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Improving FLC Properties. Simplicity, Planarity, and Rigidity in New Chiral Oxazoline Derivatives

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Abstract: In an attempt to develop new dopants for improved ferroelectric properties in liquid crystals, aryloxazolines have been chosen as chiral moieties. They were prepared in optically active form from (*S*)-β-amino alcohols via a short stereospecific synthesis and incorporated into mesogenic systems. Mesogenic and ferroelectric properties of 11 compounds in five series of chiral oxazoline derivatives [**I(OH)**, **I(H)**, **II(OH)**, **II(H)**, and **III(OH)**] have been studied. In order to establish the relationship between the molecular structure and ferroelectric properties, an in-depth structural investigation of both H-bonded and non-H-bonded phenyloxazoline moieties was carried out (by means of semiempirical calculations—AM1—and spectroscopic studies—IR, UV and ^{1}H NMR). These studies have proved a planar structure for both types of structures, which should have a strong influence on ferroelectric properties. These properties have been evaluated in 10 mol % binary mixtures. The highest Ps values were measured for compounds of series **I(OH)** [P_s max$_{\mathrm{I(OH)a}}$ = 16.7 nC/cm^2, P_s max$_{\mathrm{I(OH)b}}$ = 13.2 nC/cm^2] containing a hydrogen bond, which makes the chiral part of the molecule more rigid. Compound **III(OH)a** shows a wide SmC* phase range which supercools well below room temperature, and it has been studied as a ferroelectric liquid crystal in the pure state. The P_s max measured is appreciably high: 225 nC/cm^2. Its special thermal behavior (showing a glass transition at −28 °C) makes this compound very interesting from the point of view of practical applications and will be the target of further studies.

Introduction

One of the ideal ways for a chemist devoted to materials synthesis to work would be to know, *"a priori"*, the properties of given structures. In this way, we could design the most suitable molecules for a specific property. In spite of this situation being remote, important efforts have been made during the last few years in order to probe more deeply into the understanding of structure−activity relationships. In the specific field of liquid crystals, research on ferroelectric materials has provided considerable information about such relationships. In many cases, this knowledge can be extended to other related fields such as NLO properties, piezoelectricity, and pyroelectricity, which might also take advantage of the polar order shown by the SmC* phase.[1]

The search for new structures for liquid crystals with good ferroelectric properties implies looking for mesogenic molecules containing a chiral unit which must show some special features, i.e., if this chiral part incorporates a strong dipole moment with a significant component perpendicular to the long molecular axis, and if, additionally, intra and intermolecular dipole interactions occur in such a way that strong coupling is favored, good ferroelectric behavior should be guaranteed.[1]

In recent years, a small number of mesogenic ferroelectric compounds with a chiral center in a ring system, such as γ-lactones,[2] β-lactams,[3]-dioxolan-4-ones,[4] dioxanes,[5] and oxazolines,[6] have been synthesized. These heterocycles have a strong dipole in a rigid chiral structure which favors good ferroelectric behavior as discussed above. In our search for new highly-effective chiral moieties we expected OXAZOLINES to be good candidates. They are five-membered heterocycles with a planar structure and a strong dipole moment due to two heteroatoms.[7] Moreover, oxazolines can be easily prepared in optically active form from enantiomerically pure and commercially available amino alcohols.[8,9] The oxazoline ring appears to be a versatile chiral terminal unit with a very

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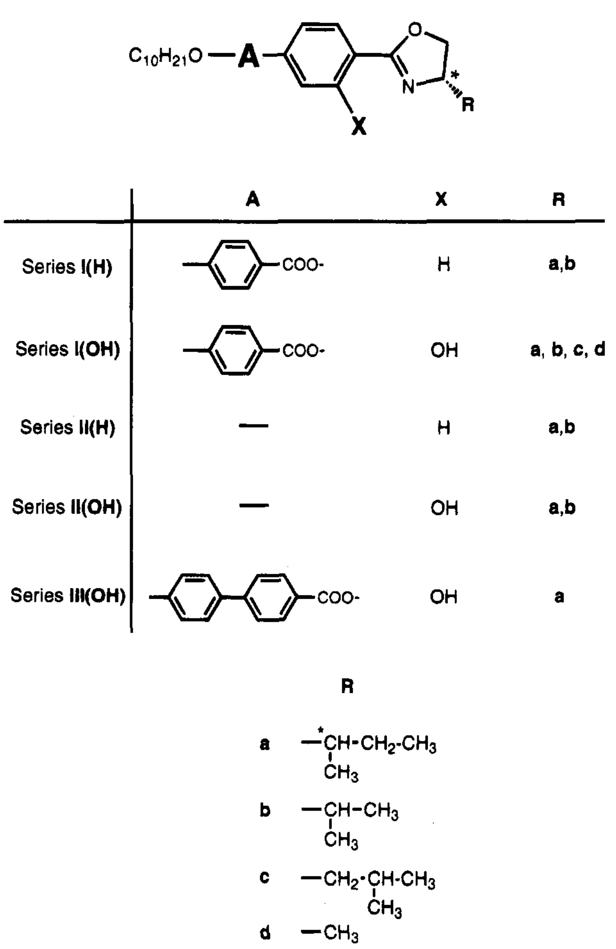
Chart 1



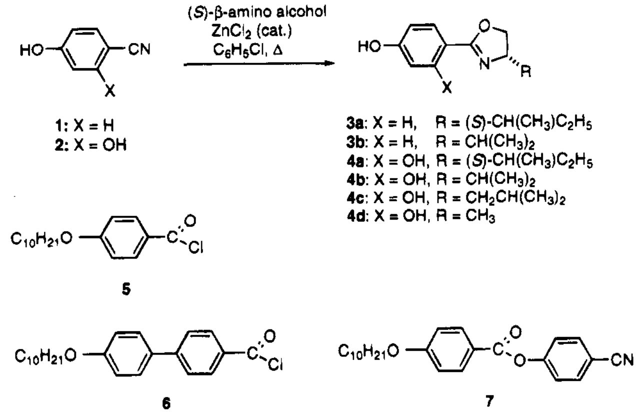
interesting structural possibility: the heterocycle can be fixed by means of a strong six-membered chelate ring through a hydrogen bond. Consequently, this structure fulfills the conditions mentioned previously which lead to a rigid chiral moiety and, hence, favor intra- and intermolecular dipole coupling within the ferroelectric phase.

As a secondary objective we have studied the influence of the different central cores of the oxazoline derivatives on the ferroelectric and mesogenic properties when these compounds are used as chiral dopants in ferroelectric mixtures.

In this paper we describe the synthesis and mesogenic and ferroelectric properties of 11 different oxazoline derivatives (Chart 1). The investigation of three fundamental factors was intended: (1) the conceivability of using oxazolines as chiral terminal units, (2) the importance of chelation through an intramolecular H-bond, and (3) the influence of the different central cores on mesogenic and ferroelectric properties.

All the compounds [series **I(H/OH)**, **II(H/OH)**, and **III(OH)**] were the target of a study which helped to elucidate the most important factors of the structure–activity relationship. In order to carry out this structural study, both spectroscopic techniques (^{1}H NMR, IR, and UV) and computer calculations were employed. They latter have already proved to be very helpful when dealing with structure–activity relationships. In previous studies,[10,11] we introduced molecular mechanic empirical calculations as a useful tool for deeply studying the influence of the possible conformations of the aliphatic chiral tail on P_s values. Our present work is focused on chiral structures with their asymmetric centers located in a heterocyclic ring directly bonded to the rigid aromatic core. The existence of unsaturation and conjugation in these oxazoline-derived chiral moieties led us to consider quantum mechanical calculations, such as MINDO/3,[12] MNDO,[13] or AM1.[14] The molecules in question have two main structural characteristics which made MINDO/3 and MNDO programs unsuitable: the presence of heteroatoms and the hydrogen bond, respectively. AM1 has proved to be very accurate for calculations of heats of formation, rotational barriers and dipole moments, even when molecules contain both a nitrogen and an oxygen atom and a hydrogen bond, as they do in our case.

Scheme 1



Results and Discussion

Synthesis. The condensation of substituted nitriles with β-amino alcohols in the presence of a metal catalyst is a general stereospecific route to 2-oxazolines.[8,9,15] For the syntheses of compounds in series **I(H/OH)**, **II(H/OH)**, and **III(OH)** optically active **3** and **4** were key intermediates. Refluxing a chlorobenzene solution of hydroxybenzonitriles **1** or **2** and the corresponding amino alcohol in the presence of a catalytic amount of zinc dichloride afforded 2-oxazolinyl phenols **3a,b** and **4a–d** respectively, in 41–60% yield (Scheme 1).

Esterification of **3** or **4** with 4-decyloxybenzoyl chloride (**5**) in the presence of NEt_3 gave compounds in series **I(H)** and **I(OH)**, respectively, in fair to good yield (29–71%). Following the same procedure using **4a** and **6** provided **III(OH)a**.

Compounds **II(H)a,b** were obtained by zinc-catalyzed condensation of **7** with isoleucinol or valinol, respectively. Apparently, oxazoline formation with ester **7**, a compound which is readily available through the reaction of **1** with **5**, proceeds predominately at the activated ester carbonyl and not, as expected, at the nitrile group.

Compounds of series **II(OH)** were synthesized by alkylation of **4** with decyl iodide and potassium hydroxide in DMSO.

