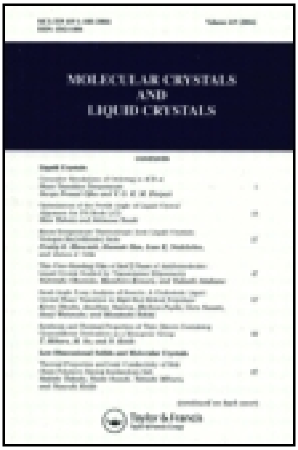


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

# Synthesis and Electro-Optical Properties of Some Ferroelectric Liquid Crystals Derived from Lactic Acid

Bengt Otterholm [a], Christer Alstermark [a], Kurt Flatischler [b], Anders Dahlgren [b], Sven T. Lagerwall [b] & K. Skarp [b]

[a] Department of Organic Chemistry, Chalmers University of Technology, S-412 96, Goteborg, Sweden

[b] Department of Physics, Chalmers University of Technology, S-412 96, Goteborg, Sweden

Version of record first published: 13 Dec 2006.

To cite this article: Bengt Otterholm, Christer Alstermark, Kurt Flatischler, Anders Dahlgren, Sven T. Lagerwall & K. Skarp (1987): Synthesis and Electro-Optical Properties of Some Ferroelectric Liquid Crystals Derived from Lactic Acid, Molecular Crystals and Liquid Crystals, 146:1, 189-216

To link to this article: http://dx.doi.org/10.1080/00268948708071813

*Mol. Cryst. Liq. Cryst.*, 1987, Vol. 146, pp. 189–216
Photocopying permitted by license only

Printed in the United States of America

# Synthesis and Electro-Optical Properties of Some Ferroelectric Liquid Crystals Derived from Lactic Acid

BENGT OTTERHOLM,† CHRISTER ALSTERMARK,† KURT FLATISCHLER,‡ ANDERS DAHLGREN,‡ SVEN T. LAGERWALL‡ and K. SKARP‡

*†Department of Organic Chemistry and ‡Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden*

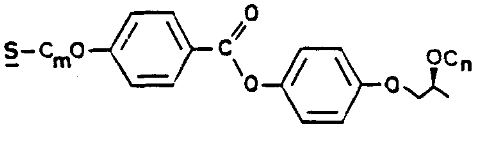
(*Received October 10, 1986*)

We have synthesized two series of liquid crystals, *viz.* 4'-(ω-(2-ethoxy)propoxy)alkoxyphenyl 4-alkoxybenzoate, *2*, (abbreviated $C_m$-$C_n$-OEt*) and 4'-(ω-(2-chloro)propoxy)alkoxyphenyl 4-alkoxybenzoate, *3*, (abbreviated $C_m$-$C_n$-Cl*). Compounds belonging to the latter mainly exhibit smectic A and B phases while the former show enantiotropic smectic C* at or near room temperature as well as A and smectic phases of higher order. The magnitude of the spontaneous polarization is moderate (~4 nC/cm$^2$). There is no alteration in sign for the spontaneous polarization and for the helical pitch as function of the *n* value. The $C_m$-$C_3$-OEt* and $C_m$-$C_5$-OEt* compounds are exhibiting unusually long helical periodicity for a pure compound (30–50 μm). Compounds of series 2 also show a close relationship between spontaneous polarization and tilt angle giving a practically temperature independent ratio $P/\theta$, making the definition of a material constant $P_o = P/\theta$ meaningful.

## INTRODUCTION

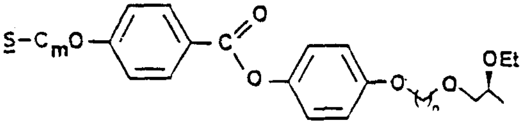
The design and synthesis of ferroelectric liquid crystals are to a large extent based on empirical data relating macroscopic properties, such as the spontaneous polarization, to the molecular structure. Recently, however, several tentative ideas aiming towards a basic understanding of the origin of the spontaneous polarization have been put forward[1–3] which will serve as guidelines in the future design of ferroelectric liquid crystal materials. The findings of Walba *et al.*[3]

concerning the ferroelectric liquid crystal materials possessing a nonracemic 2-alkoxy-1-propoxy tail unit (*1*) prompt us to disclose our investigations of the new homologous series *2* and *3*.



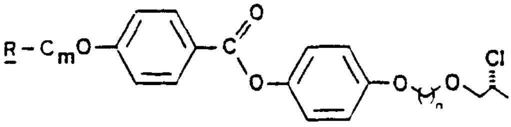
*1*

m=9-12; n=1-3



*2*

m=8-14; n=3-5



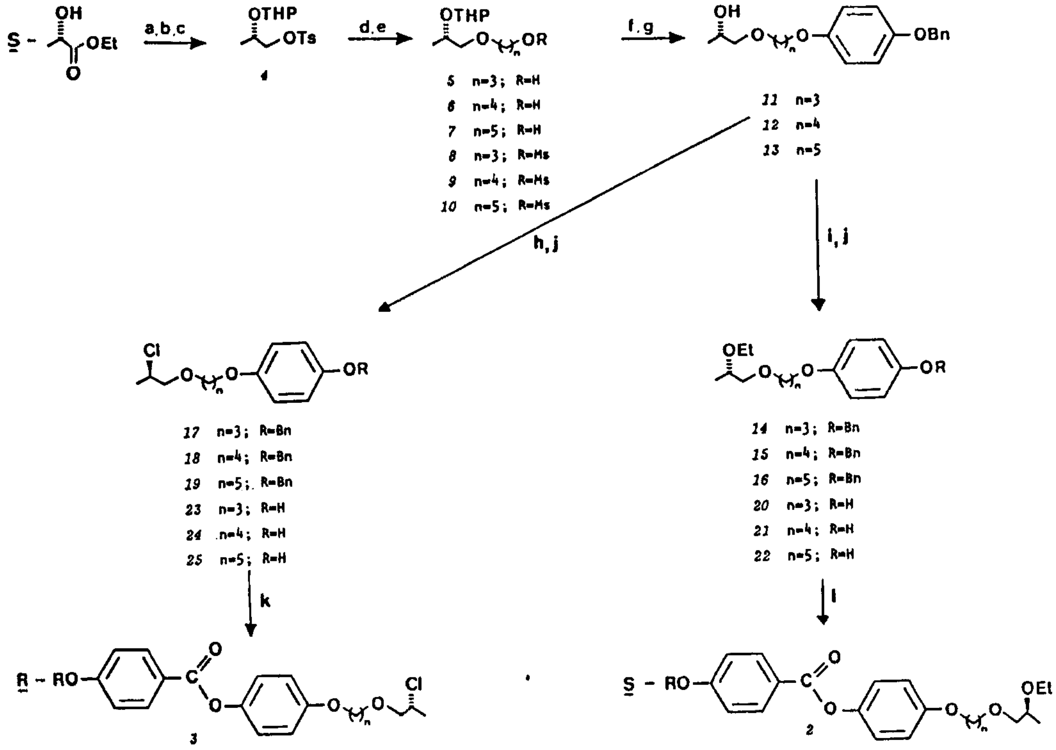
*3*

m=8-14; n=3-5

## SYNTHESIS

The chiral starting material for the two series is (*S*)-ethyl lactate, readily available in high enantiomeric purity. The synthesis is carried out as outlined in Scheme 1.

The secondary hydroxy group of ethyl lactate is protected as a tetrahydropyranyl ether according to the method of Paquette and Scott[4] and is subsequently reduced by lithium aluminum hydride affording (*S*)-2-tetrahydropyranyloxypropanol. The primary alcohol is converted into its tosylate, *4*, after which the tosyl group is displaced by the monoanion of the appropriate diol furnishing mesylates *8–10* after mesylation. Displacement of the mesyl group, this time by so-



SCHEME 1 a. DHP, conc. HCl; b. LiAlH$_4$, Et$_2$O; c. p-TsCl, py; d. 1,3-propanediol, 1,4-butanediol or 1,5-pentanediol, NaH, DMF; e. MsCl, Et$_3$, CH$_2$Cl$_2$; f. p-Benzyloxyphenol, NaH, DMF; g. PPTS, EtOH; h. SOCl2, py, CH$_2$Cl$_2$; i. EtBr, NaH, DMF; j. 10% Pd-C, H$_2$, HOAc; k. THF, Et$_3$N, ArCOCl; l. THF, NaH, ArCOCl.

dium 4-benzyloxyphenolate, and subsequent removal of the tetrahydropyranyl group catalyzed by PPTS[5] afforded secondary alcohols *11–13* which were either converted into ethers *14–16* under standard Williamson etherification conditions, or chlorinated with inversion of configuration[6] by thionyl chloride assisted by pyridine producing chlorides *17–19*. Debenzylation of ethers *14–16* and chlorides *17–19* gave phenols *20–22* and *23–25* which were coupled with 4-alkoxybenzoyl chlorides affording the target molecules *2* and *3*, respectively, in 15–25% overall yields.

## PHASE BEHAVIOUR

Phase transitions for the substances *2* and *3* are shown in Tables I and II, respectively. A clear correlation for the stability of the chiral

TABLE I

Phase transitions of series 2; X = crystal; L = isotropic liquid, N* = cholesteric; A = smectic A; B = smectic B; C* = chiral smectic C; $S_2$ = unidentified smectic phase; $S_3$ = unidentified tilted smectic phase

| m | n | Phase transitions[a] |
|---|---|---|
| 8 | 3 | X <RT ($S_2$ 6.9) A 30.9 L[b] |
| 9 | 3 | X 28.1 ($S_2$ 14.2) A 31.1 L |
| 10 | 3 | X 21.7 ($S_2$21) A 33–34 L[c] |
| 12 | 3 | X 21.4 $S_3$ 30.6 C* 31.3 A 39.5 L |
| 13 | 3 | X 42 ($S_3$ 34.1 C* 36.3 A 40) L |
| 14 | 3 | X 35 $S_3$ 39.5 C* 40.5 A 42 L |
| 8 | 4 | X 27.9 ($S_2$ 16.9) A 45.2 N* 50.3 L |
| 9 | 4 | X 25.2 (B 24.2) C* 28.5 A 47.3 N* 49.6 L |
| 10 | 4 | X 34.6 (B 30) C* 36 A 51.9 N* 52.1 L |
| 11 | 4 | X 32 (B 31.2) C* 45.3 A 50.9 L |
| 12 | 4 | X 32.2 B 38.3 C* 51.5 A 54.7 L |
| 13 | 4 | X 44.1 (B 40.5) C* 53.9 A 55.5 L |
| 14 | 4 | X 44.4 $S_3$ 45.4 C* 55.8 A 56.1 L |
| 8 | 5 | X 18.4 ($S_2$8.5) A 45.6 L |
| 9 | 5 | X 35.5 ($S_2$20) A 47.2 L |
| 10 | 5 | X 43 ($S_2$29.3) A 52 L |
| 11 | 5 | X 54 ($S_2$34.5 A 52.6) L |
| 12 | 5 | X 41 (B 40) C* 42.5 A 54.4 L |
| 13 | 5 | X 48.6 (B 42.7) C* 50.9 A 54.4 L |
| 14 | 5 | X 47 (B 46) C* 53.9 A 55.7 L |

[a] Temperatures in degrees Celsius. Phases identified by texture.

