β-Chlorohydrins vs α-Chloroacids as Chiral Tails for Ferroelectric Liquid Crystals. MM2 Approach. 2[1]

T. Sierra, M. B. Ros, A. Omenat, and J. L. Serrano*

Química Orgánica, Facultad de Ciencias, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009-Zaragoza, Spain

Received January 5, 1993. Revised Manuscript Received April 9, 1993

A new series of β-chlorohydrin-derived chiral compounds (series **ET**) has been synthesized and their mesogenic properties and Ps values studied. Their ferroelectric behavior is compared with that of homologous α-chloroacid derivatives (series **ES**), by means of 10 mol % binary mixtures with a common achiral matrix. Only a slight decrease in the Ps values is observed in the compounds of series **ET** with regard to the compounds in series **ES**. Molecular mechanics empirical calculations (MM2) were carried out in order to determine the importance of steric factors on the Ps values.

Introduction

The search for a model that explains the factors that influence ferroelectric properties is an important target in ferroelectric liquid-crystal research.[2-6]

In a previous paper,[1] we approached this subject by means of empirical calculations. Molecular mechanics empirical calculations allowed us to study the different conformations of several α-X-acid-derived chiral tails and proved to be a successful tool to understand the influence of structural factors on ferroelectric behavior. In this paper we concluded that the steric factors of the chiral tail have an important influence on the values of spontaneous polarization (Ps), by controlling the molecular arrangement within the SmC* phase, and, hence, on the intermolecular interactions of the molecular dipoles.

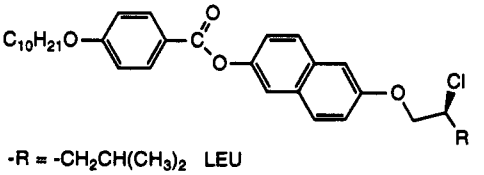
In fact, results from the MM2 study of the α-X-acids showed that the dipoles associated with the C=O and C—X bonds did not add up, but, on the contrary, were mostly in an "anti" position, specially when X had a small volume (e.g., fluorine and chlorine atoms).

Consequently, we believe that a comparative study between the α-chloroacid compounds (already described in the previous paper, series **ES**) and some analogous compounds (series **ET**), in which the C=O group is replaced by a methylene group (see Chart I), would help to corroborate our former conclusion.

With this in mind, we synthesized three new compounds with β-chlorohydrin-chiral tails derived from three natural α-amino acids: leucine, isoleucine, and valine. Their ferroelectric behavior was determined and contrasted with the conformational analysis of the chiral tails (MM2 calculations).

Chart I

SERIES ET

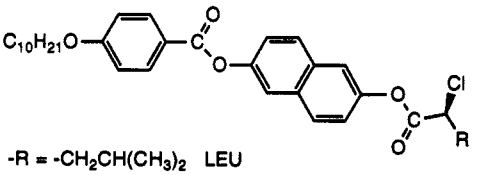


-R = -$CH_2CH(CH_3)_2$ LEU

-*$CH(CH_3)CH_2CH_3$ ILEU

-$CH(CH_3)_2$ VAL

SERIES ES[1]



-R = -$CH_2CH(CH_3)_2$ LEU

-*$CH(CH_3)CH_2CH_3$ ILEU

-$CH(CH_3)_2$ VAL

Results and Discussion

Synthesis. The full synthetic scheme of the new compounds in series **ET** is outlined in Scheme I.

The β-chlorohydrins introduced in these compounds as chiral tails were all prepared from the corresponding commercial L-α-amino acids (**1**) readily available in high enantiomeric purity: L-leucine, L-isoleucine, and L-valine. The α-chloro acids (**2**) were synthesized by means of a nucleophilic substitution of the amino group by the chlorine atom via the diazonium salt, and using 6 N HCl as a reducing medium.[7] Reduction of the acid group, using $AlLiH_4$ as a reductor agent and dry ether as a solvent,[8] afforded the corresponding β-chlorohydrins (**3**).