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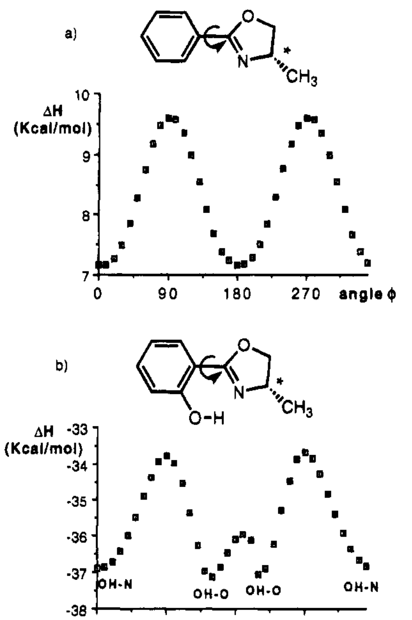

Figure 1. Potential energy curve describing the internal rotation of the phenyl group with respect to the oxazoline ring for the chosen models, (4*S*)-2-phenyl-4-methyloxazoline (a) and (4*S*)-2-(2′-hydroxyphenyl)-4-methyloxazoline (b), calculated by AM1.

Structural Characterization. Conformation and Hydrogen Bond. AM1 calculations provided evidence for a planar geometry of the oxazoline ring in accordance with the microwave data in the literature.[7] When a phenyl group is directly bonded to carbon-2 of the heterocycle, a planar conformation of the whole molecule was also calculated to be the most probable. The potential energy curve describing the internal rotation of the phenyl group with respect to the oxazoline ring (ϕ angle) is represented in Figure 1a. The plot shows two minima corresponding to two equivalent planar conformations ($\phi = 0°$ and $\phi = 180°$). Nevertheless, the possibility of independent rotation of the phenyl ring at the mesophase temperature still exists, considering the low calculated rotational barriers (<2.4 Kcal/mol). When studying the structure of the 2-hydroxyphenyl oxazoline derivatives, three energy minima were obtained by AM1 calculation of the energy path describing the same internal rotation as before (Figure 1b). One of the minima corresponds to a planar geometry ($\phi = 0°$) with an H-bond involving the nitrogen atom of the oxazoline ring. The other two energy wells can be explained in terms of the formation of an H-bond with one of the lone electron pairs of the oxygen atom. In this case, the resulting conformations depart from planarity by 30°. Obviously, given the chiral character of the molecule, two stable diastereomeric conformations are discernible: $\phi = +30°$ and $\phi = -30°$. Interchange between the three relative minima are separated by quite low rotational barriers (~3.5 Kcal/mol). From the heats of formation calculated by AM1 (ca. −37 and 7 Kcal/mol, respectively), it can be deduced that the H-bonded structure is stabilized in comparison to the non-H-bonded analogue.

It is known that, in general, semiempirical calculations underestimate electrostatic interactions against steric ones. For this reason, and in order to rigorously establish the nature of the H-bond, **spectroscopic studies** were carried out.

The presence of hydrogen-bonding in compounds of series **I(OH)**, **II(OH)**, and **III(OH)** can be deduced from their corresponding IR and UV spectra. Whereas IR frequencies between 1649 and 1652 cm^{-1} were found for the C=N bond in the compounds of series **I(H)** and **II(H)**, a shift to lower frequences ($\bar{\nu}$ = 1639−1644 cm^{-1}) was observed for all seven compounds of series **I(OH)**, **II(OH)**, and **III(OH)**. This shift indicated the presence of a hydrogen bond which weakens the oxazoline C=N bond. UV spectra were recorded for all five compounds having a *sec*-butyl group (**a**) in the chiral center. Maximum absorption wavelengths and extinction coefficients are gathered in Table 1. Compounds **I(H)a** and **II(H)a**, without a hydroxyl group, show similar spectra. In each case the most important band appears at 261.5 and 257.5 nm, respectively, which corresponds to a $\pi-\pi^*$ transition. A shoulder at 272.5 and 275.5 nm, respectively, corresponding to a n$-\pi^*$ transition, appears in both cases. The presence of an *ortho* hydroxyl group hardly modifies the position of the $\pi-\pi^*$ band, whereas the n$-\pi^*$ band is strongly affected. Thus, in compounds **I(OH)a** and **II(OH)a** a peak appears at 302.0 and 300.0 nm, respectively, corresponding to the n$-\pi^*$ transition. This effect clearly indicates the importance of the intramolecular H-bond in the molecular structure. Usually an OH group in the *ortho* position gives rise to a bathochromic shift of around 7 nm. In our case this effect is enhanced by the presence of the intramolecular chelate ring resulting in a bathochromic shift of around 25 nm. Formation of this chelate ring encourages a planar structure which extends the conjugation through the whole molecule, thus increasing the molecular polarizability. In the case of compound **III(OH)a**, containing a biphenyl system, the effect of the extension of the conjugation is greater and, consequently, $\pi-\pi^*$ and n$-\pi^*$ transitions appear together. In the case, it is only possible to detect a very intense band at 302.4 nm.

Table 1. UV Data for Compounds Derived from L-Isoleucinol (**I(OH)a**, **I(H)a**, **II(OH)a**, **II(H)a** and **III(OH)a**), Recorded in Pentane Solution

	λ_1 (log ϵ) (nm)			λ_2 (log ϵ) (nm)	λ_3 (log ϵ) (nm)
I(OH)a	261.2 (4.56)				302.0 (3.17)
I(H)a	261.5 (4.59)	267.0sh	272.5sh		
II(OH)a	257.0 (4.26)			265.5 (4.29)	300.0 (3.98)
II(H)a	257.5 (4.34)	275.5sh			
III(OH)a	250.4 (4.17)			261.2 (4.18)	302.4 (4.58)

The strength of the hydrogen bond was calculated from ^{1}H NMR data using the Schaefer equation[16] (eq 1)

$$E = \Delta\delta + 0.4 \pm 0.2 \qquad (1)$$

$$(\Delta\delta = \delta_{\mathrm{OH}} - \delta_{\mathrm{OHphenol}}, \text{ in } \mathrm{CHCl_3})$$

Energy values for the hydrogen bond of every compound in series **I(OH)**, **II(OH)**, and **III(OH)** were determined to be around 8.3 Kcal/mol. When comparing these values with those in the literature for similar *o*-hydroxybenzene derivatives,[17,18] the presence of strong hydrogen bonds which force the corresponding part of the molecule to arrange in a coplanar way can be deduced.

To establish with certainty whether the H-bond forms with either the nitrogen or the oxygen atom (or both), **NOE** experiments were carried out on compound **I(OH)b**. If an H-bond involving the nitrogen atom occurs, a planar conformation of the chiral moiety, as represented in Figure 2(OH−N), is expected to be present in the molecule. In this situation, a strong through-space-coupling between the methyl protons (**a**, **a′**) and the hydroxyl proton (**c**) should be detectable by NMR

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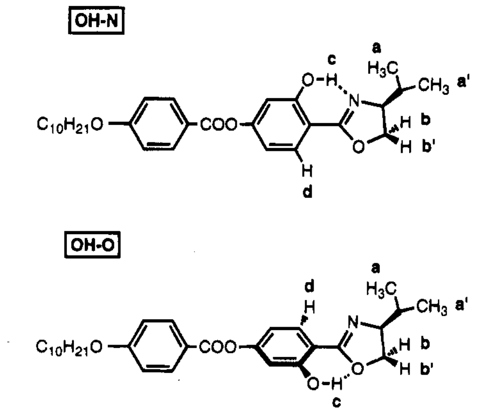

Figure 2. Possible conformations of the chiral moiety, 2-(2'-hydroxyphenyl)-4-isopropyloxazoline, depending on whether the H-bond involves the nitrogen (**OH-N**) or the oxygen (**OH-O**) atom of the oxazoline ring.

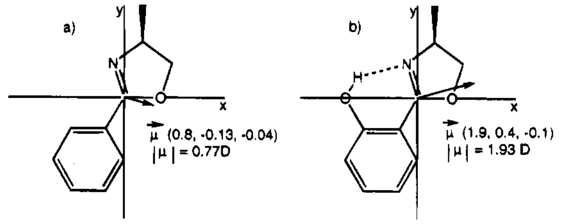

Figure 3. Dipole moments of the chosen models, (4*S*)-2-phenyl-4-methyloxazoline (a) and (4*S*)-2-(2'-hydroxyphenyl)-4-methyloxazoline (b), calculated by AM1 and drawn according to the physical convention.

spectroscopy. On the other hand, coupling between methylene protons (**b**, **b'**) and the hydroxyl proton (**c**) should be observable if the H-bond is formed with the oxygen atom, giving rise to a conformation which deviates by 30° [Figure 2(OH−O)] or −30° from planarity. When the signal corresponding to the methyl protons, **a**, **a'**, is saturated (irradiated at $\delta = 0.98$ ppm), a strong nuclear Overhauser enhancement is observed for the hydroxyl proton **c** ($\delta = 12.5$ ppm) and logically, also for the **b**, **b'** protons. In contrast, when the signal corresponding to the methylene protons **b**, **b'** is saturated (irradiated at $\delta = 4.13$ ppm), only arene proton **d** ($\delta = 7.67$ ppm) is affected (apart from protons **a**, **a'**) and the hydroxyl proton **c** remains unaltered. Basing ourselves on these results, we conclude that the H-bond, besides being very strong, only involves the nitrogen atom and hence, the chiral moiety is entirely planar for the compounds in series **I(OH)**, **II(OH)**, and **III(OH)**.

Dipole Moments. In order to study the influence of both steric and dipolar factors on ferroelectric behavior by means of AM1 calculations, we chose two simplified models of the corresponding mesogenic structures (Figure 3). The benzoate group was not considered taking into account the low-effective disposition of the dipole moment of the central ester group and its independent mobility which must lead to a cancellation of its steric and dipolar contribution to P_s values; similar energy values are obtained for very different conformations when calculations are performed on the whole phenyl benzoate molecule, which justifies the above reasoning.