[b] The material did not crystallize even at −50° C.

[c] Broad clearing point interval in spite of extensive purification.

TABLE II

Phase transitions for series 3; abbreviations see Table I

| m | n | Phase transitions[a] |
|---|---|---|
| 12 | 3 | X 48.3 (B 45.4) A 50.1 L |
| 13 | 3 | X 53.3 (B 48.6 A 50.8) L |
| 14 | 3 | X 54 (B 52.2) L |
| 8 | 4 | X 35.6 (B 18.2) A 48.7 N* 61.6 L |
| 10 | 4 | X 44.9 (B 36.6) A 59.6 N* 62.6 L |
| 11 | 4 | X 55.2 (B 40.4) A 61.4 N* 62 L |
| 12 | 4 | X 54.5 (B 46.5) A 64.5 L |
| 13 | 4 | X 63 (B 51) A 65 L |
| 14 | 4 | X 60.6 (B 55.4) A 66.3 L |
| 11 | 5 | X 58.3 (B 39.2) A 58.7 L |
| 12 | 5 | X 50.3 (B 45.8) A 61.1 L |
| 13 | 5 | X 55.2 (B 49.8) A 61.8 L |
| 14 | 5 | X 56.6 (B 54.8) A 63.3 L |

[a] Temperatures in degrees Celsius. Phases identified by texture.

smectic C phase of series *2* and the length of the aliphatic tail of the molecule, especially emphasized for the $C_m$-$C_4$-OEt* homologous series, is seen in Table I, (*cf.* also Figures 3 and 6). For the $C_m$-$C_4$-OEt* series a maximum phase stability is found around $m = 12$.

Comparing compounds *2* with the corresponding series (*1*) lacking the spacer unit[3] (*cf.* Table III) it is noticed that the spacer group exerts a stabilizing effect on the C* phase. Whereas compounds *1* exhibit only monotropic C*, most higher homologs of series *2* show thermodynamically stable C* phases. Furthermore, the overall smectic stability is increased by some 5–10 degrees. The odd-even effect,[7] ubiquitous in liquid crystalline homologous series, is not as pronounced for the materials presented in this paper. The effect is hardly discernible in series *2*, $n = 4$, and for $n = 3{,}5$ the clearing point curves are quite irregular. This seems also to be the case for series *3* but the number of homologs within each individual series ($n = 3{,}4{,}5$) is too small to establish the proper clearing point behaviour. A comparision of the two series *2* and *3* reveals one important feature: an ethoxy substituent at the penultimate carbon atom (*2*) gives an abundant C* phase whereas in the chlorine-substituted series (*3*) tilted phases are absent. The reason for this is not easily conceivable since both series have molecular features generally believed to promote the occurrence of a smectic C phase[8]: alkoxy-aryl-alkoxy system, branching (the chlorine is sterically comparable to a methyl group) of the alkoxy chains and terminal dipoles perpendicular to the mo-

TABLE III

Phase transitions of series *1*; 6* = smectic 6; S = unidentified smectic phase; for other abbreviations see Table I

| m | n | Phase transitions[a] (from ref. 3) |
|---|---|---|
| 9 | 1 | X 45 (A 38) L |
| 9 | 2 | X 38 (A 36) L |
| 9 | 3 | X ? A 12 L |
| 10 | 1 | X 40 (C* 30) A 51 L |
| 10 | 2 | X 36.7 (G* 9 C* 27.8) A 39.4 L |
| 10 | 3 | X 29 A 31 L |
| 11 | 1 | X 42 A 48.5 L |
| 11 | 2 | X 95 L |
| 11 | 3 | X 28 A 32 L |
| 12 | 1 | X 43 (A 42) L |
| 12 | 2 | X 44 (C* 34.8) A 46 L |
| 12 | 3 | X 35 (S 25 C* 37.5) A 42 L |

[a] Temperatures in degrees Celsius.

lecular long axis. Anyway, a close inspection of the CPK space filling models gives at hand that the chlorine atom, as the molecule rotates around its long axis, comes in close proximity to the adjacent layer in the case of tilted molecules. This may be the driving force acting to suppress the formation of tilted phases in these chlorine-substituted compounds. The methyl group of series *2*, on the other hand, can very well be accomodated within the space between the alkyl chains (*cf.* Figure 1).

Furthermore, the dipolar character of the two series differ both with respect to strength and direction. The dipole moment of the carbon-chlorine bond is *ca.* 2.1 D while the dipole moment of the ether linkage is about 1.2 D[9] besides being conformationally more flexible. Since the $C_2C_3$ bond (*cf.* Figure 14) in both series are *gauche* favoured[10] the lateral dipole component of series *3* becomes even more dominant.

The same situation, *i.e.* that tilted phases are suppressed when the 2-chloropropyl group is utilized as a structure element, is found in several other examples. For instance, substitution of the ethoxy group of series *1*[3] by a chlorine, results in the disappearance of the C* phase in favour of an orthogonal B phase.[11] Other striking examples are when the 2-methylbutyl of the phenyl benzoate series[12] *26* and the

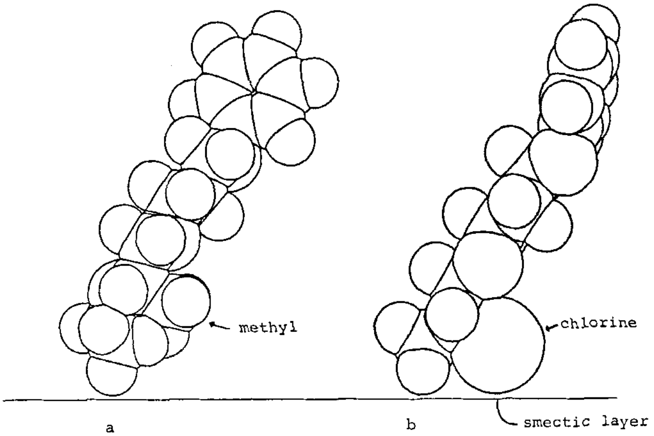
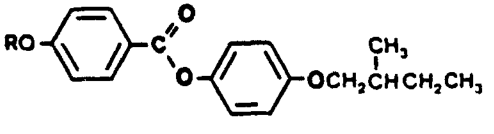
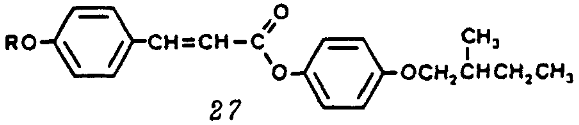


FIGURE 1 CPK space filling model of a: chiral tail unit of series 2 and b: chiral tail unit of series 3.

phenyl cinnamate series[13] 27, with abundant C* phases, is replaced by the 2-chloropropyl group yielding only orthogonal phases (A and B).[11]



**26**



## PHYSICAL PARAMETERS

For the three homologous series *2* with $n = 3,4,5$ the spontaneous polarization, tilt angle and optical response times were measured in an experimental setup described in more detail in Ref. 14. For the measurements, a sample cell that consists of two ITO-coated glass plates with a specially designed electrode pattern was used. The overlapping active area in the sample cell is 16.8 mm$^2$. The distance between the glass plates was maintained by evaporated silicon monoxide spacers of 2 μm thickness. The electrode pattern was coated with a 1000 Å thick uniform protective layer of SiO, evaporated with the incident beam normal to the glass surface. The liquid crystals are oriented in the bookshelf geometry (standing smectic layers) by shearing[15]; the top glass plate is moved in a longitudinal shear-motion relative to the bottom plate. The sample cell holder is assembled and placed in a Mettler FP 52 hot stage for temperature control. The temperature is separately monitored by a Pt-100 sensor drilled into the assemblage holder.

For the spontaneous polarization measurements a calibrated AC-bridge circuit was used. The principle is to balance out the linear part of the current response and to retain only the non-linear part originating from the ferroelectric dipole switching in the sinusoidal driving voltage, resulting in a hysteresis curve. To minimize the influence from ionic impurities in the liquid crystals, the driving voltage and frequency were chosen to be in the range 20–40 volts peak value and 100–200 Hz, respectively.

Tilt angle measurements as function of temperature for the different compounds where carried out on well-aligned samples, under a polarizing-microscope with crossed polarizers. The (field on) tilt angle is equal to the half angle read from the scale on the microscope turntable, between the two extreme optical states, corresponding to the two polarities of the DC-field applied across the sample cell.

The electro-optic response time is defined to correspond to the change between 10% and 90% of the light-transmission through crossed polarizers on application of a square-wave voltage across the sample cell. For comparison purposes, a standard field strength of 15 V/μm was chosen.

The C* phase helical pitch was measured by light diffraction. A thick bookshelf-aligned sample is placed in a monochromatic light beam the direction of which is thus perpendicular to the unquenched helix in the middle of the sample, and the diffraction pattern is viewed on a screen. The Bragg relation $Z \cdot \sin\theta = N \cdot \lambda$ and simple geometry gives

$$Z = N\lambda\,[1+(b/a)^2]^{1/2}$$

where $Z$ = pitch; $N$ = order of diffraction; $\lambda$ = wavelength of light; $b$ = distance from sample to screen; $a$ = distance on the screen to the $N$:th diffracted beam. The substance is sandwiched between glass plates with mylar spacers.