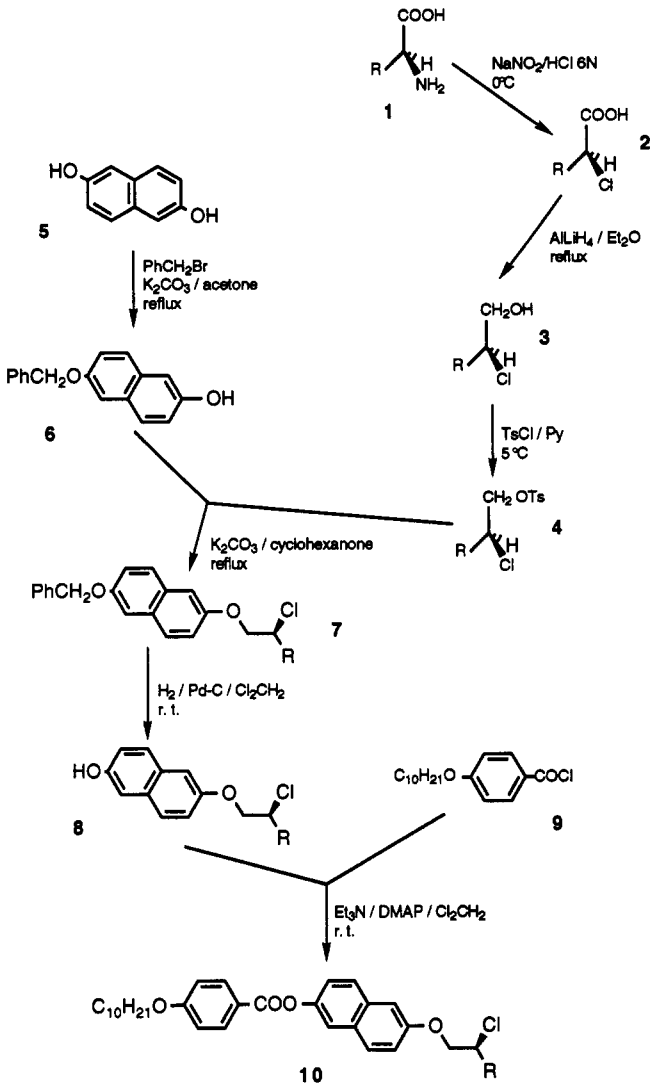
The tosylated β-chlorohydrins were introduced in 2-hydroxy-6-(benzyloxy)naphthalene (**6**) according to the

* Author for correspondence.

(1) Sierra, T.; Serrano, J. L.; Ros, M. B.; Ezcurra, A.; Zubía, J. *J. Am. Chem. Soc.* **1992**, *114*, 7645.
(2) Walba, D. M.; Slater, S. C.; Thurmes, W. N.; Clark, N. A.; Handshy, M. A. Supon, F. *J. Am. Chem. Soc.* **1986**, *108*, 5210.
(3) Lagerwall, S. T.; Otterholm, B.; Skarp, K. *Mol. Cryst. Liq. Cryst.*, **1987**, *152*, 503.
(4) Beresnev, L. A.; Blinov, L. M.; Osipov, M. A.; Pikin, S. A. *Mol. Cryst. Liq. Cryst.* **1988**, *158A*, 3.
(5) Koden, M.; Kuratate, T.; Funada, F.; Awane, K.; Sakaguchi, K.; Shiomi, Y. *Mol. Cryst. Liq. Cryst., Lett.* **1990**, *7*, 79.
(6) Walba, D. M. *Ferrolectric Liquid Crystals. A Unique State of Matter.* In *Advances in the Synthesis and Reactivity of Solids*; Mallouk, T. E., Ed.; JAI Press Ltd.: Greenwich, CT, 1991; Vol. 1, p 173.
(7) Fu, S. C. J.; Birnbaum, S. M.; Greenslein, I. P. *J. Am. Chem. Soc.* **1954**, *76*, 6054.
(8) Eliel, E. L., *J. Am. Chem. Soc.* **1976**, *78*, 1193.

0897-4756/93/2805-0938$04.00/0

Scheme I



Williamson method.[9] The protected hydroxy group (**7**) was debenzylated by hydrogenation (**8**), so that it could be esterified with 4-decyloxybenzoyl chloride (**9**), yielding the final compounds (**10**).

All attempts at introducing the chiral tail into the previously prepared mesogenic nucleus, 6-(4-(decyloxy)-benzoyloxy)-2-hydroxynaphthalene, by means of the Mitsunobu reaction[10] or the Williamson method,[9] were unsuccessful.

^{1}H NMR spectroscopy enabled us to verify the nonexistence of diastereoisomers in the isoleucine derivative due to partial racemization in some of the synthetic steps. We assumed that since the synthetic process is the same, all the three compounds behave similarly as far as optical purity is concerned.

The syntheses of the three α-chloroacid derivatives, as well as their spectroscopic data, are reported in ref 1.

Mesophase Characterization. The mesophases of the three ether compounds were identified according to their textures, which were observed by optical microscopy.

From the isotropic liquid the Ch phase appears in cell and oily streaks textures. On cooling, the SmA phase appears in a focal conic texture which remains in the SmC*

(9) Alabart, J. L.; Marcos, M.; Meléndez, E.; Serrano, J. L. *Ferroelectrics* **1984**, *58*, 37.
(10) Mitsunobu, O., *Synthesis* **1981**, 1.

Table I. Transition Temperatures (°C) for the Compounds in Series ET in the Second Heating and Cooling Processes

compound	C	SmC*	SmA	Ch	I
ET-LEU	● 77.3	(● 61.9)[a,b]	● 83.4	● 85.4	●
ET-ILEU	● 79.5	(● 43.8)[a]	● 62.5	● (64.5)[b]	●
ET-VAL	● 71.7		● 76.2	● 83.6	●

[a] Optical microscopy data. [b] In parentheses: Monotropic transition.