The dipole moments of both optimized geometries are represented in Figure 3. The molecular dipole lies mainly in the plane of the molecule in both cases. Differences between dipole moduli are also noteworthy and have an important influence on ferroelectric behavior as will be discussed below.

The planar conformations which are favored must cause an advantageous lack of steric hindrance for a close lateral approach of contiguous molecules within the SmC* phase. This fact should favor the dipolar coupling of the neighbor molecules and contribute to increase the P_s values in the materials, in agreement with previous results that prove the contribution to the P_s values of both magnitude of the dipolar moment in the chiral tails and the way that these dipoles interact sterically with those of contiguous molecules.[10,11]

Table 2. Transition Temperatures (°C) for the Compounds in Series **I(OH/H)** and **II(OH/H)** Obtained from the Second Heating and Cooling Processes Determined by Differential Scanning Calorimetry

compd	heating process	cooling process
I(OH)a	**X**$_2$ 12.3 **X**$_1$ 43.0 **I** + **X** 65.0^b **I**	**I** 47.9 **Ch** 5.6 **X**
I(OH)b	**X**$_2$ 41.6^a **X**$_1$ 71.0 **I**	**I** 55.7 **Ch** 36.4 **X**
I(OH)c	**X** 49.0 **I**	**I** 30.2 **Ch** 24.8 **X**
I(OH)d	**X** 55.8 **I**	**I** 26.3 **Ch** 20.6 **X**
I(H)a	**X** 64.4 **I**	**I** 63.7 **Ch** 48.2 **X**
I(H)b	**X** 74.8 **I**	**I** 66.3 **X**
II(OH)a	**X** 25.6 **I**	**I** 8.1 **X**
II(OH)b	**X** 32.3 **I**	**I** 23.4 **X**
II(H)a	**X**$_2$ −7.1 **X**$_1$ 1.9 **X** 14.8 **I**	**I** −9.6 **X**
II(H)b	**X**$_1$ 3.7 **X** 21.7 **I**	**I** −0.7 **X**
III(OH)a	**g** −28.0 **Sm1** −5.7 **SmC*** 9.1^a **X**$_5$ 38.7 **X**$_6$ 43.2 **SmC*** 111.2 **Ch** 168.1^b **BP** 172.5 **I**	**I** 171.2 **BP** 170.3^b **Ch** 117.7 SmC* −11.5 **Sm1** −28.0 **g**

[a] Cold recrystallization. [b] Optical Data.

Mesogenic Properties. Pure Compounds. Thermal data corresponding to the 11 compounds synthesized are gathered in Table 2.

When only one aromatic ring is present in the molecule [series **II(OH)** and **II(H)**] a large decrease in melting temperatures is observed in comparison with the corresponding two-ring analogues [series **I(OH)** and **I(H)**]. Most of the compounds of series **II(OH)** and **II(H)** crystallize well below room temperature, which is very interesting in terms of their utilization as dopants in FLC mixtures.

Neither the compounds in series **I(OH/H)** nor those in series **II(OH/H)** show the potentially ferroelectric SmC* phase. Cholesteric monotropic behavior is exhibited by all four compounds in series **I(OH)**. The widest cholesteric range is seen when a *sec*-butyl group is incorporated into the oxazoline ring. Cholesteric behavior is also shown by one of the two compounds in series **I(H)** which happens to have the *sec*-butyl group in the oxazoline stereogenic center. The other compound in series **I(H)** is not cholesteric.

In an attempt to obtain the SmC* phase in a pure compound, a third aromatic ring was incorporated into the structure **I(OH)a**. Thus, compound **III(OH)a**, derived from the biphenylic acid, shows a wide-range SmC* phase, which supercools well below room temperature. In addition, **III(OH)a** drew our attention because of its special thermal behavior, which is graphically represented by its DSC scans in Figure 4. The crystalline substance was heated at a rate of 10 °C/min (Figure 4a). During the melting process, rich polymorphism was detected before the ferroelectric mesophase was observed (**X**$_1$ 43.5 **X**$_2$ 49.8 **X**$_3$ 56.9 **X**$_4$ 74.1 °C **SmC***). A cholesteric phase appears upon heating the SmC* phase ($t_{\mathrm{SmC^*\text{-}Ch}} = 114.1$ °C), transforming into a blue phase at 170.3 °C which lasts two degrees before isotropization ($t_{\mathrm{BP\text{-}I}} = 172.5$ °C). The second scan (Figure 4b) represents the cooling process from the isotropic liquid. The same phase sequence is encountered on cooling. The SmC* phase stands on cooling, becoming highly viscous at 25 °C. At a temperature of −11.5 °C, the SmC* phase transforms into an unidentified crystalline smectic phase (**Sm1**) which turns into the glassy state on cooling by a few degrees. The Tg is much easier to detect in the second heating process (Figure 4c). On

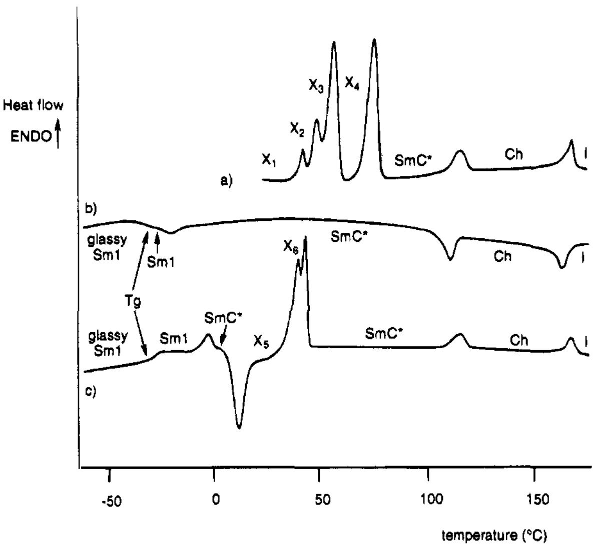

Figure 4. DSC scans [first heating (a), first cooling (b), and second heating (c)] for compound **III(OH)a**, recorded at a rate of 10 °C/min.

Table 3. Transition Temperatures (°C) for the Mixtures Containing 10 mol % of the Chiral Dopants of Series **I(OH/H)**, **II(OH/H)**, and **III(OH)** Obtained from the Cooling Process Determined by Differential Scanning Calorimetry

chiral dopant	I	→	Ch	→	SmA	→	SmC*	→	SmB_h	→	X
I(OH)a	•	82.5	•	71.0	•	69.9	•	32.0	•	18.0	•
I(OH)b	•	84.1	•	70.5	•	69.8	•	33.5	•	17.5	•
I(OH)c	•	83.0	•	70.5	•	67.5	•	34.0	•	18.0	•
I(OH)d	•	80.8	•	66.0	•	64.0	•	31.2	•	13.3	•
I(H)a	•	86.7	•	81.3	•	70.8	•	42.4	•	23.8	•
I(H)b	•	85.7	•	81.0	•	70.0	•	42.8	•	25.2	•
II(OH)a	•	77.0	•	62.2	•	55.0	•	30.4	•	26.5	•
II(OH)b	•	77.5	•	60.7	•	51.0	•	30.5	•	26.2	•
II(H)a	•	79.1	•	70.9	•	57.5	•	33.2	•	27.5	•
II(H)b	•	76.8	•	68.0	•	54.2	•	32.0	•	27.1	•
III(OH)a	•	93.7	•	83.6	•	77.0	•	38.7	•	18.7	•

increasing the temperature at a rate of 10 °C, the glass transforms into the Sm1 phase inducing a step in the curve whose inflexion point was calculated to be −28 °C. The SmC* phase appears at −5.7 °C and remains for a few degrees before undergoing cold crystallization at 9.1 °C. The subsequent melting process occurs through two crystalline phases, and the ferroelectric SmC* phase reappears at 50 °C. The phase sequence SmC*-Ch-BP-I can then be observed again.

Binary Mixtures. Binary mixtures were prepared in order to evaluate the potential ferroelectric behavior of all the compounds synthesized. Mixtures (10 mol %) were made by blending the chiral dopant with an achiral SmC matrix at the temperature of the isotropic state. 6-Hexyloxyphenyl 4′-decyloxybenzoate[19] was chosen as the achiral matrix, which shows a wide SmC phase range close to room temperature, in addition to a mesogenic sequence advantageous for obtaining good planar alignment: Ch-SmA-SmC*.

The mesogenic behavior of the 11 binary mixtures is shown in Table 3.

All 11 mixtures retain the phase sequence of the achiral matrix: I-Ch-SmA-SmC*-SmB_{hex}-X. However, the presence of the H-bond in the structure of chiral dopants in series **I(OH)**, **II(OH)**, and **III(OH)** seems to cause a considerable shortening of the SmA range when compared with series **I(H)** and **II(H)**. A decrease in clearing temperatures is observed for the compounds containing one-benzene-ring [series **II(OH)** and **II(H)**] in contrast to their corresponding two-ring analogues [series **I(OH)** and **I(H)**, respectively], which have the same mesogenic core as the achiral matrix. The widest SmC* phase range was obtained for the mixture containing the compound **III(OH)a**, which shows the ferroelectric phase in its pure form.

