water and dried over anhydrous magnesium sulphate. After removal of the solvent the crude product was distilled on a Fischer Spaltrohr 500 apparatus to afford 45 per cent of (*S*)-1-bromo-6-methyloctane (51–53°C/1 mm Hg). Lit. [28] b.p.$_{14}$ 101°C. $[\alpha]_D$ + 5·73° (*c* 0·80, benzene), Lit. [28] $[\alpha]_D$ + 2·16° (neat); ^{1}H N.M.R. (270 MHz, $CDCl_3$): δ 0·86 (m, 6 H), 1·08–1·42 (m, 9 H), 1·86 (quintet, 2 H), 3·40 (t, J = 6·8 Hz, 2 H); I.R. ($CHCl_3$): 2920, 2850, 1460, 1375, 1260, 640 cm^{-1}; M.S. (70 eV; m/Z (per cent rel. int.)): 208 (1, M^+ + 2), 206 (1, M^+), 151 (45), 149 (47), 97 (64), 57 (100), 55 (85).

Chiral 4-alkoxy-2-hydroxybenzaldehydes, general procedure. (*S*)-2-Methylbutyl tosylate, (*S*)-4-methylhexyl tosylate or (*S*)-1-bromo-6-methyloctane (0·024 mol) and 2,4-dihydroxybenzaldehyde (3 g, 0·024 mol) were dissolved in dry DMF (50 ml). Potassium carbonate (4·5 g, 0·033 mol) was added and the reaction mixture was refluxed for 45 min. After cooling the reaction mixture was diluted with water and extracted three times with diethyl ether. The combined organic layers were washed once with water and then extracted twice with aqueous sodium hydroxide (5 per cent). The alkaline solution was washed once with diethyl ether and then neutralized with concentrated hydrochloric acid and extracted three times with diethyl ether. The combined organic layers were washed twice with water and dried over anhydrous magnesium sulphate. After removal of the solvent the crude aldehydes were purified

by column chromatography (63–200 μm silica gel, dichloromethane) to afford 40–45 per cent 4-alkoxy-2-hydroxybenzaldehydes.

Analytical data: (*S*)-4-(2-Methylbutyloxy)-2-hydroxybenzaldehyde: $[\alpha]_D$ + 11·6° (*c*. 2·74, benzene); ^{1}H N.M.R. (270 MHz, $CDCl_3$): δ 0·95 (t, *J* = 7·5 Hz, 3 H), 1·02 (d, *J* = 6·8 Hz, 3 H), 1·28 (m, 1 H), 1·53 (m, 1 H), 1·88 (m, 1 H), 3·79 (dd, J_{vic} = 6·3 Hz, J_{gem} = 9·0 Hz, 1 H), 3·88 (dd, J_{vic} = 5·9 Hz, J_{gem} = 9·0 Hz, 1 H), 6·41 (d, J_m = 2·3 Hz, 1 H), 6·53 (dd, J_o = 8·6 Hz, J_m = 2·3 Hz, 1 H), 7·40 (d, J_o = 8·6 Hz, 1 H), 9·70 (s, 1 H), 11·4 (s, 1 H); I.R. ($CHCl_3$): ≈3100 (broad), 2950, 2860, 1630, 1510, 1495, 1365, 1290, 1165, 1115 cm^{-1}; M.S. (70 eV; *m*/*Z* (per cent rel. int.)): 208 (27, M^+), 139 (45), 138 (96), 137 (100), 71 (18), 55 (27).

(*S*)-4-(4-Methylhexyloxy)-2-hydroxybenzaldehyde: $[\alpha]_D$ + 8·64° (*c*. 3·01, $CHCl_3$); ^{1}H N.M.R. (270 MHz, $CDCl_3$): δ 0·88 (m, 6 H), 1·13–1·58 (m, 5 H), 1·82 (m, 2 H), 3·99 (t, *J* = 6·6 Hz, 2 H), 6·41 (d, J_m = 2·3 Hz, 1 H), 6·51 (dd, J_o = 8·7 Hz, J_m = 2·3 Hz, 1 H), 7·41 (d, J_o = 8·7 Hz, 1 H), 9·70 (s, 1 H), 11·5 (s, 1 H); I.R. ($CHCl_3$): ≈3100 (broad), 2950, 2920, 2860, 1630, 1510, 1495, 1365, 1290, 1165, 1115 cm^{-1}; M.S. (70 eV; *m*/*Z* (per cent rel. int.)): 236 (32, M^+), 139 (44), 138 (100), 137 (71), 69 (32), 57 (90).