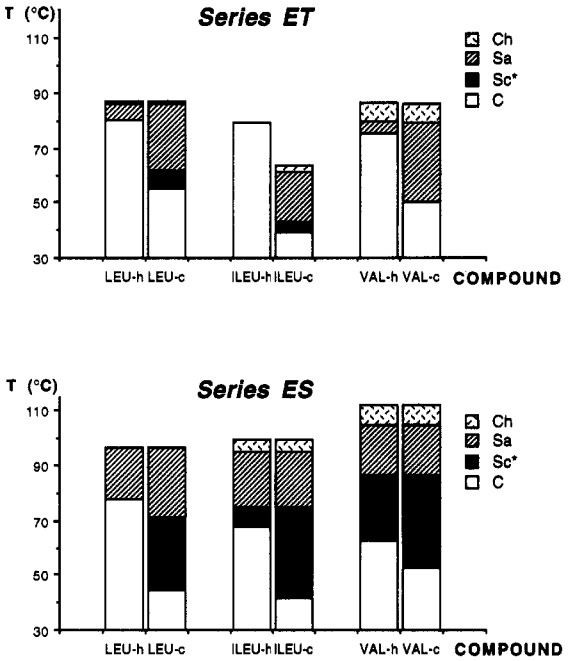


Figure 1. Mesophase ranges of the compounds in series **ET** and **ES** in the heating (h) and cooling (c) processes.

shown by leucine- (ET-LEU) and isoleucine- (ET-ILEU) derived compounds.

Mesogenic Properties. The transition temperatures of the three new compounds were determined by differential scanning calorimetry and optical microscopy in the case of the second-order transition SmA–SmC*. The temperatures are gathered in Table I. All the three compounds show a Ch phase above a SmA phase. The potentially ferroelectric SmC* phase is shown monotropically by **ET-LEU** and **ET-ILEU** compounds within a short temperature range, whereas the shorter chiral tail in the **ET-VAL** compound seems to impede the appearance of the SmC* phase. **ET-ILEU** only behaves as a liquid crystal in the cooling process.

The mesogenic behavior of these three compounds is represented in the diagram in Figure 1a, top. By comparison with the mesogenic behavior of the α-chloroacid derivatives (diagram in Figure 1, bottom) we can infer the important role played by the C=O group in the appearance of the SmC phase. This group incorporates an important transversal dipole moment to the molecule that favors the lateral molecular interaction necessary for the smectic arrangement.[11]

Spontaneous Polarization. We were able to evaluate only the spontaneous polarization for compound **ET-LEU** (i.e., 12.6 nC/cm^2), but the rapid crystallization of its monotropic SmC* phase prevented its Ps saturation value from being reached.

(11) Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals*; Leonard-Hill, Ed.; Glasgow, 1984.

Table II. Spontaneous Polarization Values (Ps(max) and Ps($T - T_c$ = -10 °C)) Observed for the Six Mixtures and Extrapolated for the Corresponding Pure Chiral Compounds

mixture	chiral dopant	transition temp, °C: I → Ch → S_A → S_C^* → C				%[a]	Ps(max)[b] (nC/cm²)	Ps(ext)[c] (nC/cm²)	Ps[b,d] (nC/cm²)	Ps(ext)[c,d] (nC/cm²)
M1	ET-LEU	97.9	93.2	74.0	38.0	10.4	4.0	38	3.0	29
M2	ET-ILEU	95.9	91.0	71.9	43.0	10.5	8.6	82	5.5	53
M3	ET-VAL	97.8	92.2	73.6	40.0	10.4	7.5	72	4.8	46
M4	EST-LEU	86.5	82.9	73.5	40.7	10.1	4.0	40	3.2	32
M5	EST-ILEU	87.6	82.6	73.3	37.6	10.1	9.8	97	7.1	70
M6	EST-VAL	87.6	81.9	72.0	39.1	10.0	9.2	92	6.0	60

[a] Molar percentage of the chiral component in the mixture. [b] Experimentally observed Ps values. [c] Ps values extrapolated for the pure compounds. [d] Ps values 10 °C below the transition SmA–SmC*.

To obtain data of the potential ferroelectric behavior of these β-chlorohydrin derivatives, they were used as dopants in 10 mol % binary mixtures with a common achiral compound, i.e., 4-hexyloxyphenyl 4′-(decyloxy)benzoate (X: 62.5 °C, SmC; 78.2 °C, SmA; 84.5 °C, N; 90.5 °C, I).

Since our aim was to make a comparative study of the three β-chlorohydrin derivatives versus the three α-chloroacid derivatives in terms of the structural factors–ferroelectric behavior relationship, and to ensure the validity of our conclusions, we also prepared and evaluated the corresponding 10 mol % binary mixtures of the three α-chloroacid derivatives in the same achiral matrix as above.