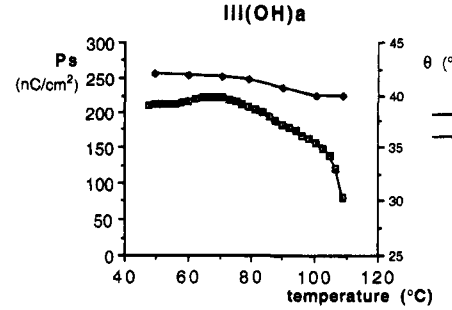

Figure 5. Temperature dependence of the spontaneous polarization (P_s) and tilt angle (θ) in compound **III(OH)a** in the SmC* phase.

The alkyl group (**R**) at the stereogenic center has no significant influence on mesogenic properties. Only a slight decrease in transition temperatures is observed when the alkyl group is drastically shortened (compound **I(OH)d**, R = $-CH_3$).

Ferroelectric Properties. Pure Compounds. Compound **III(OH)a**, which showed special mesogenic behavior, has been studied in the pure state as a ferroelectric liquid crystal. The measured P_s max is high: 225 nC/cm^2. Assuming a density of 0.8 g/cm^3 the measured polarization is approximately equivalent to 0.84 D/molecule. The calculated molecular dipole of the hydroxy oxazoline group is 1.9 D (Figure 3), if we suppose that this dipolar moment is perfectly aligned along P (macroscopic dipole density) fully 42% of the important molecular functional array is oriented along P in the tilted phase.[20] These results strongly agree with those obtained in molecules with similar structure and length published by Walba et al.,[21] indicating in both cases a quite efficient dipolar moment orientation in the mesophase. The presence of a cholesteric phase above the SmC* phase and the corresponding first order transition gives rise to a particular dependence of P_s and θ against temperature (Figure 5). The spontaneous polarization increases sharply over a few degrees below the Ch-SmC* transition, and it reaches 156 nC/cm^2 at t−tc = −10 °C. The tilt angle, θ, is quite large and reaches 42° at the temperature of the P_s max value (67 °C) and 40° ten degrees below the Ch-SmC* transition. This ferroelectric behavior, together with its special mesogenic characteristics, makes compound **III(OH)a** very interesting from the point of view of practical applications. An in-depth study of the physical properties of this pure compound is beyond the scope of this paper and will be the target of further work.

Binary Mixtures. The ferroelectric properties of all the mixtures are gathered in Table 4: spontaneous polarization (maxima and t−tc = −10 °C values), switching times (t−tc = −10 °C), and viscosity values (t−tc = −10 °C).

Tilt angles (θ) were also measured for all the mixtures and are included in Table 4. There is a significant difference between the tilt angles of materials with chiral dopants containing different mesogenic cores.

The well-established strong coupling between P_s and θ is taken into account in the P_0 values[22] (reduced polarization, eq

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Table 4. Spontaneous Polarization [P_s (max, t−tc = −10 °C), nC/cm^2], Tilt Angle [θ(max, t−tc = −10 °C)], Reduced Polarization [P_o (max, t−tc = −10 °C), nC/cm^2], Response Time [τE (t−tc = −10 °C), μsV/μm], and Rotational Viscosities [γ_c (t−tc = −10 °C), Pa.s] for the 11 Binary Mixtures Containing 10 mol % of the Chiral Dopants of Series **I(OH/H)**, **II(OH/H)**, and **III(OH)**

chiral dopant	P_s max	θ max	$P_s(-10)$	$\theta(-10)$	P_o max	$P_o(-10)$	$\tau(-10)$	$\gamma_c(-10)$
I(OH)a	−16.7	26.5	10.2	25.5	37.4	23.7	452	0.0261
I(OH)b	−13.2	25.5	8.8	25.7	30.7	20.3	589	0.0291
I(OH)c	−14.7	26.5	9.0	23.9	32.9	22.2	441	0.0225
I(OH)d	−6.7	23.3	5.4	22.6	16.9	14.1	802	0.0245
I(H)a	−5.0	23.7	3.8	21.9	12.4	10.2	768	0.0162
I(H)b	−4.1	22.5	3.5	21.0	10.7	9.8	704	0.0132
II(OH)a	−7.5	22.3	4.2	19.5	19.6	12.6	704	0.0175
II(OH)b	−5.5	21.4	3.8	19.5	15.1	11.4	917	0.0190
II(H)a	−4.5	20.0	3.0	19.6	13.2	8.9	785	0.0131
II(H)b	−3.8	19.0	2.8	18.5	11.7	8.8	830	0.0134
III(OH)a	−12.3	27.5	8.5	23.3	26.5	21.5	471	0.0228

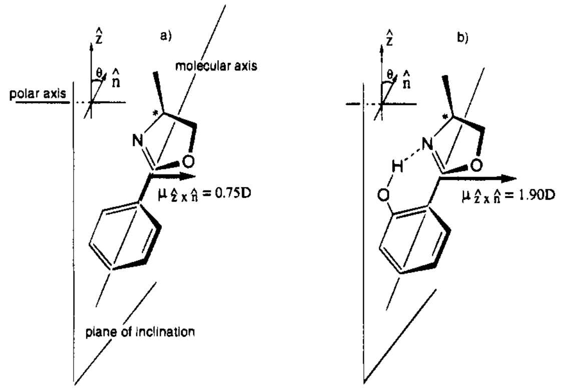

Figure 6. Representation of the disposition of the chiral part of the oxazoline-derived molecules within the SmC* phase. The planar asymmetric group is situated in a plane perpendicular to the plane of inclination. Thus the molecular axis is contained in this plane and a significant dipole component exists along the polar axis of the ferroelectric mesophase.

2) whose consideration allows a more accurate comparative study of the different structures. Furthermore, studies on P_o

$$P_o = P_s/\sin\theta \qquad (2)$$

point out its independence of the nature of the achiral host,[23,24] especially when the dipole moment of the chiral dopant is small or moderate, and so the ferroelectric behavior represented by the P_o value should only correspond to the structure of the chiral dopant, which is the subject of our study.

As mentioned above (Figure 3), the dipole moments of these structures are only significant in the plane of the molecule. Consequently, effective contribution of the corresponding dipole to the P_s value can only be achieved if a molecular disposition similar to that represented in Figure 6 is considered in the SmC* phase. A large number of the molecules situate the dipolar moment of their chiral center in a plane perpendicular to the plane of inclination. In this arrangement, a significant dipole component exists parallel to the polar axis of the chiral phase, which accounts for the existence of a nonzero macroscopic polarization.

As previously mentioned in the structural characterization section, an important difference exists between the dipole components associated to the rigid chiral moieties of compounds in series **I(H)** and **II(H)** and those of compounds in series **I(OH)** and **II(OH)**. We therefore expected a strong increase in P_s values in compounds of the latter series. Indeed, when we examined the experimental P_o data of mixtures of series **I(OH)**, we found that they showed the highest P_s values, which are more than three times those of their homologues in series **I(H)**. However this increase, which would be expected to be of the same order in the other related H-bonded structures, did not occur to the same extent in compounds of series **II(OH)**. These results must correspond to a different behavior of the H-bonded and non-H-bonded chiral moieties depending on the structure of the mesogenic core of the dopant. Whereas series **I(H)** and **II(H)** show almost equal moderate P_o values independently of their structure, a reasonable difference is found among P_o values of related compounds in series **I(OH)** and **II(OH)**. This distinct behavior led us to think about molecular steric factors becoming more significant for molecules which have a high dipole moment with a strong component lying along the polar axis of the SmC* arrangement. The highest P_o values correspond to mixtures of compounds in series **I(OH)** which happen to have the most similar structure to that of the achiral host (P_o max = 37.4 nC/cm^2). In this situation, the dopant-host steric interactions must give rise to a homogeneous composition of the SmC* layer increasing the order parameter, which may lead to a convenient coupling of dipoles, favoring high P_s values. Molecules in series **II(OH)** are significantly shorter than the achiral host molecule and show a marked lower P_o value (P_o max = 19.6 nC/cm^2). To confirm this idea about the structural homogeneity, we can also compare with the P_o value measured for the mixture of **III(OH)a**, which has an identical chiral moiety. The only difference is the third aromatic ring in the core which lengthens the molecule with respect to the achiral host. Also in this case the P_o value (P_o max = 26.5 nC/cm^2) is clearly lower than this for compound **I(OH)a**. Since it concerns 10% molar mixtures the relation dipole moment/unit volume is very similar in the different mixtures. As a consequence in this particular case the structural factors are possibly mainly responsible for the different ferroelectric properties observed in homologous derivatives. When the structures of host and quest are more similar, a higher homogeneity is obtained in the SmC*-layer, resulting in a higher order parameter; consequently an increase of the spontaneous polarization is achieved.

The overview of P_o data in Table 4 gives us an extensive idea of the potential ferroelectric properties of these chiral oxazolines. The effectiveness of the H-bond in making the chiral oxazoline moiety more rigid is clear. If we compare those results with those obtained for other dopants with related structures and high P_s chiral tails (Table 5), we can confirm the effectiveness of the H-bonded oxazoline structures. Traditional chiral tails giving rise to high P_s values (such as 2-octanol and 2-chloro-3-methylpentanoic acid) have been included in dopants for mixtures consisting of the same achiral matrix which we have employed in the present study.[25] In spite of the dopant "core" being the same, P_s and P_o values are much lower than those of the oxazoline analogues [**I(OH)a** and **I(OH)b**].