As a standard, we have used 225 μm thickness. Surface anchoring[16] will affect the pitch in too thin samples. The sample is placed in a heated copper holder with openings for the light beam, and aligned by cooling in a magnetic field of 2 *T*, with the field parallel to the glass plates. During the alignment process we can view the sample via a long-distance polarizing microscope, and this gives us a valuable cheque of phase transitions and alignment. We usually achieve good alignment for substances with an isotropic–smectic A transition. For substances with an uncompensated cholesteric phase, the alignment is poorer, but may still be good enough for measurements. After the alignment, the entire sample-holder is placed in a He-Ne laser beam, giving the chiral smectic C phase diffraction pattern. The intensity of the diffraction pattern depends, as is conceivable, on the polarization direction of the laser beam, with maximum variation for the direction of polarization perpendicular to the helix direction.

## RESULTS

### Polarization and Tilt Angle

Our results for the spontaneous polarization as a function of temperature for the three homologous series *2* with $n = 3,4,5$ are shown in Figures 2, 3 and 4, respectively.

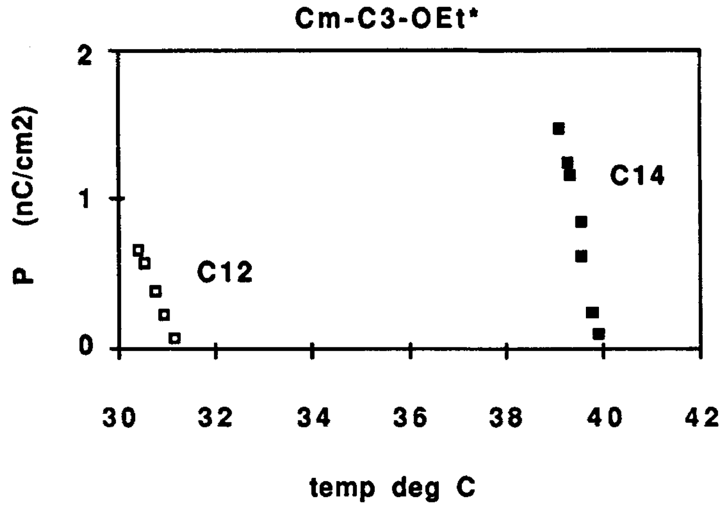


FIGURE 2 Spontaneous polarization for the two members C12-C3-OEt* and C14-C3-OEt* of the homologous series 2, $n = 3$.

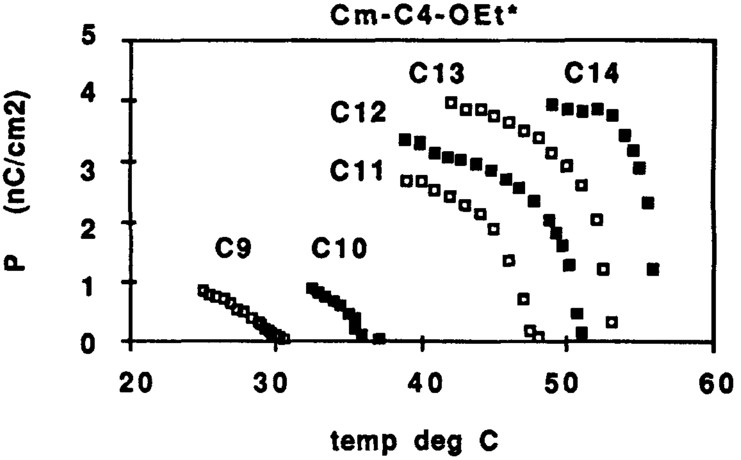


FIGURE 3 Spontaneous polarization as a function of temperature for the homologous series 2, $n = 4$.

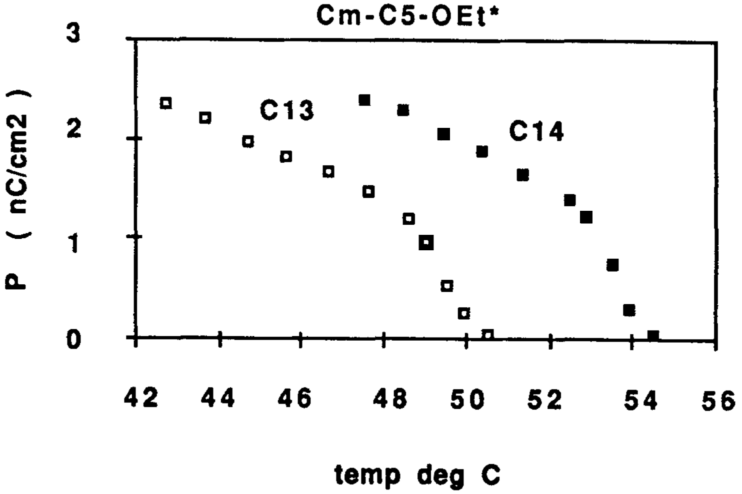


FIGURE 4 Spontaneous polarization as a function of temperature for the two members C13-C5-OEt* and C14-C5-OEt* of the homologous series 2, $n = 5$.

The sign[17] of the spontaneous polarization, as defined by the relation $P = P_0\, \hat{z} \times \hat{n}$ is found to be positive, for all members within the same homologous series as well as for the three different series. (Here $\hat{n}$ is the director and $\hat{z}$ is the smectic layer normal). A odd-even effect on the sign of the spontaneous polarization related to whether the chiral center is moved outwards or inwards from the core of the molecule is thus not observed.

In Figures 5, 6 and 7 is shown the tilt angle as a function of temperature for the three series.

The relation between polarization and tilt angle can be expected to be approximately linear and indeed, this is found even at quite large values of tilt. The quotient polarization / tilt angle is practically

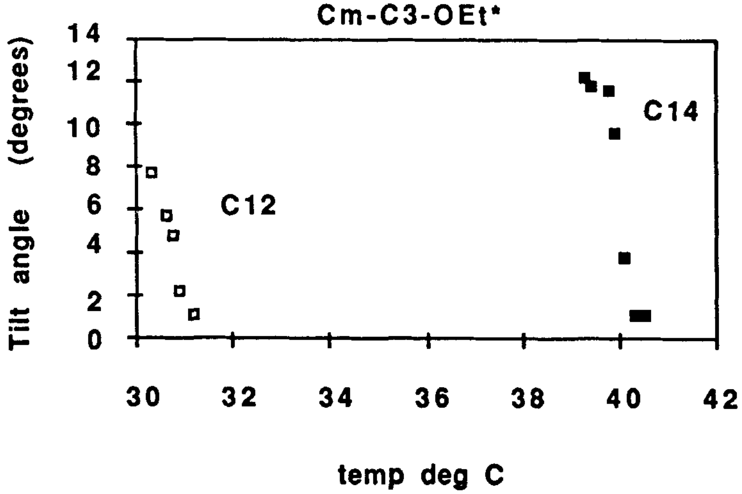


FIGURE 5 Tilt angle as a function of temperature for the two members C12-C3-OEt* and C14-C3-OEt* of the homologous series 2, $n=3$.

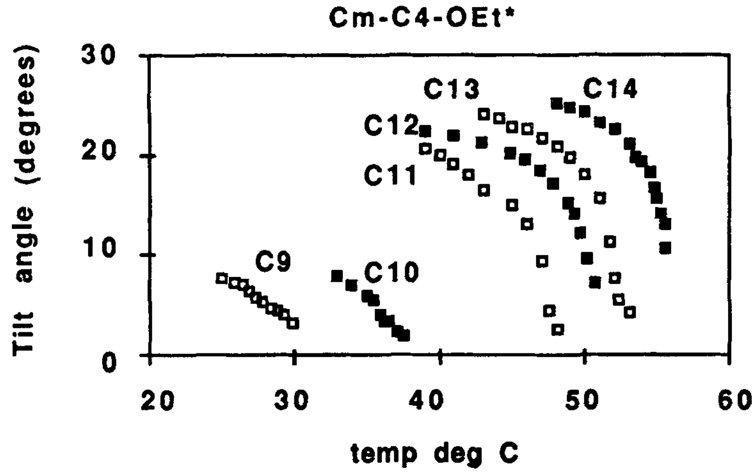


FIGURE 6 Tilt angle as a function of temperature for the homologous series 2, $n=4$.

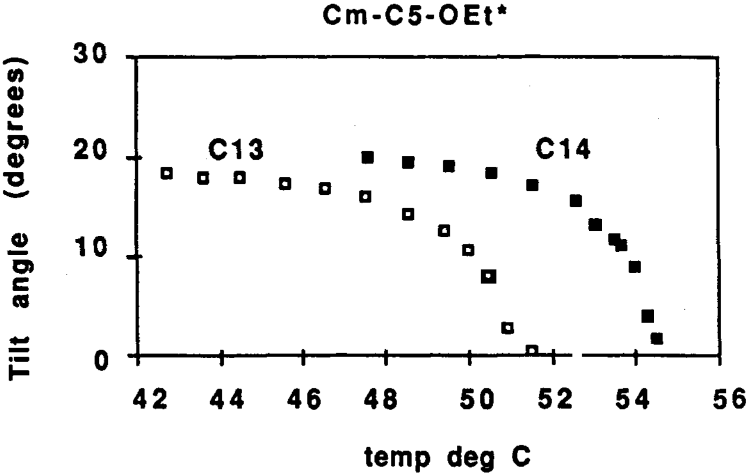


FIGURE 7 Tilt angle as a function of temperature for the two members C13-C5-OEt* and C14-C5-OEt* of the homologous series 2, $n=5$.