The maxima and $T_c - T$ = 10 °C Ps values observed for the six evaluated mixtures, as well as their 100 mol % extrapolated values, considering a linear dependence with the concentration, are gathered in Table II together with the transition temperatures.

X-ray measurements were carried out in the SmC* phases in order to determine the tilt angle. Powder diffraction patterns were obtained in the SmA and SmC* mesophases. The interlayer spacing was calculated from the measured low-angle diffraction maxima (2θ = 2.8–2.9°). The data obtained indicate that in the SmC* mesophase, the layer thickness is only slightly thinner (1 or 2 Å at most) than in the SmA mesophase and decreases gradually as the temperature is decreased. By comparing the layer thickness in the SmA and SmC* phases, a maximum value for the tilt angle in the SmC* phase of the six mixtures between 15° and 17° ($T_c - T$ = 10 °C) can be estimated.

The highest Ps values were obtained for isoleucine derivatives in both series, followed by valine-derived mixtures, and the lowest Ps values were measured in leucine derivatives. With regard to the presence or absence of the C=O group in the chiral tail, there is a slight decrease in the Ps values in the compounds in series **ET**.

Spontaneous Polarization–Steric Factors Relationship. To study the molecular structure–ferroelectric activity relationship of the chiral dopants, some aspects should be noticed. First, the fact that Ps extrapolated values for **ES** compounds agree quite well with the values measured for the pure compounds[1] and that the P_0 = Ps/sin θ of induced SmC* phases are only dependent on the structure of the chiral dopant.[12] Furthermore, the similar ranges and transition temperatures of all the mixtures make it possible to rule out the influence of temperature.

The MM2 program allows the calculation of the different conformers of a σ-bond and their relative abundance.[13] In 1989 a modification of this program—MM2PRIME—was published.[14] With the "tree coverage" option, included therein, up to six bonds may be rotated twice every 120°, so that all three staggered rotamers (one anti and two gauche for every rotated σ-bond) can be minimized. This is done automatically for all combinations over the specified bonds. 3^n rotamers are all generated and minimized. Their relative abundance is calculated from the corresponding minima steric energy values.

We have minimized the three chiral tails of ether compounds (series **ET**) using the corresponding β-chlorohydrin as models. In these models the rest of the molecule is replaced by an H atom so that the calculations can be simplified. This H atom has no effect on the conformational study because only the bonds directly involved in the asymmetric part of the molecule were allowed to rotate during the running of the program (see Table III).

Data concerning the most representative conformations of each chiral β-chlorohydrin, together with data corresponding to the α-chloroacid tails,[1] are gathered in Table III. Each chiral tail is represented by the two most abundant conformations that correspond, approximately, to 50% of the total conformational population. A study of the global conformational population of each tail showed that this assumption is reliable enough to be used in our discussion.

As far as the alkyl group in the chiral center of the molecules is concerned, a similar tendency is observed in both series (**ET** and **ES**). In a similar way to what occurred in α-chloroacid tails (Table III), we can observe a clear difference between the conformations of leucine-, and isoleucine-, and valine-derived tails. In the leucine-derived conformations, the corresponding isobutyl group conserves the linearity of the tail with a calculated 3–4–5–6 dihedral angle closed to the "anti" position (174–176°) in the conformations of higher percentage. In contrast, the calculated 3–4–5–6 dihedral angle in the isoleucine derivative shows mainly a "gauche" position that situates its corresponding *sec*-butyl group on the outside of the "all-anti" conformation of the skeleton of the chiral tail. In the valine derivative a clear inhomogeneity in the most abundant conformational population is observed: the isopropyl group is mostly in a "gauche" position.

The decrease in the rotational freedom in the SmC* phase favors the coupling of the oriented dipoles leading to high Ps values. This is the case of isoleucine- and valine-derived chiral tails that show a bent shape which gives rise to steric hindrance, and that is not present in the more lineal leucine-derived chiral tail.

(12) Siemensmeyer, K.; Stegemeyer, H. *Liq. Cryst.* **1989**, *5*, 1187.
(13) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *9*, 8127.
(14) Osawa, E.; Jaime, C.; Fujiyoshi, T.; Goto, H.; Imai, K. *J.C.P.E. Newsletter* **1989**, 1, Program No 9 (Backsversion).