The shortening of the alkyl group (**R**) at the stereogenic center (compound **I(OH)d**) gives rise to the lowest P_s value within its

Table 5. P_s max and P_o max of Binary Mixtures Containing 10 mol % of the Corresponding Chiral Dopant **I(OH)a** or **I(OH)b** Compared with the Same Data Evaluated for Binary Mixtures Containing 10 mol % of Related Chiral Dopants with Other Chiral Tails, 2-Octanol and 2-Chloro-3-methylpentanoic Acid

chiral dopant	P_s max (nC/cm^2)	P_o max (nC/cm^2)
$C_{10}H_{21}O\phi COO\phi(OH)OXAZ^*C^*H(CH_3)C_2H_5$ **(I(OH)a)**	16.7	37.4
$C_{10}H_{21}O\phi COO\phi(OH)OXAZ^*C^*H(CH_3)_2$ **(I(OH)b)**	13.2	30.7
$C_{10}H_{21}O\phi COO\phi OC^*H(CH_3)C_6H_{13}$ [25]	3.2	8.2
$C_{10}H_{21}O\phi COO\phi OCOC^*HClC^*H(CH_3)C_2H_5$ [25]	6.5	17.4

Table 6. Response Times (τE, μsV/μm) for the Mixtures of Four Chiral Dopants and Two Different hosts (a) 6-Hexyloxyphenyl 4′-decyloxybenzoate and (b) a Phenylpyrimidine Material

chiral dopant	phenylbenzoate host[a]	phenylpyrimidine host[b]	
	τE (t−tc = −10 °C)	τE (t−tc = −10 °C)	τE (rt)
I(OH)a	452	431	796
I(H)a	768	345	519
II(OH)a	704	628	653
II(H)a	785	551	632

series. However, this did not prevent obtaining higher polarization values than for the compounds with longer alkyl groups in the non-H-bonded materials.

With regard to the electrooptical properties of these materials, the rigid naphtho[1,2-*b*]oxazoline-like structure of the compounds in series **I(OH)**, **II(OH)**, and **III(OH)**, seems to increase their rotational viscosity when compared with the other series' (see Table 4). However, taking into account the mathematical relationship between P_s, τ, and γ_c (eq 3), the high P_s values of these compounds compensate for the viscosity effect and give rise to lower response times. The fastest responses to an electrical pulse were measured for the mixtures of compounds of series **I(OH)** (whose chiral compound has a long **R** group at the stereogenic center **-a**, **b**, **c-**) and of compound **III(OH)**.

$$\tau E = k\gamma_c/P_s \qquad (3)$$

In order to evaluate the possibility to use these compounds as chiral dopants and trying to obtain fast response times, four additional mixtures (10% weight) have been prepared. Compounds **I(OH)a**, **I(H)a**, **II(OH)a**, and **II(H)a** have been blended with a commercial phenylpyrimidine host (supplied by Displatech, Inc.). The four mixtures show an SmC* phase at room temperature. Response times have been measured under the same conditions previously used. Unfortunately, the same order of magnitude of response times has been found for the new mixtures, at t−tc = −10 °C and at room temperature (Table 6), as for mixtures with the ester-derivative host.

Contrary to what happened for mixtures with the phenylbenzoate-derived host, the lowest response times correspond to compounds without intramolecular H-bond.

As a consequence, for every mixture with different host, all factors involved in eq 3 (P_s, γ, and τ) must be considered in order to choose the most efficient dopant for ferroelectric liquid−crystalline mixtures.

Conclusions

Aryloxazolines have been tested as chiral moieties in new FLC dopants. Both H-bonded [**I(OH)**, **II(OH)**, and **III(OH)**] and non-H-bonded [**I(H)** and **II(H)**] oxazoline derivatives have been synthesized and studied. A relatively simple synthetic method allows us to obtain different derivatives with high optical purity. In the field of ferroelectric liquid crystals, the accessability of the pure material is a crucial factor from the point of view of applications.

A planar conformation has been determined by AM1 calculations for all aryloxazolines. In this planar geometry, the molecular dipole mainly lies in the plane of the molecule. As a consequence, an effective contribution of the dipole moment to the spontaneous polarization (P_s) can only be achieved if the disposition of the planar chiral moiety is perpendicular to the plane of inclination within the SmC* phase.

Spectroscopic studies have proved the existence of a strong intramolecular H-bond between the hydroxyl group and the nitrogen atom of the oxazoline ring. This H-bond plays a fundamental role in the improved ferroelectric behavior of the corresponding mixtures for two reasons. Firstly, the increased rigidity of the planar structure of the compounds of series **I(OH)**, **II(OH)**, and **III(OH)** with respect to compounds of series without an H-bond [**I(H)** and **II(H)**] and, secondly, the significant increase in the molecular dipole moduli observed in H-bonded structures.

Another significant point concerns a steric factor related to the structural similarity between the dopant and matrix molecules. Compounds in series **I(OH)**, with the most similar structure to the achiral matrix, show the highest P_s values. These P_s values [$P_s\text{max}_{\mathrm{I(OH)a}} = 16.7$ nC/cm^2, $P_s\text{max}_{\mathrm{I(OH)b}} = 13.2$ nC/cm^2] are much higher than those found in similar binary mixtures containing compounds with chiral tails traditionally used for obtaining high P_s values: 2-octanol and 2-chloro-3-methylpentanoic acid.

Finally, a combination of the mesogenic and ferroelectric behavior of all the mixtures proved that these oxazoline derivatives are, in general, very interesting compounds to be used as FLC dopants. Among them, compounds of series **I(OH)**, which crystallize close to room temperature and give the highest P_s/P_o values in mixtures, are the best candidates. Nevertheless, the promising characteristics of compounds of series **II(OH)** and **II(H)**, with only one aromatic ring, must be also emphasized. In addition to their low melting temperatures (they remain liquid at room temperature), they have the simplest structure of the compounds studied, and give rise to considerably high P_s/P_o values in mixtures.

Experimental Section

Synthesis. General Methods. All reactions were carried out in flame-dried glassware under argon using anhydrous solvents which were purified according to the published methods.[26] 2,4-Dihydroxybenzaldehyde and 4-hydroxybenzonitrile (**1**) were purchased from Fluka. 4-Decyloxybenzoyl chloride (**5**) and 4′-decyloxy-4-phenylbenzoyl chloride (**6**) were prepared from the corresponding commercially available hydroxy acids. Amino alcohols were synthesized from the corresponding amino acids following published procedures.[27] Thin-layer chromatography (TLC) was performed on Macherey & Nagel

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silicagel 60 (Alugram SIL G/UV_{254}) TLC plates. For column chromatography silica gel C 560 (35−70 μm; Chemische Fabrik Uetikon) was used. Products were detected by UV or revealed by coloration with phosphomolybdic acid (PMA) followed by heating.

2,4-Dihydroxybenzonitrile (2). A solution of 2,4-dihydroxybenzaldehyde (55.3 g, 0.4 mol) in 150 mL of ethanol was treated with a concentrated aqueous solution of hydroxylamine hydrochloride (41.7 g, 0.6 mol) followed by slow addition of a concentrated aqueous solution of Na_2CO_3 (63.6 g, 0.6 mol). Ethanol was added until a homogeneous solution was obtained. The resulting mixture was stirred at ambient temperature for 0.5 h. After standing overnight, colorless crystals were obtained. They were isolated by filtration, dried *in vacuo*, and recrystallized from water to give 57.3 g (94%) of the corresponding oxime. The solid was then dissolved and refluxed in 350 mL of acetic anhydride for 3 h. After cooling to ambient temperature the solvent was removed under reduced pressure, and the remaining solid was dissolved in 200 mL of CH_2Cl_2. The solution was washed with a concentrated aqueous solution of $NaHCO_3$ until no further gas evolution (CO_2) was observed. The organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. The crude product (81.8 g) was treated with aqueous KOH solution (70 g of KOH in 300 mL of water), and the resulting solution, which slowly turned black, was stirred for 3 days at ambient temperature. Careful acidification (pH 2) with diluted sulfuric acid (20 vol.%) was followed by extraction with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. Recrystallization from chloroform gave 33.1 g (61%) of **2** as a colorless solid: sublimation 152 °C; ^1H NMR (300 MHz, acetone-d_6) δ 9.4 (s, br, 2H), 7.4 (d, J = 8.5 Hz, 1H), 6.5 (m, 2H); ^{13}C NMR (75 MHz, acetone-d_6): δ 163.5, 162.3, 135.4, 117.7, 109.3, 103.6, 92.1; EIMS *m/z* (rel intensity) 136 (10), 135 (M^+, 100), 108 (33), 107 (32), 80 (15), 79 (21), 52 (43). Anal. Calcd for $C_7H_5NO_2$: C, 62.22; H, 3.73; N, 10.37. Found: C, 62.32; H, 3.65; N, 10.48.

Preparation of (4′-Hydroxyphenyl)-2-oxazolines 3a,b. According to the general procedure for the synthesis of bis(2-oxazolines)[9b] using zinc chloride (0.68 g, 5 mmol), nitrile **1** (10 mmol), and amino alcohol (12 mmol) in 30 mL of chlorobenzene. After 18 h under reflux the solvent was removed *in vacuo*, and the residue was dissolved in acetone. Silica gel (2 g) was added, the solvent was removed, and the remaining solid was carefully dried. The products were purified by column chromatography on silica gel (petroleum ether/EtOAc 2:1).

(4*S*)-4,5-Dihydro-2-(4′-hydroxyphenyl)-4-[(*S*)-1-methylpropyl]oxazole (3a). Obtained from 4-hydroxybenzonitrile (**1**) and L-isoleucinol in 52% yield as a colorless solid: mp 149 °C; $[\alpha]^{20}_{589}$ −30.4° (*c* 1.28, acetone); ^1H NMR (300 MHz, $CDCl_3$) δ 9.36 (s, br, 1H), 7.72 (d, J = 8.8 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 4.43−4.19 (m, 3H), 1.79−1.72 (m, 1H), 1.52−1.43 (m, 1H), 1.26−1.13 (m, 1H), 0.90 (t, J = 7.4 Hz, 3H), 0.84 (d, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4, 160.8, 130.3, 117.3, 115.6, 69.4, 69.3, 38.5, 26.0, 13.7, 11.7. Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.10; H, 7.90; N, 5.91.