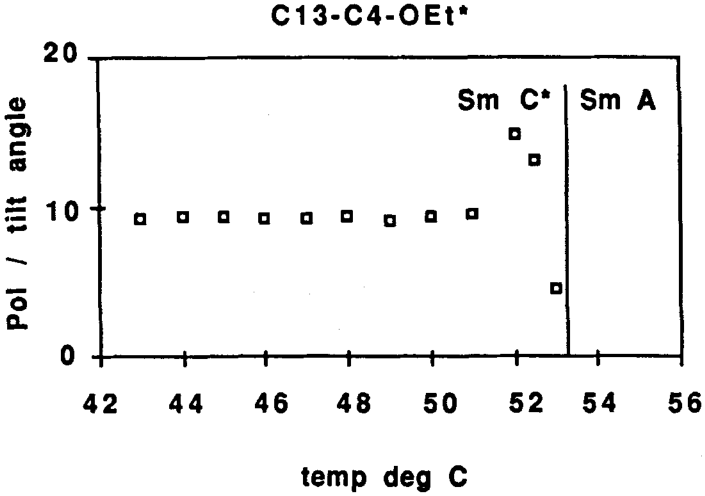


FIGURE 8 The quotient polarization / tilt angle versus temperature for the C13-C4-OEt* compound.

independent of temperature (*cf.* Figures 8, 9 and 10) exept near the phase transition smectic A smectic C*. It should however be noted, that the accuracy of the measurements of both tilt angle and polarization is especially low near the phase transition. From Table IV we can infer a correlation between the length of the non-chiral aliphatic

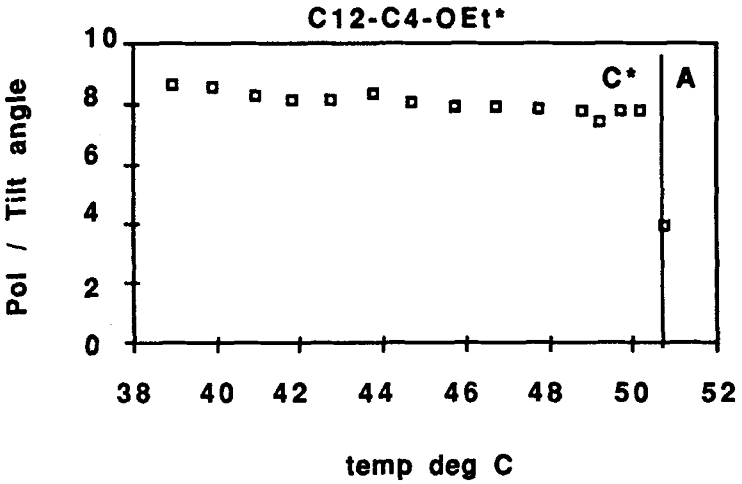


FIGURE 9 The quotient polarization / tilt angle versus temperature for the C12-C4-OEt* compound.

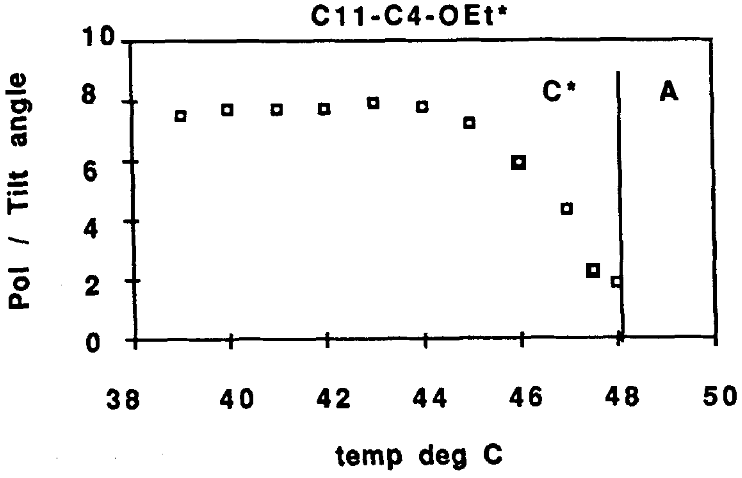


FIGURE 10 The quotient polarization / tilt angle versus temperature for the C11-C4-OEt* compound.

tail (*m* value) and the material constant $P_o$ ($P/\theta$). $P_o$ is increasing with increasing *m* value for this class of compounds.

### Response Time

Our rise time measurements are presented in Table V for the three series. The relative short response times, taking account of the low

TABLE IV

| Compound Cm-Cn-OEt* | | Polarization/tilt angle P/θ (mean values) | |
|---|---|---|---|
| m | n | nC/cm²rad | standard deviation |
| 12 | 3 | 5.0 | 0.5 |
| 14 | 3 | 5.7 | 0.3 |
| 9 | 4 | 5.6 | 0.5 |
| 10 | 4 | 5.2 | 0.8 |
| 11 | 4 | 7.6 | 0.3 |
| 12 | 4 | 8.0 | 0.3 |
| 13 | 4 | 9.3 | 0.1 |
| 14 | 4 | 9.8 | 0.4 |
| 13 | 5 | 6.3 | 0.8 |
| 14 | 5 | 5.9 | 0.6 |

TABLE V

| Compound Cm-Cn-OEt* | | Rise time | $(T-T_c)$ | Field strength |
|---|---|---|---|---|
| m | n | μs | C° | V/μm |
| 12 | 3 | 21 | −0.5 | 15 |
| 14 | 3 | 53 | −0.5 | 15 |
| 9 | 4 | 126 | −3 | 15 |
| 10 | 4 | 175 | −3 | 18 |
| 11 | 4 | 105 | −3 | 20 |
| 12 | 4 | 120 | −3 | 18 |
| 13 | 4 | 100 | −3 | 15 |
| 14 | 4 | 125 | −3 | 15 |
| 13 | 5 | 175 | −3 | 15 |
| 14 | 5 | 150 | −3 | 15 |

polarization values, indicate a relatively low rotational viscosity for this class of compounds, *cf.* Table VI. From the rise time, tilt angle and spontaneous polarization measurements one can estimate the rotational viscosity.

$$\lambda \sim P\,E\,\tau$$

($P$ = Spontaneous polarization; $E$ = Electric field strength; and $\tau$ = Rise time.)

TABLE VI

| Compound | | (T-Tc) | rotational viscosity |
|---|---|---|---|
| Cm-Cn-OEt* | | C° | Centipoise |
| m | n | | γ (P) |
| 12 | 3 | −0.5 | 1.2 |
| 14 | 3 | −0.5 | 5 |
| 9 | 4 | −3 | 9.6 |
| 10 | 4 | −3 | 19 |
| 11 | 4 | −3 | 39 |
| 12 | 4 | −3 | 48 |
| 13 | 4 | −3 | 38 |
| 14 | 4 | −3 | 70 |
| 13 | 5 | −3 | 39 |
| 14 | 5 | −3 | 37 |

### The Smectic C* Pitch

The measurements of helical pitch versus temperature for the smectic C* phases of the three homologous series are presented in Figures 11, 12 and 13.

We also determined the handedness of the helical pitch both for the cholesteric and for the smectic C* phases of the different series. The sign[18] of the helical pitch was determined on a wedge shaped

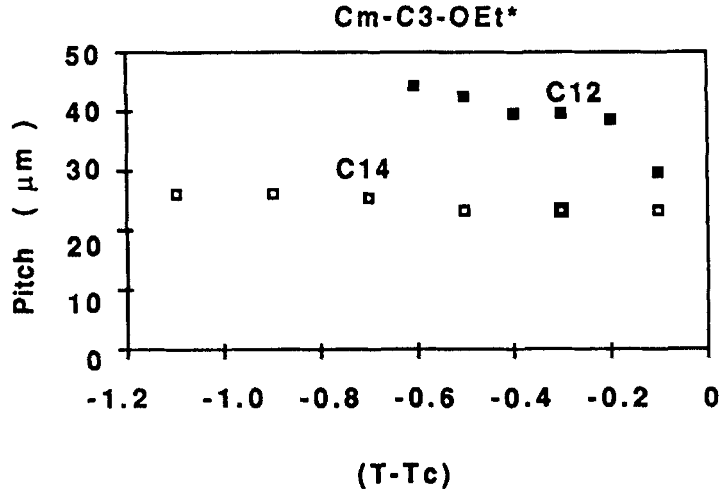


FIGURE 11 Helical pitch versus temperature for the two members C12-C3-OEt* and C14-C3-OEt* of the series 2, $n=3$.

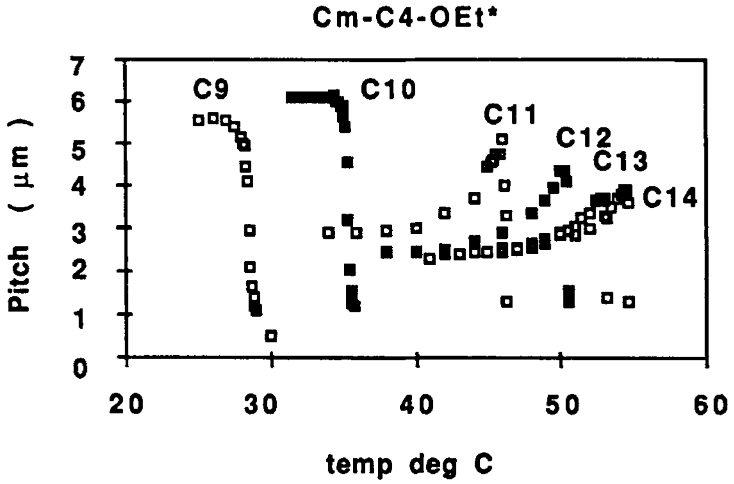


FIGURE 12 Helical pitch versus temperature for the homologous series 2, $n=4$.

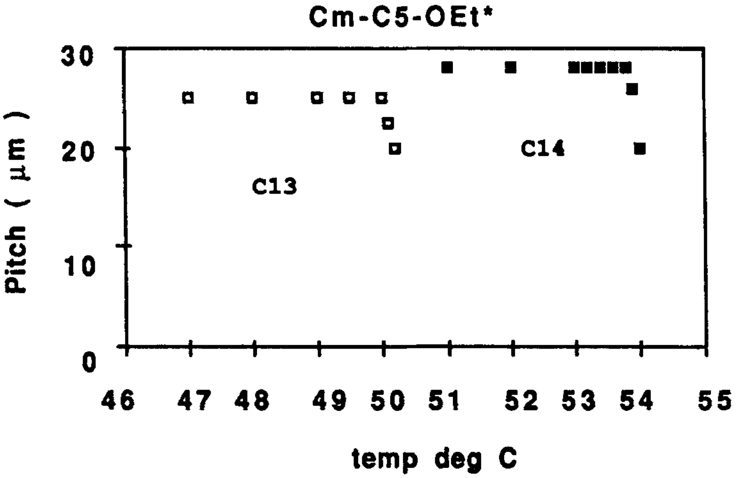


FIGURE 13 Helical pitch versus temperature for the two compounds C13-C5-OEt* and C14-C5-OEt* of the series 2, $n=5$.

sample between crossed polarizers, with the layers parallel to the glass plates and the helical axis standing up towards the observer. The sign (determined from the rotation of the polarization plane of light) was found to be minus, corresponding to lefthandedness, both in the N* phase and in the C* phase and the same for all three homologous series. Thus the sign of the helix in accordance with the sign of the spontaneous polarization does not show any alternation with odd and even chain length for this class of compounds, whereas there is a big difference in the values of the helical pitch (C*) between the *2*, $n=4$ series (3−6 μm), the *2*, $n=5$ (~30μm) and the *2*, $n=3$ series (~40μm).