Table III. Abundance, Dihedral Angles, and Module of the Dipole Moments of the Most Representative Conformations for Each β-Chlorohydrin and α-Haloacid Minimized by MM2 (Bonds Marked with an Arrow Allowed To Rotate during the Running of the Program)

	leucine derivatives						isoleucine derivatives						valine derivatives				
ET	%[a]	2-3-4-5[b]	3-4-5-6[b]	4-5-6-7[b]	2-3-4-Cl[b]	μ[c]	%[a]	2-3-4-5[b]	3-4-5-6[b]	4-5-6-7[b]	2-3-4-Cl[b]	μ[c]	%[a]	2-3-4-5[b]	3-4-5-6[b]	2-3-4-Cl[b]	μ[c]
	26	-170.1	176.6	176.3	67.7	3.2	28	-163.2	-60.5	173.6	71.1	3.1	34	-164.3	- 60.7	70.4	3.1
	20	55.3	174.3	177.8	-69.9	3.1	12	- 55.1	-60.6	173.5	178.5	2.1	21	51.7	174.3	-73.8	3.0
EST	%[a]	2-3-4-5[b]	3-4-5-6[b]	4-5-6-7[b]	2-3-4-Cl[b]	μ[c]	%[a]	2-3-4-5[b]	3-4-5-6[b]	4-5-6-7[b]	2-3-4-Cl[b]	μ[c]	%[a]	2-3-4-5[b]	3-4-5-6[b]	2-3-4-Cl[b]	μ[c]
	23	113.6	172.0	-61.3	-12.3	0.4	32	129.7	-64.5	170.2	1.0	0.2	31	117.7	-64.6	-10.6	0.3
	22	156.9	174.4	-59.1	30.8	0.9	15	137.4	-75.3	59.0	6.5	0.3	30	128.3	-64.6	- 0.2	0.2

[a] Percentage of the corresponding conformation in the conformational population. [b] Torsional angle defined by the atoms whose numbers are indicated in the figure above. [c] Dipole moment of the conformation in Debye.

With regard to the presence or absence of the carbonyl group, experimental results indicate a slight decrease in the Ps values from ester materials to ether ones. Basing ourselves on our previous results in which the C=O group has no favorable orientation to reinforce the molecular dipole, an increase in the Ps values might be expected if the group is suppressed. However, in view of the experimental results (evaluated Ps values), other considerations, such as steric factors, must be taken into account.

Considering the calculated 2–3–4–5 dihedral angles, a noticeably more abundant twisted conformation is present in the tails of ester materials in comparison with the ether ones, where a more linear disposition seems to be more probable. In the last case, the whole chiral tail will be located inside the hypothetical cylinder defined by the mesogenic molecule. However, the more twisted alkyl tail of ester materials might not completely fit into the cylinder, giving rise to a decrease in the rotational freedom which favors higher Ps values.

These results corroborate the fact that steric factors have a decisive effect on the Ps values of ferroelectric liquid crystals, overcoming, in some cases, dipolar considerations.

Experimental Section

Synthesis. The procedures for obtaining 2(*S*)-2-chloroalkanoic acids (**2**) and analytical data were reported in ref 1.

Representative Procedure for Obtaining 2(S)-2-Chloroalkanols (3). 2(S)-2-Chloro-4-methylpentanol: To a refluxing suspension of 1.3 equiv of $AlLiH_4$ in dry ethyl ether, 1 equiv of the 2(*S*)-2-chloro-4-methylpentanoic acid is added dropwise. When the addition is over, the reaction mixture is refluxed for another 2 h. It is then allowed to cool down, and 10% H_2SO_4 is added. The ether phase is separated, and the aqueous phase is extracted three times with ethyl ether. The organic phases are gathered and dried over $MgSO_4$. After filtering, the solvent is removed under vacuum and the crude is purified by distillation, yield 54%. bp 105 °C/15 mmHg. ^1H NMR (200 MHz, $CDCl_3$) δ 0.96 (d, *J* = 6.6 Hz, 3 H), 0.98 (d, *J* = 6.6 Hz, 3 H), 1.3–1.7 (m, 3 H), 2.1 (s, 1 H), 3.7 (d, *J* = 6.2 Hz, 2 H), 4.0 (m, 1 H). IR (neat) 3362, 1076 cm^{-1}. $[\alpha]_D^{20}$ −41.3° (neat).

Analytical Data for Other Compounds 3. 2(S),3(S)-2-Chloro-3-methylpentanol: yield 38%. bp 130 °C/15 mmHg. ^1H NMR (200 MHz, $CDCl_3$) δ 0.9 (t, *J* = 6.6 Hz, 3 H), 1.0 (d, *J* = 6.6 Hz, 3 H), 1.5 (m, 3 H), 1.9 (s, 1 H), 3.8 (m, 3 H). IR (neat) 3380, 1077 cm^{-1}. $[\alpha]_D^{20}$ −6.3° (neat).

2(S)-2-Chloro-3-methylbutanol: yield 51%. bp 150 °C/760 mm Hg. ^1H NMR (200 MHz, $CDCl_3$) δ 0.94 (d, *J* = 6.6 Hz, 3 H), 0.97 (d, *J* = 6.6 Hz, 3 H), 2.1 (m, 1 H), 2.4 (s, 1 H), 3.8 (m, 3 H). IR (neat) 3352, 1073 cm^{-1}. $[\alpha]_D^{20}$ +1.8° (neat).