(*S*)-4-(6-Methyloctyloxy)-2-hydroxybenzaldehyde: $[\alpha]_D$ + 6·05° (*c*. 2·33, benzene); ^{1}H N.M.R. (270 MHz, $CDCl_3$): δ 0·86 (m, 6 H), 1·03–1·48 (m, 9 H), 1·78 (m, 2 H), 4·00 (t, *J* = 6·6 Hz, 2 H), 6·41 (d, J_m = 2·3 Hz, 1 H), 6·52 (dd, J_m = 2·3 Hz, J_o = 8·7 Hz, 1 H), 7·40 (d, J_o = 8·7 Hz, 1 H), 9·70 (s, 1 H), 11·5 (s, 1 H); I.R. ($CHCl_3$): ≈3100 (broad), 2950, 2920, 2860, 1630, 1510, 1495, 1365, 1290, 1165, 1115 cm^{-1}; M.S. (70 eV; *m*/*Z* (per cent rel. int.)): 264 (20, M^+), 139 (29), 138 (100), 137 (43), 71 (32), 57 (62).

(S)-4-(6-Methyloctyloxy)benzaldehyde. The procedure described previously was followed using 4-hydroxybenzaldehyde (recrystallized from water) instead of 2,4-dihydroxybenzaldehyde affording 4-(6-methyloctyloxy)benzaldehyde (83 per cent) as a colourless liquid. $[\alpha]_D$ + 6·80° (*c*. 7·0, $CHCl_3$), Lit. [29] $[\alpha]_D$ + 5·71°; ^{1}H N.M.R. (270 MHz, $CDCl_3$): δ 0·86 (m, 6 H), 1·07 (m, 2 H), 1·2–1·4 (m, 7 H), 1·82 (quintet, 2 H), 4·04 (t, *J* = 6·6 Hz, 2 H), 6·98 (d, *J* = 8·8 Hz, 2 H), 7·80 (d, *J* = 8·8 Hz, 2 H), 9·87 (s, 1 H); I.R. ($CHCl_3$): 2920, 2850, 1680, 1595, 1575, 1260, 1155 cm^{-1}; M.S. (70 eV; *m*/*Z* (per cent rel. int.)): 248 (27, M^+), 123 (100), 122 (76), 121 (75).

Oximes of 4-alkylacetophenones, general procedure. Potassium carbonate (16·6 g, 0·12 mol) dissolved in water (180 ml) was added slowly to hydroxylamine hydrochloride (13·9 g, 0·2 mol). After the evolution of carbon dioxide has subsided 4-alkylacetophenone (0·08 mol) was added. Ethanol was then added until a clear solution was obtained (*c*. 250 ml) and the resulting mixture was refluxed for 4·5 hours. After cooling the reaction mixture was extracted three times with diethyl ether and the combined organic layers were washed once with hydrochloric acid (2 M) and twice with water and dried over anhydrous magnesium sulphate. The solvent was evaporated and the resulting solid was recrystallized from hexane to yield 40–75 per cent of oxime which was used in the following step without further characterization.

4-Alkylanilines, general procedure. The oxime (0·04 mol) was dissolved in dry diethyl ether (85 ml). Phosphorus pentachloride (11·7 g, 0·056 mol) was added carefully and the reaction mixture was stirred under anhydrous conditions for 4 hours and then poured into ice/water and extracted twice with diethyl ether. The combined organic layers were washed once with water, once with aqueous sodium hydrogen carbonate and twice with water and dried over anhydrous magnesium sulphate. Evaporation of the solvent afforded the crude anilide which was dissolved in ethanol

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(320 ml). Concentrated hydrochloric acid (36 ml) was added and the reaction mixture was refluxed for 15 hours. After neutralization with aqueous sodium hydroxide (10 per cent) and addition of water the reaction mixture was extracted three times with diethyl ether. The combined organic layers were washed twice with water and dried over anhydrous magnesium sulphate. Evaporation of the solvent and distillation at reduced pressure using a Kugelrohr apparatus afforded 4-alkylanilines in 50 per cent yields.