## DISCUSSION

The lack of conformational rigidity generally prevents any prediction of the direction of the spontaneous polarization. However, assuming the zig-zag model of Bartolino *et al.*[19] and following the discussion of Walba *et al.*[3] the positive sign of $P$ can be interpreted as follows: the predominant conformation of the $C_2C_3$ bond is left-handed *gauche* ($g^-$) and the optic tilt ($\theta_o$) is larger than the steric tilt ($\theta_s$) *or*, the predominant conformation is right-handed *gauche* ($g^+$) and $\theta_s$ is larger than $\theta_o$ (see Figure 14). Then to maintain the positive sign of $P$, as the asymmetric center is moved sequentially away from the core, the predominant conformation will change alternately between $g^-$ and $g^+$ if the relation between the steric and optic tilt remains the same. Or conversely, if the conformation remains the same, the relation between the optic and steric tilt will change, which however seems less likely (*cf.* Figure 15).

This is in sharp contrast to the cases described by Goodby *et al.*[1,2] which show an alternation of the sign of the spontaneous polarization as the asymmetric carbon is moved incrementally along the carbon chain of the molecule. However, this situation was found to be valid

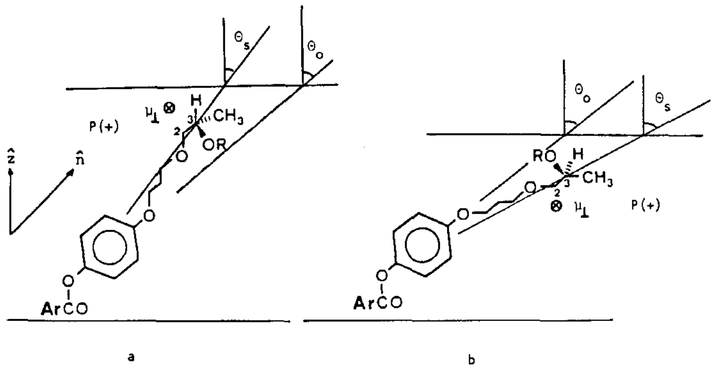


FIGURE 14 a. $n=3$, conformation of $C_2C_3$-bond is $g^-$ and $\theta_o$ is larger than $\theta_s$ b. $n=3$, conformation of $C_2C_3$-bond is $g^+$ and $\theta_s$ is larger than $\theta_o$

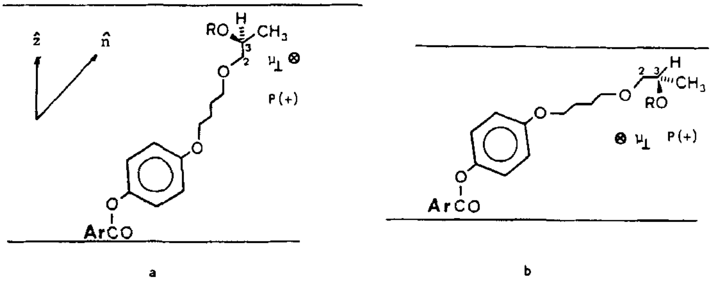
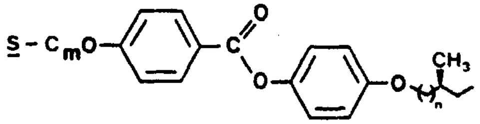


FIGURE 15 a. $n=4$, conformation of $C_2C_3$-bond is $g^+$ and $\theta_o$ is larger than $\theta_s$ b. $n=4$, conformation of $C_2C_3$-bond is $g^-$ and $\theta_s$ is larger than $\theta_o$

only for compounds possessing the relatively non-polar chiral 2-methylbutyl unit.

It is presently an important task to explore the range of applicability of the different structural models with respect to different systems. In this context one should note that different conventions regarding the direction of the dipole moment is used: the group at Bell Labs[1,2] takes the dipole as to be directed from + to − whereas we are using (like Walba *et al.*[3]) the opposite (physical) convention.

As for the strength of the polarization we remark that when the asymmetric center is moved away from the core only a fairly weak decrease in the *P*-value is observed. For instance, the compounds belonging to series *1* are characterized by polarization values around 6–10 nC/cm$^2$ (*cf.* ref. 3), whereas the compounds belonging to series *2* have values around 4 nC/cm$^2$. Even more relevant would be a comparison of the $P_0$ values, *cf.* for instance the values for compounds $C_{14}$-$C_4$-OEt* and $C_{14}$-$C_5$-OEt* from our Table IV. A strikingly different behaviour is quite common, for instance in systems like the phenyl benzoate series[12] where the polarization strength falls off



drastically[20] when *n* increases from 1 to 3. Our interpretation is that in this latter case the dipole moments contributing to the polarization have their origin in the core system and feel an asymmetric influence from the "chiral part" which is rapidly decreasing as the asymmetric center is moved away. In the series *2*, on the other hand, the major contributing dipoles are directly attached to the asymmetric center and thus less dependent on the location relative to the core. The small decrease in $P$ as $n$ increases can be attributed to increased internal rotation of the tail.

## EXPERIMENTAL

NMR spectra were recorded on a Bruker WH-270 instrument at 270 MHz or on a Varian XL-400 instrument at 400 MHz and high resolution mass spectra were recorded on a ZAB/HF VG analytical spectrometer. IR spectra were taken on a Perkin-Elmer 197 spectrometer and specific rotations (values for compounds *2* and *3* are shown in Tables VII and VIII, respectively) were obtained on a Perkin-Elmer 141 or a Perkin-Elmer 241 polarimeter. Texture observations were made using an Olympus BHA polarizing microscope and phase transitions were determined using a Perkin-Elmer DSC7 apparatus. Chromatographic purifications were performed using flash chromatography on Merck 40–63 μ normal phase silica gel with pentane/diethyl ether (P/E) mixtures as eluent. Diethyl ether and tetrahydrofurane (THF) were distilled from sodium and dimethylformamide (DMF), dichloromethane and pyridine were distilled from calcium hydride prior to use. *p*-Alkoxybenzoic acids were purchased from Frinton Laboratories or obtained from *p*-hydroxybenzoic acid under standard Williamson etherification conditions. The corresponding acid chlorides were prepared by treatment of the acids with freshly distilled oxalyl chloride in dry benzene and subsequent distillation on a Kugelrohr apparatus.

*(S)-Ethyl 2-(tetrahydropyranyloxy)propionate.* Dihydropyrane (14.4 ml, 0.16 mol, distilled prior to use) was added to (*S*)-ethyl lactate (20.0 g, 0.17 mol) *via* syringe at 0° C and under argon. Concentrated HCl (10 drops) was added and the reaction mixture was stirred for three hours at room temperature. The reaction mixture was diluted with diethyl ether and the resulting solution was washed with 10% NaOH and dried over anhydrous sodium sulfate. After evaporation of the solvent the residue was distilled (104–8 °C/8 mmHg) to afford 28.6 g (84%) of (*S*)-ethyl 2-(tetrahydro-2-pyranyloxy)propionate.

$[\alpha]_D$-39.7° (3.08, $CHCl_3$), NMR (270, $CDCl_3$)[21]: δ 1.28 (two t, J = 6.5 Hz, 3H), 1.39 and 1.46 (two d, J = 6.7 Hz, 3H), 1.5 – 1.9 (m, 6H), 3.48 (m, 1H), 3.87 (m, 1H), 4.19 (m, 2H), 4.19 and 4.4 (two

TABLE VII

Specific rotations of series *2*

| n | m | $[\alpha]_D$[a] | C[b] |
|---|---|---|---|
| 3 | 8 | +0.53 | 2.62[c] |
| 3 | 9 | +0.38 | 1.82[d] |
| 3 | 10 | +1.61 | 6.88[e] |
| 3 | 12 | +0.45 | 3.75[c] |
| 3 | 13 | +0.42 | 2.37[d] |
| 3 | 14 | +0.47 | 2.74[d] |
| 4 | 8 | −0.84 | 2.37[d] |
| 4 | 9 | — | — |
| 4 | 10 | −0.70 | 0.713[d] |
| 4 | 11 | −0.51 | 2.37[d] |
| 4 | 12 | +1.17 | 0.942[e] |
| 4 | 13 | −0.25 | 3.22[d] |
| 4 | 14 | −0.38 | 2.12[d] |
| 5 | 8 | +0.69 | 3.90[e] |
| 5 | 9 | −1.00 | 1.79[d] |
| 5 | 10 | −0.76 | 1.71[d] |
| 5 | 11 | +0.64 | 4.03[c] |
| 5 | 11 | −0.73 | 5.45[d] |
| 5 | 12 | −0.98 | 2.05[d] |
| 5 | 13 | −0.82 | 2.44[d] |
| 5 | 14 | −0.77 | 2.21[d] |
| 5 | 14 | +0.41 | 1.21[e] |

[a] grad cm$^3$ g$^{-1}$ dm$^{-1}$;
[b] g (100 cm$^3$)$^{-1}$;
[c] $CDCl_3$;
[d] $CHCl_3$;
[e] $CH_2Cl_2$.

q, 1H), 4.7 (m, 1H), IR ($CDCl_3$): 2940, 2860, 1730, 1200, 1120, 1035, 1020, 980 cm$^{-1}$.