Representative Procedure for Obtaining 2(S)-2-Chloroalkyl Tosylates (4). 2(S)-2-Chloro-4-methylpentyl tosylate: To an ice-bathed solution of 1 equiv of the β-chlorohydrin in pyridine (1 mL/mmol), 2 equiv of *p*-toluenesulfonyl chloride are added. The mixture is stirred for 1 h in the ice bath and kept 12 h longer at 0 °C in the freezer. Then, the mixture is diluted with water and extracted several times with ethyl ether. The organic phases are gathered and washed with 10% H_2SO_4 and water. The solution is dried over $MgSO_4$ and filtered, and the solvent was removed under vacuum. The product can be used in the next step without further purification; yield 80%. IR (neat) 1495, 1367, 1189, 1176 cm^{-1}.

Analytical Data for Other Compounds 4. 2(S),3(S)-2-Chloro-3-methylpentyl tosylate: yield 79%. IR (neat) 1494, 1365, 1189, 1177 cm^{-1}.

2(S)-2-Chloro-3-methylbutyl tosylate: yield 87%. IR (neat) 1495, 1366, 1190, 1177 cm^{-1}.

2-(Benzyloxy)-6-hydroxynaphthalene (6). To a suspension of 76 mmol (12 g) of 2,6-dihydroxynaphthalene and 76 mmol (10.5 g) of finely pulverized K_2CO_3 in dry acetone, 76 mmol (13 g) of benzyl bromide are added. After stirring for 24 h, the reaction mixture is allowed to cool. Water (150 mL) is added, and the precipitated filtered and washed with water. The product is purified by flash chromatography using methylene chloride as an eluent; yield 30%. mp 141 °C. ^1H NMR (200 MHz, $CDCl_3$) δ 5.15 (s, 2 H), 5.29 (s, 1 H), 7.05–7.22 (m, 4 H), 7.33–7.48 (m, 5 H), 7.59 (d, *J* = 9.0 Hz, 1 H), 7.62 (d, *J* = 9.0 Hz, 1 H). IR (Nujol) 3316, 1605, 1514, 1230 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_2$: C 81.57; H 5.65. Found: C 82.00; H 5.43.

Representative Procedure for Obtaining 2-(Benzyloxy)-6-(2′(S)-2′-chloroalkyloxy)naphthalene (7). 2-Benzyloxy-6-(2′(S)-2′-chloro-4′-methylpentyloxy)naphthalene. To a suspension of 6.8 mmol (1.7 g) of 2-(benzyloxy)-6-hydroxynaphthalene and 10.8 mmol (1.5 g) of K_2CO_3 in 35 mL of cyclohexanone, 8.2 mmol of the appropriate tosylate derivative (**4**) are added. After stirring under reflux for 4 h, the reaction mixture is allowed to cool, and the precipitate filtered off. The solvent is removed at reduced pressure, and the crude is purified by flash chromatography using the appropriate methylene chloride/ethyl acetate mixture and recrystallized from hexanes. Eluent: methylene chloride/hexanes [5:95]. Yield 66%. mp 81 °C. ^1H NMR (200 MHz, $CDCl_3$) δ 0.95 (d, *J* = 6.6 Hz, 3 H), 0.99 (d, *J* = 6.6 Hz, 3 H), 1.76 (m, 2 H), 2.0 (m, 1 H), 4.12–4.32 (m, 3 H), 5.15 (s, 2 H), 7.09–7.25 (m, 4 H), 7.34–7.50 (m, 5 H), 7.64 (d, *J* = 8.7 Hz, 2 H). IR (Nujol) 1603, 1242, 1164 cm^{-1}. Anal. Calcd for $C_{23}H_{25}O_2Cl$: C 74.87; H 6.84. Found: C 74.80; H 7.0.

Analytical Data for Other Compounds 7. 2-(Benzyloxy)-6-(2′(S),3′(S)-2′-chloro-3′-methylpentyloxy)naphthalene. Eluent: methylene chloride/hexanes [2:98]; yield 36%. bp 74

°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, J = 7.5 Hz, 3 H), 1.65 (m, 2 H), 1.96 (d, J = 6.8 Hz, 1 H), 2.05 (m, 1 H), 4.07 (m, 1 H), 4.26 (m, 2 H), 5.15 (s, 2 H), 7.09–7.25 (m, 4 H), 7.33–7.50 (m, 5 H), 7.63 (d, J = 8.9 Hz, 1 H), 7.64 (d, J = 8.9 Hz, 2 H). IR (Nujol) 1605, 1241, 1166 cm^{-1}. Anal. Calcd for $C_{23}H_{25}O_2Cl$: C 74.87; H 6.84. Found: C 74.92; H 6.80.