^{1}H N.M.R. (270 MHz, $CDCl_3$): δ 0·88 (t, J = 6·5 Hz, 3 H), 1·26 (m, 4, 6, 8 or 12 H), 1·55 (m, 2 H), 2·48 (t, J = 7·6 Hz, 2 H). 3·49 (broad s, 2 H), 6·60 (d, J = 8·3 Hz, 2 H), 6·95 (d, J = 8·3 Hz, 2 H); I.R. ($CHCl_3$): 3430, 3360, 2920, 2850, 1620, 1510, 1265, 820 cm^{-1}. Mass spectral data: 4-pentylaniline: M.S. (70 eV; m/Z (per cent rel. int.)): 163 (15, M^+), 107 (10), 106 (100); 4-hexylaniline: M.S. (70 eV; m/Z (per cent rel. int.)): 177 (7, M^+), 107 (9), 106 (100); 4-heptylaniline: M.S. (70 eV; m/Z (per cent rel. int.)): 191 (5, M^+), 107 (5), 106 (100); 4-nonylaniline: M.S. (70 eV; m/Z (per cent rel. int.)): 219 (8, M^+), 107 (8), 106 (100).

*Preparation of target imines (**1–3**), general procedure.* Equimolar amounts of aldehyde and aniline were refluxed for 4 hours in dry benzene (10–15 ml/mmol substrate) containing 4 Å molecular sieves. The molecular sieves were filtered off and the solvent was removed by evaporation. The crude imines were recrystallized several times from absolute ethanol until a clearing point interval of *c.* 0·5°C was obtained.

Analytical data: MBRA n: ^{1}H N.M.R. (270 MHz, $CDCl_3$): δ 0·88 (t, J = 6·6 Hz, 3 H), 0·95 (t, J = 7·4 Hz, 3 H), 1·02 (d, J = 6·8 Hz, 3 H), 1·30 (m, ($2n$ − 5) H), 1·58 (m, 3 H), 1·88 (m, 1 H), 2·61 (t, J = 7·6 Hz, 2 H), 3·77 (dd, J_{vic} = 6·6 Hz, J_{gem} = 9·0 Hz, 1 H), 3·86 (dd, J_{vic} = 6·1 Hz, J_{gem} = 9·0 Hz, 1 H), 6·46 (m, 3 H), 7·2 (m, 4 H), 8·50 (s, 1 H), 13·8 (broad s, 1 H); MHxRA n: ^{1}H N.M.R. (270 MHz, $CDCl_3$): δ 0·90 (m, 9 H), 1·30 (m, ($2n$ − 1) H), 1·62 (m, 2 H), 1·82 (m, 2 H). 2·62 (t, J = 7·7 Hz, 2 H), 3·98 (t, J = 6·7 Hz, 2 H), 6·46 (m, 3 H), 7·19 (m, 4 H), 8·52 (s, 1 H), 13·9 (broad s, 1 H); MORA n: ^{1}H N.M.R. (270 MHz, $CDCl_3$): δ 0·87 (m, 9 H), 1·15 (m, 2 H), 1·30 (m, ($2n$ + 1) H). 1·62 (m, 2 H), 1·82 (m, 2 H), 2·62 (t, J = 7·7 Hz, 2 H), 3·99 (t, J = 6·6 Hz, 2 H), 6·46 (m, 3 H), 7·21 (m, 4 H), 8·51 (s, 1 H), 13·8 (broad s, 1 H); I.R. ($CDCl_3$, identical for all compounds of type **1–3**): 2920, 2850, 1620, 1600, 1510, 1190 cm^{-1}.

Preparation of imines **4**. The imines **4** were obtained analogously to the preparation of imines **1–3**. ^{1}H N.M.R. (270 MHz, $CDCl_3$): δ 0·90 (m, 9 H), 1·1–1·7 (m, ($2n$ + 5) H), 1·81 (quintet, 2 H), 2·61 (t, J = 7·6 Hz, 2 H), 4·02 (t, J = 6·6 Hz, 2 H), 6·95 (d, J = 8·8 Hz, 2 H), 7·20 (AA′BB′, 4 H), 7·81 (d, J = 8·8 Hz, 2 H), 8·38 (s, 1 H); I.R. ($CHCl_3$): 2920, 2850, 1595, 1505, 1245, 1160 cm^{-1}.

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