*(S)-2-(Tetrahydro-2-pyranyloxy)propanol.* A suspension of lithium aluminum hydride (4.04 g, 0.106 mol) in dry diethyl ether (90 ml) was cooled to 0° C. A solution of (*S*)-ethyl 2-(tetrahydro-2-pyranyloxy)propionate (28.6 g, 0.142 mol) in dry diethyl ether (40 ml) was added during one hour. The reaction mixture was allowed to come to room temperature and stirred for an additional 4 hours. Water and 10% NaOH were added until a white solid was formed which was filtered off and the filtrate was dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was distilled

TABLE VIII

Specific rotations of series *3*

| n | m | $[\alpha]_D$[a] | C[b] |
|---|---|---|---|
| 3 | 12 | −3.34 | 2.04 |
| 3 | 13 | −4.47 | 2.17 |
| 3 | 14 | −4.32 | 2.08 |
| 4 | 8 | −4.24 | 2.03 |
| 4 | 10 | −4.03 | 1.76 |
| 4 | 11 | −3.98 | 2.84 |
| 4 | 12 | −3.68 | 9.25 |
| 4 | 13 | −3.21 | 1.43 |
| 4 | 14 | −3.72 | 3.89 |
| 5 | 11 | −3.77 | 1.17 |
| 5 | 12 | −3.58 | 1.62 |
| 5 | 13 | −3.40 | 2.77 |
| 5 | 14 | −3.35 | 4.24 |

[a] grad $cm^3\ g^{-1}\ dm^{-1}$;
[b] $g\ (100\ cm)^{-3}$, $CH_2Cl_2$.

(101–5° C/8 mmHg) to yield 16.8 g (74%) of (*S*)-2-(tetrahydro-2-pyranyloxy)propanol.

NMR (270, $CDCl_3$)[21]: δ 1.17 and 1.124 (two d, J = 6.7 Hz, 3H), 1.5–1.9 (m, 6H), 2.07 (dd, 1H), 3.53 (m, 3H), 3.91 (m, 2H), 4.57 and 4.74 (two t, 1H), IR ($CDCl_3$): 3580, 3400, 2940, 2850, 1130, 1075, 1020 $cm^{-1}$.

*(S)-2-(Tetrahydro-2-pyranyloxy)propyl tosylate 4.* (*S*)-2-(Tetrahydro-2-pyranyloxy)propanol (35.1 g, 0.219 mol) was dissolved in pyridine (45 ml). *p*-Tosyl chloride (41.8 g, 0.22 mol) was added in small portions at 0° C. The resulting slurry was stirred for one hour at 0° C and then placed in the refrigerator over night. The reaction mixture was diluted with water and extracted twice with diethyl ether. The combined organic layers were washed several times with aqueous copper sulfate, once with brine and dried over anhydrous sodium sulfate. Evaporation of the solvent and drying in vacuum afforded 62.0 g (90%) of tosylate *4*.

NMR (400, $CDCl_3$)[21]: δ 1.12 and 1.20 (two d, J = 6.7 Hz, 3H), 1.45–1.8 (m, 6H), 2.45 (s, 3H), 3.47 (m, 1H), 3.81 (m, 1H), 3.95 (m, 2H), 3.95 and 4.10 (two m, 1H), 4.62 and 4.68 (two t, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), IR ($CDCl_3$): 2950, 1350, 1210, 1175 $cm^{-1}$.

*General procedure for preparing primary alcohols 5–7.* Sodium hydride (1.45 g, *ca* 33.3 mmol) (55% dispersion in oil) was washed several times with dry pentane and was then suspended in dry DMF (30 ml). The suspension was cooled to 0° C and the appropriate diol (*ca* 80 mmol) dissolved in dry DMF (40 ml) was added *via* syringe. The reaction mixture was stirred at 0° C and under argon for one hour and tosylate *4* (3.96 g, 16.6 mmol) dissolved in dry DMF (30 ml) was added *via* syringe. After refluxing two hours the reaction mixture was diluted with water and extracted three times with diethyl ether. The combined organic layers were washed twice with aqueous sodium hydrogencarbonate and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was flash chromatographed (E containing 1% triethylamine) to yield 40–60% of alcohols *5–7*.

Physical data compound *5*[21]: $[\alpha]_D$+3.08° (3.38, $CHCl_3$), NMR (400, $CDCl_3$): δ 1.15 and 1.22 (two d, J = 6.7 Hz, 3H), 1.5–1.8 (m, 6H), 1.83 (quintet, J = 6.3 Hz, 2H), 3.4–3.55 (m, 2H), 3.6–4.05 (m, 7H), 4.69 and 4.76 (two t, 1H), IR ($CDCl_3$): 3500, 2940, 2860, 1120, 1075, 1030 $cm^{-1}$.

Physical data compound *6*[21]: $[\alpha]_D$+2.56° (4.50, $CHCl_3$), NMR (270, $CDCl_3$): δ 1.16 and 1.23 (two d, J = 6.7 Hz, 3H), 1.5–1.9 (m, 10H), 3.4–3.7 (m, 6H), 3.9 (m, 3H), 4.72 and 4.78 (two t, 1H), IR ($CDCl_3$): 3500, 2940, 2860, 1120, 1075, 1030 $cm^{-1}$.

Physical data compound *7*[21]: $[\alpha]_D$−1.61° (2.48, $CHCl_3$), NMR (400, $CDCl_3$): δ 1.16 and 1.22 (two d, J = 6.7 Hz, 3H), 1.4–1.9 (m, 12H), 3.3–3.7 (m, 6H), 3.95 (m, 3H), 4.72 and 4.80 (two t, 1H), IR ($CDCl_3$): 3620, 2940, 2860, 1120, 1075, 1020 $cm^{-1}$.

*General procedure for mesylation of alcohols 5–7.* Alcohol *5–7* (10 mmol) was dissolved in dry dichloromethane (40 ml) and cooled to 0° C and kept under argon. Freshly distilled triethylamine (1.3 equ.) and mesyl chloride (1.3 equ.) (distilled prior to use) were added *via* syringe and the resulting mixture was stirred at 0° C for one hour. Diethyl ether (60 ml) was added and the organic solution was washed with brine and dried over anhydrous sodium sulfate. Evaporation of the solvent and drying in vacuum furnished mesylates *8–10* in quantitative yields.

Physical data compound *8*[21]: $[\alpha]_D$ +2.09° (3.58, $CHCl_3$), NMR (400, $CDCl_3$): δ 1.15 and 1.21 (two d, J = 6.7 Hz, 3H), 1.5–1.9 (m, 6H), 2.0 (quintet, J = 6.3 Hz, 2H), 3.02 (s, 3H), 3.4–3.7 (m, 5H), 3.95 (m, 2H), 4.35 (two t, 2H), 4.70 and 4.77 (two t, 1H), IR ($CDCl_3$): 2940, 2860, 1350, 1330, 1170, 1120 $cm^{-1}$.

Physical data compound *9*[21]: $[\alpha]_D -5.99°$ (3.67, $CHCl_3$), NMR (270, $CDCl_3$): δ 1.15 and 1.22 (two d, J = 6.7 Hz, 3H), 1.4 – 1.9 (m, 10H), 3.02 (s, 3H), 3.3–3.6 (m, 5H), 3.92 (m, 2H), 4.77 (two t, 2H), 4.72 and 4.77 (two t, 1H), IR ($CDCl_3$): 2940, 2860, 1350, 1330, 1170, 1120 $cm^{-1}$. Physical data compound *10*[21]: $[\alpha]_D$ $-1.44°$ (3.75, $CHCl_3$), NMR (400, $CDCl_3$): δ 1.16 and 1.22 (two d, J = 6.7 Hz, 3H), 1.45–1.9 (m, 12H), 3.02 (s, 3H), 3.35 – 3.6 (m, 5H), 3.95 (m, 2H), 4.22 (t, 2H), 4.72 and 4.79 (two t, 1H) IR ($CDCl_3$): 2940, 2860, 1350, 1330, 1170, 1120 $cm^{-1}$.

*General procedure for preparing secondary alcohols 11–13.* A suspension of sodium hydride (8 mmol) (55% dispersion in oil, washed several times with dry pentane) in DMF (10 ml) was cooled to 0° C and kept under argon. 4-Benzyloxyphenol (1.23 g, 6.15 mmol) dissolved in DMF (15 ml) was added *via* syringe and the resulting mixture was stirred under argon and at 0° C for one hour. Mesylate *8–10* (6.15 mmol) dissolved in dry DMF (10 ml) was added *via* syringe and the reaction mixture was refluxed for one hour. Water was added and the resulting suspension was extracted three times with diethyl ether and the combined organic layers were washed two times with 5% NaOH and once with brine. Evaporation of the solvent left a yellow oil which was dissolved in ethanol (15 ml) and pyridinium *p*-toluene sulfonate (10 mol%) was added and the reaction mixture was stirred at 55° C for 4 hours. Evaporation of the solvent and flash chromatography (P/E 1:3) afforded *ca* 80% of alcohols *11–13* as white solids which were recrystallized from ethanol.

Physical data for compound *11*: Mp. 59–60.5° C, $[\alpha]_D + 11.0°$ (2.64, $CHCl_3$), NMR (400, $CDCl_3$): δ 1.14 (d, J = 6.7 Hz, 3H), 2.04 (quintet, J = 6.3 Hz, 2H), 2.38 (d, 1H), 3.25 (dd, $J_{gem}$ = 10 Hz, $J_{vic}$ = 6 Hz, 1H), 3.46 (dd, $J_{gem}$ = 10 Hz, $J_{vic}$ = 5 Hz, 1H), 3.56 (m, 2H), 3.97 (m, 1H), 4.02 (t, 2H), 5.02 (s, 2H), 6.83 (d, J = 9.2 Hz, 2H), 6.90 (d, J = 9.2 Hz, 2H), 7.39 (m, 5H), IR ($CDCl_3$): 3570, 2930, 2850, 1500, 1375, 1220, 1110, 1020, 820 $cm^{-1}$.

Physical data compound *12*: Mp. 62–63.5° C, $[\alpha]_D + 9.40$ (3.32, $CHCl_3$), NMR (270, $CDCl_3$): δ 1.16 (d, J = 6.7 Hz, 3H), 1.78 (m, 2H), 1.83 (m, 2H), 2.38 (d, 1H), 3.21 (dd, $J_{gem}$ = 10 Hz, $J_{vic}$ = 6 Hz, 1H), 3.42 (dd, $J_{gem}$ = 10 Hz, $J_{vic}$ = 5 Hz, 1H), 3.52 (m, 2H), 3.93 (m, 1H), 3.95 (t, 2H), 5.02 (s, 2H), 6.83 (d, J = 9.2 Hz, 2H), 6.90 (d, J = 9.2 Hz, 2H), 7.39 (m, 5H), IR ($CDCl_3$): 3570, 2930, 2850, 1500, 1375, 1220, 1110, 1020, 820 $cm^{-1}$.