2-Benzyloxy-6-(2′(S)-2′-chloro-3′-methylbutyloxy)naphthalene. Eluent: methylene chloride/hexanes [5:95]; yield 40%. mp 85 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.03 (d, J = 6.6 Hz, 3 H), 1.09 (d, J = 6.6 Hz, 3 H), 2.31 (m, 1 H), 4.26 (m, 3 H), 5.15 (s, 2 H), 7.09–7.23 (m, 4 H), 7.34–7.50 (m, 5 H), 7.62 (d, J = 8.8 Hz, 1 H), 7.63 (d, J = 8.8 Hz, 1 H). IR (Nujol) 1605, 1241, 1165 cm^{-1}. Anal. Calcd for $C_{22}H_{23}O_2Cl$: C 74.45; H 6.54. Found: C 75.00; H 6.83.

Representative Procedure for Obtaining 2-(2′(S)-2′-Chloroalkyloxy)-6-hydroxynaphthalene (8). 2-(2′(S)-2′-Chloro-4-methylpentyloxy)-6-hydroxynaphthalene. To a suspension of 0.8 g of 10% Pd–C under H_2 atmosphere, 4 mmol of 2-benzyloxy-6-(2′(S)-2′-chloro-4′-methylpentyloxy)naphthalene is added via syringe. The reaction is followed by TLC. When it is over, the mixture is filtered through Celite and the solvent removed under vaccum. The crude is purified by flash chromatography. Eluent: hexanes/ethyl acetae [98:2]; yield 70%. mp 92 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.96 (d, J = 6.5 Hz, 3 H), 0.99 (d, J = 6.6 Hz, 3 H), 1.77 (m, 2 H), 2.06 (m, 1 H), 4.13–4.36 (m, 3 H), 5.30 (s, 1 H), 7.07–7.17 (m, 4 H), 7.60 (d, J = 9.3 Hz, 1 H), 7.63 (d, J = 9.3 Hz, 1 H). IR (Nujol) 3365, 1609, 1230 cm^{-1}. Anal. Calcd for $C_{16}H_{19}O_2Cl$: C 68.92; H 6.88. Found: C 69.20; H 6.90.

Analytical Data for Other Compounds 8. 2-(2′(S),3′(S)-2′-Chloro-3′-methylpentyloxy)-6-hydroxynaphthalene: Eluent: hexanes/ethyl acetate [98:2]; yield 50%. mp 82 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, J = 7.4 Hz, 3 H), 1.09 (d, J = 6.8 Hz, 3 H), 1.64 (m, 2 H), 2.04 (m, 1 H), 4.26 (m, 3 H), 7.06–7.16 (m, 4 H), 7.59 (d, J = 8.8 Hz, 1 H), 7.63 (d, J = 8.8 Hz, 1 H). IR (Nujol) 3363, 1610, 1234 cm^{-1}. Anal. Calcd for $C_{16}H_{19}O_2Cl$: C 68.92; H 6.88. Found: C 68.44; H 6.80.

2-(2′(S)-2′-Chloro-3′-methylbutyloxy)-6-hydroxynaphthalene. Eluent: hexanes/ethyl acetate [95:5]; yield: 56%. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.04 (d, J = 6.8 Hz, 3 H), 1.11 (d, J = 6.6 Hz, 3 H), 2.32 (m, 1 H), 4.23 (m, 3 H), 4.89 (s, 1 H), 7.07–7.17 (m, 4 H), 7.59 (d, J = 8.4 Hz, 1 H), 7.64 (d, J = 8.4 Hz, 1 H). IR (Nujol) 3365, 1608, 1230 cm^{-1}. Anal. Calcd for $C_{15}H_{17}O_2Cl$: C 68.04; H 6.48. Found: C 69.00; H 7.12.

Representative Procedure for Obtaining 2-(2′(S)-2′-Chloroalkyloxy)-6-(4′-(decyloxy)benzoyloxy)naphthalene (10). 2-(2′(S)-2′-Chloro-4-methylpentyloxy)-6-(4′-(decyloxy)benzoyloxy)naphthalene. To a solution of 2 mmol of 2-(2′(S)-chloroalkyloxy)-6-hydroxynaphthalene and 2.3 mmol (0.23 g) of triethylamine in 20 mL of dry methylene chloride, (dimethylamino)pyridine is added in catalytic amount. To this solution, 2.5 mmol (0.74 g) of 4-decyloxybenzoyl chloride in 5 mL of methylene chloride is added. After stirring, at room temperature, for 6 h, the solvent is removed under vacuum. The crude is purified by flash chromatography and two recrystallizations from hexanes and ethanol respectively. Eluent: methylene chloride/hexanes [30:70]; yield 72%. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, J = 6.4 Hz, 3 H), 0.99 (t, J = 6.9 Hz, 6 H), 1.10–1.57 (m, 14 H), 1.57–1.87 (m, 4 H), 1.87–2.0 (m, 1 H), 4.05 (t, J = 6.6 Hz, 2 H), 4.18–4.33 (m, 3 H), 6.99 (d, J = 8.9 Hz, 2 H), 7.17–7.35 (m, 3 H), 7.61 (d, J = 2.1 Hz, 1 H), 7.73 (d, J = 8.7 Hz, 1 H), 7.77 (d, J = 8.7 Hz, 1 H), 8.21 (d, J = 8.9 Hz, 2 H). IR (Nujol) 1718, 1605, 1223, 1170, 1116 cm^{-1}. Anal. Calcd for $C_{33}H_{43}O_4Cl$: C 73.50; H 8.05. Found: C 73.93; H 8.45.