(4*S*)-4,5-Dihydro-2-(4′-hydroxyphenyl)-4-isopropyloxazole (3b). Obtained from 4-hydroxybenzonitrile (**1**) and L-valinol in 41% yield as a colorless solid: mp 145 °C; $[\alpha]^{20}_{589}$ −46.0° (*c* 1.19, acetone); ^1H NMR (300 MHz, $CDCl_3$) δ 10.05 (s, br, 1H), 7.70 (d, J = 8.8 Hz, 2H), 6.71 (d, J = 8.8 Hz, 2H), 4.44−4.39 (m, 1H), 4.23−4.12 (m, 2H), 1.93−1.89 (m, 1H), 0.98 (d, J = 6.7 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 160.9, 130.2, 117.1, 115.6, 70.9, 69.9, 32.4, 18.7, 17.6; EIMS *m/z* (rel intensity) 205 (M^+, 5), 163 (10), 162 (100), 134 (17), 107 (33); CIMS (NH_3) *m/z* (relative intensity) 206 ($M + 1^+$, 100). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.83. Found: C, 70.07; H, 7.17; N, 6.76.

Preparation of (2′,4′-Dihydroxyphenyl)-2-oxazolines 4a−d and Compounds of Series II(H). According to the general procedure for the preparation of bis(2-oxazolines)[9b] using zinc chloride (34 mg, 0.25 mmol), nitrile **2** or **7** (10 mmol), and amino alcohol (12 mmol) in 30 mL of chlorobenzene. After 18 h under reflux the products were isolated as described.[9b] Purification by column chromatography (petroleum ether/EtOAc 10:1) was followed by high vacuum distillation.

(4*S*)-4,5-Dihydro-2-(2′,4′-dihydroxyphenyl)-4-[(*S*)-1-methylpropyl]oxazole (4a). Obtained from 2,4-dihydroxybenzonitrile (**2**) and L-isoleucinol in 60% yield as a colorless solid: mp 58 °C; $[\alpha]^{20}_{589}$ +5.0° (*c* 2.16, ethanol); ^1H NMR (300 MHz, $CDCl_3$) δ 9.0 (s, br, 2H), 7.49 (d, J = 8.6 Hz, 1H), 6.47 (d, J = 2.4 Hz, 1H), 6.35 (dd, J = 8.6, 2.3 Hz, 1H), 4.40 (dd, J = 8.6, 7.5 Hz, 1H), 4.21−4.07 (m, 2H), 1.67−1.53 (m, 2H), 1.26−1.14 (m, 1H), 0.93 (t, J = 7.3 Hz, 3H), 0.87 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 162.4, 160.6, 129.5, 107.1, 103.6, 103.1, 69.9, 69.3, 39.3, 25.9, 14.7, 11.3; EIMS *m/z* (rel intensity) 235 (M^+, 54), 178 (100), 150 (35), 137 (85). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.31; H, 7.40; N, 6.05.

(4*S*)-4,5-Dihydro-2-(2′,4′-dihydroxyphenyl)-4-isopropyloxazole (4b). Obtained from 2,4-dihydroxybenzonitrile (**2**) and L-valinol in 55% yield as a colorless solid: mp 113 °C; $[\alpha]^{20}_{589}$ +20.9° (*c* 2.20, ethanol); ^1H NMR (300 MHz, acetone-d_6) δ 7.49−7.46 (m, 1H), 6.42−6.38 (m, 2H), 4.50−4.45 (m, 1H), 4.19−4.10 (m, 2H), 1.80−1.70 (m, 1H), 0.99 (d, J = 6.7 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, acetone-d_6) δ 165.9, 162.9, 162.8, 130.1, 107.8, 103.9, 103.2, 72.0, 70.4, 33.7, 18.8; EIMS *m/z* (rel intensity) 221 (M^+, 32), 178 (100), 150 (47). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.16; H, 6.63; N, 6.37.

(4*S*)-4,5-Dihydro-2-(2′,4′-dihydroxyphenyl)-4-(2-methylpropyl)oxazole (4c). Obtained from 2,4-dihydroxybenzonitrile (**2**) and L-leucinol in 50% yield as a colorless solid: mp 96 °C; $[\alpha]^{20}_{589}$ +50.2° (*c* 2.01, ethanol); ^1H NMR (300 MHz, $CDCl_3$) δ 8.9 (s, br, 2H), 7.52 (d, J = 8.5 Hz, 1H), 6.46 (d, J = 2.4 Hz, 1H), 6.37 (dd, J = 8.5, 2.4 Hz, 1H), 4.49 (dd, J = 9.2, 7.8 Hz, 1H), 4.45−4.33 (m, 1H), 3.95 (t, J = 7.8 Hz, 1H), 1.88−1.81 (m, 1H), 1.69−1.60 (m, 1H), 1.45−1.36 (m, 1H), 1.00 (d, J = 6.6 Hz, 3H), 0.99 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 162.2, 160.6, 129.5, 107.1, 103.8, 103.1, 72.5, 63.0, 45.3, 25.6, 22.9, 22.4; EIMS *m/z* (rel intensity) 235 (M^+, 23), 178 (100), 150 (30), 137 (14). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.16; H, 7.03; N, 5.74.

(4*S*)-4,5-Dihydro-2-(2′,4′-dihydroxyphenyl)-4-methyloxazole (4d). Obtained from 2,4-dihydroxybenzonitrile (**2**) and L-alaninol in 55% yield as a colorless solid: mp 113 °C; $[\alpha]^{20}_{589}$ +37.0° (*c* 1.95, ethanol); ^1H NMR (300 MHz, acetone-d_6) δ 10.5 (s, br, 2H), 7.49−7.46 (m, 1H), 6.42−6.39 (m, 2H), 4.56−4.51 (m, 1H), 4.45−4.37 (m, 1H), 3.96 (t, J = 7.7 Hz, 1H), 1.31 (d, J = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, acetone-d_6) δ 165.7, 162.9, 162.7, 130.1, 107.8, 103.9, 103.2, 73.8, 61.3, 21.6; EIMS *m/z* (rel intensity) 193 (M^+, 100), 178 (33), 150 (20), 135 (93). Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.18; H, 5.43; N, 7.08.

(4*S*)-4,5-Dihydro-2-(4′-decyloxyphenyl)-4-[(*S*)-1-methylpropyl]oxazole [II(H)a]. Obtained from **7** and L-isoleucinol in 32% yield as a colorless oil: bp 160 °C (0.06 mbar); $[\alpha]^{20}_{589}$ −32.6° (*c* 2.15, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 4.35 (dd, J = 8.8, 7.7 Hz, 1H), 4.33−4.16 (m, 1H), 4.11 (t, J = 7.4 Hz, 1H), 3.98 (t, J = 6.6 Hz, 2H), 1.81−1.56 (m, 4H), 1.47−1.18 (m, 15H), 0.95 (t, J = 7.3 Hz, 3H), 0.92−0.84 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.2, 161.6, 129.9, 120.0, 114.1, 70.9, 69.5, 68.1, 39.1, 31.9, 29.5, 29.4, 29.3, 29.2, 26.2, 26.0, 22.7, 14.2, 14.1, 11.6; EIMS *m/z* (rel intensity) 303 (21), 302 (100), 43 (19); CIMS (NH_3) *m/z* (rel intensity) 360 ($M + 1^+$, 100). Anal. Calcd for $C_{23}H_{37}NO_2$: C, 76.83; H, 10.37; N, 3.90. Found: C, 77.07; H, 10.60; N, 3.96.

(4*S*)-4,5-Dihydro-2-(4′-decyloxyphenyl)-4-isopropyloxazole [II(H)b]. Obtained from **7** and L-valinol in 28% yield as a colorless solid: $[\alpha]^{20}_{589}$ −43.3° (*c* 3.53, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 4.38−4.35 (m, 1H), 4.15−4.06 (m, 2H), 3.98 (t, J = 6.6 Hz, 2H), 1.87−1.75 (m, 3H), 1.47−1.27 (m, 14H), 1.02 (d, J = 6.7 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 161.7, 130.0, 119.9, 114.1, 72.3, 70.0, 68.1, 32.8, 31.9, 29.5, 29.4, 29.3, 29.1, 26.0, 22.6, 19.0, 18.0, 14.1; EIMS *m/z* (rel intensity) 303 (21), 302 (100), 43 (17); CIMS (NH_3) *m/z* (rel intensity) 346 ($M + 1^+$, 100), 302 (13). Anal. Calcd for $C_{22}H_{35}NO_2$: C, 76.48; H, 10.21; N, 4.05. Found: C, 77.28; H, 10.71; N, 3.85.

4′-Decyloxy-4-benzoyloxybenzonitrile (7). To a solution of 1.19 g (10 mmol) of 4-hydroxybenzonitrile (**1**) in 50 mL of dry pyridine was slowly added acid chloride **5** (2.97 g, 10 mmol). After stirring at ambient temperature overnight the mixture was treated with 50 mL of 5 N HCl and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by chromatography (pentane/EtOAc 10:1) gave 3.18 g (84%) of colorless crystals: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.12 (d, J = 9.0 Hz, 2H), 7.72 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 4.05 (t, J = 6.5 Hz, 2H), 1.85−1.78 (m, 2H), 1.49−1.22 (m, 14H), 0.88 (t, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 164.0, 163.9, 133.5, 132.3, 122.9, 120.4, 118.2, 114.4, 109.3, 68.3, 31.7, 29.4, 29.2, 29.1, 25.8, 22.5, 18.2, 14.0. The product was used for the preparation of compounds of series **II(H)** without further analysis.