Physical data compound *13*: Mp. 70–71° C, $[\alpha]_D + 8.83°$ (2.66, $CHCl_3$), NMR (400, $CDCl_3$): δ 1.15 (d, J = 6.7 Hz, 3H), 1.52 (m, 2H), 1.66 (m, 2H), 1.79 (m, 2H), 2.38 (d, 1H), 3.20 (dd, $J_{gem} = 10$ Hz, $J_{vic} = 6$ Hz, 1H), 3.40 (dd, $J_{gem} = 10$ Hz, $J_{vic} = 5$ Hz, 1H), 3.49 (m, 2H), 3.91 (t, 2H), 3.96 (m, 1H), 5.02 (s, 2H), 6.82 (d, J = 9.2 Hz, 2H), 6.90 (d, J = 9.2 Hz, 2H), 7.40 (m, 5H), IR ($CDCl_3$): 3560, 2940, 2860, 1500, 1230, 1210, 1110, 1020, 820 $cm^{-1}$.

*General procedure for etherification of secondary alcohols 11–13.* A suspension of sodium hydride (12.7 mmol) (55% dispersion in oil, washed several times with dry pentane) in DMF (15 ml) was cooled on ice bath and kept under argon. Alcohol *11–13* (5.06 mmol) dissolved in DMF (20 ml) was added *via* syringe and the resulting mixture was stirred at 0° C for 45 minutes. Ethyl bromide (0.95 ml, *ca* 2.5 equ.) (distilled from calcium chloride prior to use) was added *via* syringe and the reaction mixture was stirred at room temperature for 5 hours. Water was added cautiously and the resulting suspension was extracted twice with diethyl ether. The combined organic layers were washed with brine and dried over anhydrous magnesium sulfate. After evaporation of the solvent the crude product was flash chromatographed (P/E 7:3) affording 85–90% of ethers *14–16* which were debenzylated without further characterization.

*General procedure for chlorination of secondary alcohols 11–13.* Dry pyridine (0.7 ml, 1.3 equ.) and freshly distilled thionyl chloride (0.6 ml, 1.3 equ.) dissolved in dry dichloromethane (12 ml) was cooled to 0° C and kept under argon. Alcohol *11–13* (6.06 mmol) in dry dichloromethane (12 ml) was added *via* syringe. The reaction mixture was refluxed for 2.5 hours and 2M HCl was added cautiously and the resulting mixture was extracted twice with diethyl ether. The combined organic layers were washed with 2M HCl, brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent and flash chromatography (P/E 9:1) afforded chlorides *17–19* (60–75%) which were debenzylated without further characterization.

*General procedure for debenzylation of ethers 14–16.* Ethers *14–16* (9.16 mmol) was dissolved in ethanol (60 ml) and charged with palladium on carbon (10%, *ca* 1.5 g). The flask was filled with hydrogen and the reaction mixture was stirred under hydrogen atmosphere and at room temperature for 20 hours and was then filtered through Celite. The filtrate was evaporated and the residue was flash chromatographed (P/E 1:1) furnishing phenols *20–22* as colorless oils in 85–95% yields.

Physical data compound *20*: $[\alpha]_D + 4.52°$ (3.38, $CHCl_3$), NMR (400, $CDCl_3$): δ 1.14 (d, J = 6.5 Hz, 3H), 1.18 (t, J = 7 Hz, 3H), 2.02

(quintet, J = 7 Hz, 2H), 3.37 (dd, $J_{gem}$ = 10 Hz, $J_{vic}$ = 4.5 Hz, 1H), 3.46 (dd, $J_{gem}$ = 10 Hz, $J_{vic}$ = 6 Hz, 1H), 3.50–3.64 (m, 3H), 3.63 (t, J = 6.3 Hz, 2H), 3.99 (t, J = 6.3 Hz, 2H), 4.7 (broad s, 1H), 6.76 (m, 4H), IR ($CDCl_3$): 3590, 2960, 2860, 1505, 1480, 1375, 1230, 1210, 1175, 1095, 820 $cm^{-1}$.

Physical data compound *21*: $[\alpha]_D + 4.21°$ (2.85, $CHCl_3$), NMR (400, $CDCl_3$): δ 1.16 (d, J = 6.5 Hz, 3H), 1.18 (t, J = 7 Hz, 3H), 1.74 (m, 2H), 1.82 (m, 2H), 3.36 (dd, $J_{gem}$ = 10 Hz, $J_{vic}$ = 5 Hz, 1H), 3.46 (dd, $J_{gem}$ = 10 Hz, $J_{vic}$ = 6 Hz, 1H), 3.53 (t, J = 6.5 Hz, 2H), 3.50–3.64 (m, 3H), 3.92 (t, J = 6.5 Hz, 2H), 4.6 (broad s, 1H), 6.77 (m, 4H), IR ($CDCl_3$): 3590, 2960, 2860, 1510, 1430, 1330, 1230, 1210, 1175, 1100, 820 $cm^{-1}$.

Physical data compound *22*: $[\alpha]_D + 2.88°$ (3.96, $CHCl_3$), NMR (400, $CDCl_3$): δ 1.15 (d, J = 6.5 Hz, 3H), 1.20 (t, J = 7 Hz, 3H) 1.51 (m, 2H), 1.63 (m, 2H), 1.77 (m, 2H), 3.34 (dd, $J_{gem}$ = 10 Hz, $J_{vic}$ = 5 Hz, 1H), 3.45 (dd, $J_{gem}$ = 10 Hz, $J_{vic}$ = 6 Hz, 1H), 3.48 (t, J = 6.5 Hz, 2H), 3.51–3.62 (m, 3H), 3.89 (t, J = 6.5 Hz, 2H), 4.5 (broad s, 1H), 6.76 (m, 4H), IR($CDCl_3$): 3590, 2940, 2860, 1510, 1230, 1210, 1175, 1100, 820 $cm^{-1}$.

*General procedure for debenzylation of chlorides 17–19.* The benzylation of chlorides *17–19* were carried out using acetic acid as solvent otherwise the procedure of debenzylation of ethers *14–16* was followed. Flash chromatography (P/E 1:1) afforded phenols *23–25* as colorless oils in 70–80% yields.

Physical data compound *23*: $[\alpha]_D - 8.82°$ (4.23, $CH_2Cl_2$), NMR (270, $CDCl_3$): δ 1.51 (d, J = 6.7 Hz, 3H), 2.03 (quintet, J = 6.2 Hz, 2H), 3.53 (dd, $J_{gem}$ = 10 Hz, $J_{vic}$ = 6.5 Hz, 1H), 3.62 (dd, $J_{gem}$ = 10 Hz, $J_{vic}$ = 5 Hz, 1H) 3.69 (t, J = 6.5 Hz, 2H), 4.03 (t, J = 6.5 Hz, 2H), 4.12 (m, 1H), 6.78 (m, 4H), IR($CDCl_3$): 3590, 2950, 2860, 1510, 1230, 1175, 860, 820 $cm^{-1}$.

Physical data compound *24*: $[\alpha]_D - 7.88°$ (4.14, $CH_2Cl_2$), NMR (400, $CDCl_3$): δ 1.51 (d, J = 6.7 Hz, 3H), 1.76 (m, 2H), 1.83 (m, 2H), 3.53 (m, 4H), 3.93 (t, J = 6.5 Hz, 2H), 4.11 (m, 1H), 4.40 (broad s, 1H), 6.77 (m, 4H), IR($CDCl_3$): 3590, 2940, 2860, 1510, 1230, 1210, 1175, 860, 820 $cm^{-1}$.

Physical data compound *25*: $[\alpha]_D - 7.09°$ (3.58, $CH_2Cl_2$), NMR (270, $CDCl_3$): δ 1.53 (d, J = 6.7 Hz, 3H), 1.55 (m, 2H), 1.67 (m, 2H), 1.80 (m, 2H), 3.52 (m, 4H), 3.90 (t, J = 6.5 Hz, 2H), 4.11 (m, 1H), 4.36 (s, 1H), 6.77 (m, 4H), IR ($CDCl_3$): 3590, 2940, 2860, 1505, 1230, 1210, 1175, 860, 820 $cm^{-1}$.

*General procedure for coupling of phenols 20–22 with p-alkoxy-*

*benzoyl chlorides.* To a suspension of oil-free sodium hydride (2.22 mmol, washed with dry pentane) in THF (40 ml) was added phenols *20–22* (2.02 mmol) dissolved in THF (10 ml). The phenolate was generated under argon at ambient temperature for 15 minutes. Acid chloride (2.02 mmol) dissolved in THF (10 ml) was added *via* syringe and the reaction mixture was stirred at room temperature for 20 hours. The reaction mixture was diluted with water and extracted twice with diethyl ether. The combined organic layers were washed with 2M HCl, 5% NaOH and brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by flash chromatography (P/E 9:1) furnished target esters *2* in 60–93% yields. The liquid crystal materials were recrystallized from pentane until a clearing point interval of less than 0.5 degrees was obtained.

NMR and IR spectra are identical for each compound with the same value of *n* and thus the physical data are not given for each individual compound.

Physical data compound *2*, $n=3$, NMR (270, $CDCl_3$, $R=C_x$) δ 0.90 (t, J=6.5 Hz, 3H), 1.15 (d, J=6.5 Hz, 3H), 1.19 (t, J=7 Hz, 3H), 1.29 (m, 2x−8H), 1.45 (m, 2H), 1.82 (m, 2H), 2.05 (quintett, J=6.3 Hz, 2H), 3.35 (dd, $J_{gem}=10$ Hz, $J_{vic}=5$ Hz, 1H) 3.45 (dd, $J_{gem}=10$ Hz, $J_{vic}=6$ Hz, 1H), 3.4–3.6 (m, 3H), 3.62 (t, J=6 Hz, 2H), 4.03 (t, J=6.5 Hz, 2H), 4.07 (t, J=6 Hz, 2H), 6.93 (m, 4H), 7.1 (d, J=9.2 Hz, 2H), 8.13 (d, J=9.2 Hz, 2H), IR($CHCl_3$): 2920, 2850, 1720, 1600, 1500, 1250, 1190, 1160, 1075 $cm^{-1}$.