Analytical Data for Other Compounds 10. 2-(2′(S),3′(S)-2′-Chloro-3′-methylpentyloxy)-6-(4′-(decyloxy)benzoyloxy)naphthalene. Eluent: methylene chloride/hexanes [20:80]; yield 81%. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, J = 6.4 Hz, 3 H), 0.97 (t, J = 7.3 Hz, 3 H), 1.11 (d, J = 6.8 Hz, 3 H), 1.14–1.52 (m, 15 H), 1.62–1.86 (m, 2 H), 2.06 (m, 1 H), 4.05 (t, J = 8.9 Hz, 2 H), 4.29 (m, 3 H), 6.98 (d, J = 8.9 Hz, 2 H), 7.17–7.34 (m, 3 H), 7.61 (d, J = 2.4 Hz, 1 H), 7.73 (d, J = 8.3 Hz, 1 H), 7.77 (d, J = 8.3 Hz, 1 H), 8.18 (d, J = 8.9 Hz, 2 H). IR (Nujol) 1720, 1606, 1220, 1168, 1120 cm^{-1}. Anal. Calcd for $C_{33}H_{43}O_4Cl$: C 73.50; H 8.05. Found: C 73.82; H 8.64.

2-(2′(S)-2′-Chloro-3′-methylbutyloxy)-6-(4′-(decyloxy)benzoyloxy)naphthalene. Eluent: methylene chloride/hexanes [20:80]; yield: 78%. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, 3 H), 1.05 (d, J = 6.7 Hz, 3 H), 1.12 (d, J = 6.7 Hz, 3 H), 1.22–1.52 (m, 14 H), 1.79–1.86 (m, 2 H), 2.35 (m, 1 H), 4.05 (t, J = 6.6 Hz, 2 H), 4.26 (m, 3 H), 6.99 (d, J = 8.8 Hz, 2 H), 7.17–7.35 (m, 3 H), 7.61 (d, J = 1.96 Hz, 1 H), 7.73 (d, J = 8.8 Hz, 1 H), 7.77 (d, J = 8.8 Hz, 1 H), 8.18 (d, J = 8.8 Hz, 2 H). IR (Nujol) 1733, 1606, 1215, 1169, 1117 cm^{-1}. Anal. Calcd for $C_{32}H_{41}O_4Cl$: C 73.18; H 7.88. Found: C 73.57; H 8.30.

Techniques. Microanalysis was performed with a Perkin-Elmer 240B microanalyzer. Infrared spectra for all the compounds were obtained by using a Perkin-Elmer 1600 (series FTIR) spectrometer using neat samples for the alcohol and tosylate intermediates, and Nujol mulls for the final compounds, between polyethylene plates in the 360–4000-cm^{-1} spectral range. ^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200 MHz for ^{1}H. The textures of the mesophases were studied with a Nikon optical microscope equipped with a polarizing light, a Mettler FP82 hot stage, and a Mettler FP80 central processor.

Measurements of temperatures of transition were carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating and cooling rate of 10 °C/min (the apparatus was calibrated with indium, 156.6 °C, and tin, 232.1 °C).

The spontaneous polarization was obtained using the triangular wave form method.[15,16] In the experimental setup[17] the triangular wave voltage is supplied by a HP3325A function generator. The current–voltage cycles are recorded by a digital acquistion system HP7090A. All the equipment is interfaced to a microcomputer. Cells for measurements are 4 μm thick, with indium tin oxide (ITO) electrodes coated with polyimide.

Powder X-ray diffraction patterns were obtained in a Guinier diffractometer (Huber 644) operating with a Cu $K\alpha_1$ beam issued from a germanium monochromator. The samples were held in rotating Lindemann glass capillaries (ϕ = 0.5 mm) and heated with a variable-temperature attachment. The diffraction patterns were registered with a scintillation counter.

Acknowledgment. We thank Dr. J. Barberá, who carried out the X-ray measurements, and Dr. C. Jaime, for his advice on MM2 calculations. This work was financed by the CICYT (Projects MAT-90-0813 and MAT-91-0962-CO2-01).

(15) Pérez-Jubindo, M. A.; Tello, M. J.; Fernández, J. *J. Phys. D* **1981**, *14*, 2305.
(16) Miyasato, K.; Abe, S.; Takezoe, H.; Fukuda, A.; Kuze, E. *Jpn. J. Appl. Phys.* **1983**, *22*, L661.
(17) De la Fuente, M. R.; Ezcurra, A.; Pérez-Jubindo, M. A.; Zubía, J. *Liq. Cryst.* **1990**, *7*, 51.