General Procedure for the Preparation of Compounds of Series I(OH) and I(H). To a solution of acid chloride **5** (1.24 g, 4.2 mmol) in 15 mL of CH$_2$Cl$_2$ was added triethylamine (0.57 mL, 0.41 g) followed by 4 mmol of 2-oxazoline **3** or **4**. After stirring at ambient temperature overnight the mixture was poured into 10 mL of an aqueous solution of 1 N HCl. The organic layer was separated and washed twice with saturated aqueous NaHCO$_3$ solution. The combined aqueous washes were back-extracted with 30 mL of CH$_2$Cl$_2$. The organic extracts were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated *in vacuo*. The crude products were purified by MPLC on silica gel (pentane/EtOAc 50:1).

(4*S*)-4,5-Dihydro-2-[4′-(4″-decyloxybenzoyloxy)phenyl]-4-[(*S*)-1-methylpropyl]oxazole [I(H)a]. Obtained from **3a** and **5** in 71% yield: $[\alpha]^{20}_{589}$ −26.2° (c 0.15, CHCl$_3$); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.14 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 4.39 (t, J = 8.2 Hz, 1H), 4.28−4.22 (m, 1H), 4.15 (t, J = 7.6 Hz, 1H), 4.04 (t, J = 6.6 Hz, 2H), 1.84−1.19 (m, 19H), 0.97 (t, J = 7.4 Hz, 3H), 0.93−0.86 (m, 6H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 164.4, 163.5 (2C), 153.3, 132.2, 129.6, 121.6, 121.1 (2C), 114.3, 71.2, 69.7, 68.4, 39.2, 32.0, 29.6, 29.4, 29.3, 29.2, 26.2, 26.0, 22.8, 14.4, 14.2, 11.7; EIMS m/z (rel intensity) 262 (18), 261 (100), 121 (52), 43 (12); CIMS (NH$_3$) m/z (rel intensity) 481 (20), 480 (M + 1$^+$, 61), 263 (21), 220 (100). Anal. Calcd for C$_{30}$H$_{41}$NO$_4$: C, 75.12; H, 8.62; N, 2.92. Found: C, 75.04; H, 8.69; N, 2.87.

(4*S*)-4,5-Dihydro-2-[4″-(4″-decyloxybenzoyloxy)phenyl]-4-isopropyloxazole [I(H)b]. Obtained from **3b** and **5** in 52% yield as a colorless solid: $[\alpha]^{20}_{589}$ −26.5° (c 0.72, CHCl$_3$); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.13 (d, J = 8.9 Hz, 2H), 8.02 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 4.45−4.38 (m, 1H), 4.18−4.08 (m, 2H), 4.04 (t, J = 6.6 Hz, 2H), 1.91−1.77 (m, 3H), 1.49−1.24 (m, 14H), 1.04 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H), 0.89 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 164.5, 163.7, 162.7, 153.4, 132.3, 129.6, 121.7, 121.3, 121.2, 114.3, 72.6, 70.2, 68.3, 32.8, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.0, 18.9, 18.0, 14.1; EIMS m/z (rel intensity) 262 (18), 261 (100), 121 (50), 43 (15); CIMS (NH$_3$) m/z (rel intensity) 467 (M + 1$^+$, 32), 466 (M$^+$, 100), 203 (52).

(4*S*)-4,5-Dihydro-2-[4′-(4″-decyloxybenzoyloxy)phenyl]-4-[(*S*)-1-methylpropyl]oxazole [I(OH)a]. Obtained from **4a** and **5** in 40% yield as a colorless solid: $[\alpha]^{20}_{589}$ −23.6° (c 1.06, toluene); ^{1}H NMR (300 MHz, CDCl$_3$) δ 12.40 (s, broad, 1H), 8.12 (d, J = 8.9 Hz, 2H), 7.66 (d, J = 8.5 Hz, 1H), 6.97 (d, J = 8.9 Hz, 2H), 6.87 (d, J = 2.1 Hz, 1H), 6.75 (dd, J = 8.6, 2.2 Hz, 1H), 4.42 (t, J = 8.6 Hz, 1H), 4.25−4.22 (m, 1H), 4.12 (t, J = 7.9 Hz, 1H), 4.04 (t, J = 6.5 Hz, 2H), 1.84−1.79 (m, 2H), 1.66−1.60 (m, 2H), 1.47−1.22 (m, 15H), 0.98−0.86 (m, 9H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 164.6, 164.4, 163.6, 161.2, 154.9, 132.3, 128.8, 121.3, 114.3, 112.5, 110.1, 108.5, 70.1, 69.5, 68.3, 39.3, 31.9, 29.5, 29.3, 29.3, 29.1, 26.0, 25.9, 22.7, 14.7, 14.1, 11.3; EIMS m/z (rel intensity) 496 (M + 1$^+$, 5), 495 (M$^+$, 16), 262 (19), 261 (100), 121 (67). Anal. Calcd for C$_{30}$H$_{41}$NO$_5$: C, 72.70; H, 8.34; N, 2.83. Found: C, 72.86; H, 8.10; N, 2.97.

(4*S*)-4,5-Dihydro-2-[4′-(4″-decyloxybenzoyloxy)phenyl]-4-isopropyloxazole [I(OH)b]. Obtained from **4b** and **5** in 36% yield as a colorless solid: $[\alpha]^{20}_{589}$ −29.7° (c 1.13, toluene); ^{1}H NMR (300 MHz, CDCl$_3$): δ 12.50 (s, br, 1H), 8.12 (d, J = 8.9 Hz, 2H), 7.67 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 9.0 Hz, 2H), 6.87 (d, J = 2.1 Hz, 1H), 6.74 (dd, J = 8.6, 2.1 Hz, 1H), 4.44−4.38 (m, 1H), 4.15−4.09 (m, 2H), 4.03 (t, J = 6.5 Hz, 2H), 1.86−1.77 (m, 3H), 1.47−1.28 (m, 14H), 1.01 (d, J = 6.8 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 164.7, 164.3, 163.6, 161.2, 154.9, 132.3, 128.8, 121.3, 114.3, 112.5, 110.1, 108.5, 71.4, 69.8, 68.3, 33.0, 31.9, 31.9, 29.5, 29.3, 29.3, 29.1, 26.0, 22.6, 18.6, 18.5, 14.1; EIMS m/z (rel intensity) 481 (M$^+$, 15), 262 (19), 261 (100), 121 (66). Anal. Calcd for C$_{29}$H$_{39}$NO$_5$: C, 72.32; H, 8.16; N, 2.91. Found: C, 72.40; H, 8.30; N, 3.16.

(4*S*)-4,5-Dihydro-2-[4′-(4″-decyloxybenzoyloxy)phenyl]-4-(2-methyl)propyloxazole [I(OH)c]. Obtained from **4c** and **5** in 66% yield as a colorless solid: $[\alpha]^{20}_{589}$ −35.4° (c 1.04, toluene); ^{1}H NMR (300 MHz, CDCl$_3$) δ 12.40 (s, br, 1H), 8.12 (d, J = 9.0 Hz, 2H), 7.67 (d, J = 8.6 Hz, 1H), 6.96 (d, J = 8.9 Hz, 2H), 6.86 (d, J = 2.0 Hz, 1H), 6.75 (dd, J = 8.6, 2.2 Hz, 1H), 4.50 (t, J = 8.6 Hz, 1H), 4.45−4.36 (m, 1H), 4.03 (t, J = 6.5 Hz, 2H), 3.98 (t, J = 7.7 Hz, 1H), 1.91−1.77 (m, 3H), 1.70−1.61 (m, 1H), 1.49−1.28 (m, 17H), 1.00 (d, J = 6.4 Hz, 3H), 0.98 (d, J = 6.6 Hz, 3H), 0.89 (t, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 164.6, 164.4, 163.7, 161.1, 154.9, 132.3, 128.8, 121.3, 114.3, 112.5, 110.1, 108.6, 72.5, 68.4, 63.8, 45.5, 33.0, 31.9, 29.5, 29.4, 29.3, 29.1, 26.0, 25.6, 23.0, 22.7, 22.4, 14.1; EIMS m/z (rel intensity) 496 (M + 1$^+$, 5), 495 (M$^+$, 15), 262 (19), 261 (100), 121 (64). Anal. Calcd for C$_{30}$H$_{41}$NO$_5$: C, 72.70; H, 8.34; N, 2.83. Found: C, 72.90; H, 8.50; N, 2.85.

(4*S*)-4,5-Dihydro-2-[4′-(4″-decyloxybenzoyloxy)phenyl]-4-methyloxazole [I(OH)d]. Obtained from **4d** and **5** in 29% yield as a colorless solid: $[\alpha]^{20}_{589}$ −32.3° (c 1.20, toluene); ^{1}H NMR (300 MHz, CDCl$_3$) δ 12.40 (s, broad, 1H), 8.12 (d, J = 9.0 Hz, 2H), 7.67 (d, J = 8.6 Hz, 1H), 6.96 (d, J = 8.9 Hz, 2H), 6.87 (s, 1H), 6.75 (d, J = 8.6 Hz, 1H), 4.54−4.40 (m, 2H), 4.04 (t, J = 6.5 Hz, 2H), 3.95 (t, J = 7.2 Hz, 1H), 1.84−1.77 (m, 2H), 1.47−1.28 (m, 17H), 0.89 (t, J = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 164.6, 164.3, 163.6, 161.1, 154.9, 132.3, 128.8, 121.3, 114.3, 112.5, 110.1, 108.5, 73.3, 68.3, 60.8, 31.9, 29.5, 29.3, 29.3, 29.1, 26.0, 21.7, 21.4, 14.1; EIMS m/z (rel intensity) 453 (M$^+$, 14), 262 (19), 261 (100), 121 (67). Anal. Calcd for C$_{27}$H$_{35}$NO$_5$: C, 71.50; H, 7.78; N, 3.09. Found: C, 71.68; H, 7.90; N, 3.15.