$C_{14}$-$C_3$-OEt*: Mol. wt., obs. 570.393, calc. 570.392, MS [El 70 ev; m/e (% rel. int.)] 571 ($M^+$ +1, 2) 570 ($M^+$, 6), 318 (22), 317 (100), 121 (38).

Physical data compound *2*, $n=4$: NMR (400, $CDCl_3$, $R=C_x$): δ 0.89 (t, J=6.6 Hz, 3H), 1.16 (d, J=6.3 Hz, 3H), 1.20 (t, J=7 Hz, 3H), 1.27 (m, 2x−8H), 1.47 (m, 2H), 1.8 (m, 6H), 3.36 (dd, $J_{gem}=10$ Hz, $J_{vic}=5$ Hz, 1H) 3.47 (dd, $J_{gem}=10$ Hz, $J_{vic}=6$ Hz, 1H), 3.53 (t, J=6.5 Hz, 2H), 3.54–3.64 (m, 3H), 3.99 (t, J=6.3 Hz, 2H), 4.04 (t, J=6.5 Hz, 2H), 6.93 (m, 4H), 7.10 (d, J=9.2 Hz, 2H), 8.13 (d, J=9.2 Hz, 2H), IR($CHCl_3$): 2920, 2850, 1720, 1600, 1500, 1250, 1190, 1160, 1075 $cm^{-1}$.

$C_9$-$C_4$-OEt*: Mol. wt., obs. 514.331, calc. 514.329, MS [El 70 eV; m/e (% rel. int.)] 514 ($M^+$, 2), 248 (18), 247 (100), 121 (45).

Physical data compound *2*, $n=5$: NMR (270, $CDCl_3$, $R=C_x$): δ 0.88 (t, J=6.5 Hz, 3H), 1.16 (d, J=6.5 Hz, 3H), 1.20 (t, J=7 Hz, 3H), 1.29 (m, 2x−8H), 1.53 (m, 2H), 1.65 (m, 2H), 1.83 (m, 6H), 3.35 (dd, $J_{gem}=10$ Hz, $J_{vic}=5$ Hz, 1H), 3.47 (dd, $J_{gem}=10$ Hz, $J_{vic}=6$ Hz, 1H), 3.50 (t, J=6.5 Hz, 2H), 3.45–3.65 (m, 3H), 3.98 (t, J=6.5

Hz, 2H), 4.03 (t, J = 6.5 Hz, 2H), 6.93 (m, 4H), 7.10 (d, J = 9.2 Hz, 2H), 8.13 (d, J = 9.2 Hz, 2H), IR($CHCl_3$): 2920, 2850, 1720, 1600, 1500, 1250, 1190, 1160, 1075 $cm^{-1}$.

$C_{11}$-$C_5$-OEt*: Mol. wt., obs. 556.377, calc. 556.376, MS [EI 70 ev; m/e (% rel. int.)] 556 ($M^+$, 3), 276 (17), 275 (100), 121 (33).

*General procedure for coupling of phenols 23–25 with p-alkoxybenzoyl chlorides.* Acid chloride (0.82 mmol) was dissolved in THF (3 ml) and kept under argon. Phenols *23–25* (0.82 mmol) dissolved in THF (3 ml) was added *via* syringe followed by triethylamine (1.3 equ.) The reaction mixture was stirred at ambient temperature over night and was then diluted with water and extracted twice with diethyl ether. The combined organic layers were washed with 2M HCl, 5% NaOH and brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by flash chromatography (P/E 4:1) afforded target esters *3* in 70–85% yields. The liquid crystal materials were recrystallized from pentane until a clearing point interval of less than 0.5 degrees was obtained.

NMR and IR spectra are identical for each compound with the same value of *n* and thus physical data for each individual compound will not be given.

Physical data compound *3*, $n = 3$: NMR (270, $CDCl_3$, R = $C_x$): δ 0.89 (t, J = 6.6 Hz, 3H), 1.32 (m, 2x–8H), 1.50 (m, 2H), 1.52 (d, J = 6.8 Hz, 3H), 1.83 (m, 2H), 2.08 (quintet, J = 6.3 Hz, 2H), 3.45–3.65 (m, 2H), 3.71 (t, J = 6 Hz, 2H), 4.05 (t, J = 6 Hz, 2H), 4.09 (t, J = 6 Hz, 2H), 4.13 (m, 1H), 6.93 (m, 4H), 7.12 (d, J = 9.2 Hz, 2H), 8.13 (d, J = 9.2 Hz, 2H), IR ($CDCl_3$): 2920, 2850, 1720, 1600, 1500, 1250, 1190, 1160, 1075 $cm^{-1}$.

$C_{12}$-$C_3$-Cl*: Mol. wt., obs. 532.294, calc. 532.296, MS [EI 70 eV; m/e (% rel. int.)] 532 ($M^+$, 3), 290 (20), 289 (100), 121 (41).

Physical data compounds *3*, $n = 4$: NMR (400, $CDCl_3$, R = $C_x$): δ 0.89 (t, J = 6.6 Hz, 3H), 1.31 (m, 2x–8H), 1.50 (m, 2H), 1.52 (d, J = 6.8 Hz, 3H), 1.82 (m, 6H), 3.45–3.65 (m, 4H), 4.02 (t, J = 6.3 Hz, 2H), 4.05 (t, J = 6.5 Hz, 2H), 4.12 (m, 1H), 6.93 (m, 4H), 7.10 (d, J = 9.2 Hz, 2H), 8.13 (d, J = 9.2 Hz, 2H), IR ($CDCl_3$): 2920, 2850, 1720, 1600, 1500, 1250, 1190, 1160, 1075 $cm^{-1}$.

$C_{10}$-$C_4$-Cl*: Mol. wt., obs. 518.276, calc. 518.280, MS [EI 70 eV; m/e (% rel. int.)] 518 ($M^+$, 3), 262 (18), 261 (100), 121 (42).

Physical data compounds *3*, $n = 5$: NMR (400, $CDCl_3$, R = $C_x$): δ 0.88 (t, J = 6.6 Hz, 3H), 1.27 (m, 2x–8H), 1.49 (m, 2H), 1.51 (d, J = 6.8 Hz, 3H), 1.67 (m, 2H), 1.82 (m, 6H), 3.45–3.60 (m, 4H), 3.97 (t, J = 6.5 Hz, 2H), 4.03 (t, J = 6.5 Hz, 2H), 4.11 (m, 1H), 6.93

(m, 4H), 7.10 (d, J = 9.2 Hz, 2H), 8.13 (d, J = 9.2 Hz, 2H), IR ($CDCl_3$): 2920, 2850, 1720, 1600, 1500, 1250, 1190, 1160, 1075 $cm^{-1}$.

$C_{13}$-$C_5$-Cl*: Mol. wt., obs. 574.339, calc. 574.343, MS [El 70 eV; m/e (% rel. int.)] 574 ($M^+$, 3), 304 (22), 303 (100), 121 (42).

## Acknowledgments

This work was supported by the National Swedish Board of Technical Development under Grants No. 84-3691 and No. 85-3721. We also want to thank Dr. Thomas Olsson for preparing Figure 1 and Mr. Weston Pimlott for recording the MS spectra.

## References and Notes

1. J. W. Goodby, E. Chin, T. M. Leslie, J. M. Geary and J. S. Patel, *J. Am. Chem. Soc.*, **108**, 4729 (1986).
2. J. W. Goodby and E. Chin, *J. Am. Chem. Soc.*, **108**, 4736 (1986).
3. D. M. Walba, S. C. Slater, W. M. Thurmes, N. A. Clark, M. A. Handschy and F. Supon, *J. Am. Chem. Soc.*, **108**, 5210 (1986).
4. L. A. Paquette and M. K. Scott, *J. Am. Chem. Soc.*, **94**, 6751 (1972).
5. N. Miyashita, A. Yoshikoshi and P. A. Grieco, *J. Org. Chem.*, **42**, 3772 (1977).
6. J. March, *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 2nd ed. (McGraw-Hill, Tokyo, 1977) p. 302.
7. See for example G. W. Gray, *Advances in Liquid Crystals*, (Academic Press, New York, 1976, Ed. G. H. Brown) **2**, p. 1.
8. See for example G. W. Gray and J. W. Goodby, *Smectic Liquid Crystals: Texture and Structure* (Leonard Hill, Glasgow, 1985).
9. C. P. Smyth, *Dielectric Behaviour and Structure* (McGraw-Hill, New York, 1955).
10. J. Dale, *Stereochemistry and Conformation Analysis* (Universitetsforlag, Oslo, 1978).
11. C. Alstermark, M. Nilsson and B. Otterholm, to be published.
12. M. V. Loseva, B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, B. A. Strukov and N. I. Chernova, *JETP* (*Lett.*) **28**, 374 (1978); P. Keller, *Ferroelectrics*, **58**, 1 (1984).
13. T. M. Leslie, *Ferroelectrics*, **58**, 9 (1984).
14. K. Skarp and G. Andersson, *Ferroelectrics* (*Lett.*), **6**, 67 (1986).
15. K. Flatischler, K. Skarp, S. T. Lagerwall and B. Stebler, *Mol. Cryst. Liq. Cryst.*, **131**, 21 (1985).
16. K. Kondo, H. Takezoe, A. Fukuda and E. Kuze, *Jap. J. Appl. Phys.*, **21**, 224 (1982).
17. S. T. Lagerwall and N. A. Clark, *Ferroelectrics*, **59**, 25 (1984).
18. W. Kuczynski, S. T. Lagerwall, M. Matuszczyk, K. Skarp, B. Stebler and J. Wahl, submitted to *Mol. Cryst. Liq. Cryst.*
19. R. Bartolino, J. Doucet and G. Durand, *Ann. Phys.*, **3**, 389 (1978).
20. The Chalmers Liquid Crystal Group, unpublished results.
21. Approx 1:1 diastereomeric mixture.