General Procedure for the Preparation of II(OH)a,b. To a solution of KOH (0.610 g, 8.5 mmol) in DMSO (8.5 mL) was added 4.25 mmol of **4a** (**4b**) followed by decyl iodide (1.07 mL, 4.68 mmol). Stirring at ambient temperature for 17 h was followed by the addition of 40 mL of water. The mixture was extracted with diethyl ether (3 × 50 mL), and the combined organic phases were washed with brine (50 mL). The organic layer was separated and dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated *in vacuo*. The crude product was purified by two successive column chromatographies on silica gel (petroleum ether/EtOAc 10:1).

(4*S*)-4,5-Dihydro-2-(4′-decyloxy-2′-hydroxyphenyl)-4-[(*S*)-1-methylpropyl]oxazole [II(OH)a]. Obtained from **4a** and decyl iodide in 51% yield as a colorless solid: $[\alpha]^{20}_{589}$ −30.5° (c 3.0, toluene); ^{1}H NMR (300 MHz, CDCl$_3$) δ 12.54 (s, br, 1H), 7.49 (d, J = 8.6 Hz, 1H), 6.49 (d, J = 2.0 Hz, 1H), 6.43 (dd, J = 8.7, 2.0 Hz, 1H), 4.37 (t, J = 8.4 Hz, 1H), 4.21−4.04 (m, 2H), 3.95 (t, J = 6.5 Hz, 2H), 1.79−1.72 (m, 2H), 1.63−1.59 (m, 2H), 1.44−1.20 (m, 15H), 0.97−0.80 (m, 9H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 164.9, 163.3, 161.7, 128.8, 106.7, 103.6, 101.1, 69.9, 69.3, 68.1, 39.4, 31.9, 29.5, 29.3, 29.3, 29.0, 25.9, 25.9, 22.6, 14.7, 14.1, 11.3; EIMS m/z (rel intensity) 376 (M + 1$^+$, 8), 375 (M$^+$, 31), 319 (24), 318 (100), 235 (15), 178 (14), 150 (14), 57 (15), 55 (30), 43 (31), 41 (25). Anal. Calcd for C$_{23}$H$_{37}$NO$_3$: C, 73.56; H, 9.93; N, 3.73. Found: C, 73.59; H, 10.15; N, 3.93.

(4*S*)-4,5-Dihydro-2-(4′-decyloxy-2′-hydroxyphenyl)-4-isopropyloxazole [II(OH)b]. Obtained from **4b** and decyl iodide in 41% yield as a colorless solid: $[\alpha]^{20}_{589}$ −39.2° (c 3.0, toluene); ^{1}H NMR (300 MHz, CDCl$_3$) δ 12.52 (s, br, 1H), 7.51 (d, J = 8.7 Hz, 1H), 6.50 (d, J = 2.3 Hz, 1H), 6.41 (dd, J = 8.7, 2.4 Hz, 1H), 4.42−4.27 (m, 1H), 4.13−4.05 (m, 2H), 3.96 (t, J = 6.6 Hz, 2H), 1.82−1.73 (m, 2H), 1.59−1.19 (m, 15H), 1.00 (d, J = 6.6 Hz, 3H), 0.94 (d, J = 6.4 Hz, 3H), 0.88 (d, J = 6.7 Hz, 3H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 165.0, 163.3, 161.8, 128.9, 106.7, 103.6, 101.1, 71.2, 69.7, 68.1, 33.0, 31.9, 29.5, 29.3, 29.3, 29.1, 26.0, 22.7, 18.7, 18.6, 14.1; EIMS m/z (rel intensity) 362 (M + 1$^+$, 9), 361 (M$^+$, 37), 319 (20), 318 (100), 221 (18), 178 (15), 150 (15), 55 (10), 43 (10), 41 (10). Anal. Calcd for C$_{22}$H$_{35}$NO$_3$: C, 73.09; H, 9.76; N, 3.87. Found: C, 73.09; H, 9.92; N, 3.86.

(4*S*)-4,5-Dihydro-2-[(4″-decyloxybiphenyl-4′-yl-carbonyloxy)-2′-hydroxyphenyl]-4-[(*S*)-1-methylpropyl]oxazole [III(OH)a]. According to the procedure for the preparation of **I(OH/H)** using **4a** (0.471 g, 2.00 mmol), **6** (0.782 g, 2.40 mmol), and triethylamine (0.28 mL) in 15 mL of CH$_2$Cl$_2$. The crude product (0.858 g) was purified by two successive column chromatographies on silica gel (first: petroleum ether/*tert*-butylmethyl ether 3:1; second: same solvents 8:1) to give 0.359 g (31%) of **III(OH)a** as a colorless solid: $[\alpha]^{20}_{589}$ $-23.5°$ (*c* 3.0, toluene); ^{1}H NMR (300 MHz, CDCl$_3$) δ 12.58 (s, br, 1H), 8.22 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.5 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 2.2 Hz, 1H), 6.78 (dd, J = 8.5, 2.2 Hz, 1H), 4.43 (dd, J = 9.2, 8.0 Hz, 1H), 4.28−4.15 (m, 1H), 4.10 (t, J = 7.9 Hz, 1H), 4.01 (t, J = 6.6 Hz, 2H), 1.84−1.70 (m, 2H), 1.70−1.60 (m, 2H), 1.60−1.18 (m, 15H), 0.99−0.74 (m, 9H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 164.6, 161.2, 159.5, 154.6, 146.1, 131.9, 130.7, 128.8, 128.3, 127.2, 126.6, 114.9, 112.4, 110.0, 108.6, 70.1, 69.5, 68.1, 39.3, 31.9, 29.5, 29.4, 29.2, 29.1, 26.0, 25.8, 22.6, 14.7, 14.1, 11.8; EIMS *m/z* (rel intensity) 575 (5), 572 (M + 1$^+$, 10), 571 (M$^+$, 5) 338 (52), 337 (100), 197 (33), 196 (22), 43 (33). Anal. Calcd for $C_{36}H_{45}NO_5$: C, 75.63; H, 7.93; N, 2.45. Found: C, 75.30; H, 7.96; N, 2.44.

Techniques. Optical rotations were recorded on either a Perkin-Elmer 781 or a Perkin-Elmer 241 apparatus. Infrared spectra for the final compounds were obtained by using a Perkin-Elmer 1600 (series FTIR) spectrometer using Nujol mulls between polyethylene plates in the 360−4000 cm^{-1} spectral range. The UV−visible spectra for the final compounds were recorded in pentane using a Hitachi V-3400 spectrophotometer in the 200−500 nm spectral range. NMR spectra were taken on a Varian Gemini 300 or Bruker AT 200 at ambient temperature; ^{1}H NMR spectra at 300 and 200 MHz referenced to tetramethylsilane (δ 0.00 ppm); ^{13}C NMR spectra at 75 and 50 MHz referenced to the central line of CDCl$_3$ (δ 77.0 ppm). NMR-NOE experiments were carried out on a Bruker ARX 300. Mass spectra were measured on a VG 70−250 spectrometer (EIMS at 70 eV). Elemental analyses were performed using a Leco CHN-900 or a CHN-Rapid analyser (Heraeus). Medium-pressure liquid chromatography (MPLC) was carried out with Polygosil (Macherey & Nagel, 15−25 μm) using a Büchi-681 pump.

The textures of the mesophases were studied with either a Nikon or an Olympus BH-2 polarizing microscope, equipped with a Mettler hot stage FP82 and a control unit FP80 or a LINKAM hot stage THMS600 with a central processor TMS91 and a CS196 cooling system.

Measurements of transition temperatures were made using a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating or cooling rate of 10 °C/min. The apparatus was calibrated with indium (156.6 °C, 28.44 J/g) and tin (232.1 °C, 60.5 J/g).

The spontaneous polarization and the response time were obtained simultaneously using the triangular wave form method.[28] In the experimental set-up the triangular wave voltage is supplied by a HP3245A function generator. The current-voltage cycles are recorded by a digital acquisition system *tech* ADC488/16A. All the equipment was interfaced to a microcomputer. Cells for measurements are coated with polyimide and with indium tin oxide (ITO) electrodes. *Experimental details of the ferroelectric measurements:* The values of spontaneous polarization (P_s) were determined by integrating the displacement current peak which appears due to the reversal of P_s, in response to an applied triangular voltage.[28b] The maximum amplitude, frequency and cell thickness were 20 Vpp, 50 Hz, and 4 μm, respectively. Good alignment was obtained by slow cooling (0.5 or 1 °C/min) of the filled cell from the isotropic to the SmA phase.

Rotational viscosity γ_c was obtained from the parameters of the current peak calculated in the measurement of the P_s. From both values we can calculate the response time using the equation $\tau = 1.75\ \gamma_c/P_s\ E$.[29]

The sign of P_s was determined by the field reversal method through optical observation of the extinction direction by rotating the stage according to Lagerwall's convention.[30]

The tilt angles were measured as a function of temperature under crossed Nikol, as half of the rotation angle between the two extinction positions associated with oppositely directed polarization. The extinction positions were determined using a photomultiplier tube, the applied electrical dc field was 5 V/μm.

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