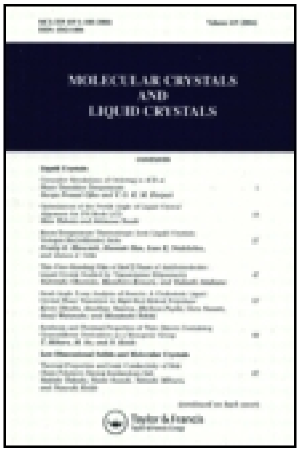

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Synthesis and Phase Behavior of Ferroelectric Chiral Imines from (*S*)-(-)-Ethyllactate

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We have synthesized new series of the Ferroelectric Chiral Imines: ($\underline{R}$)-(-)-4′-[2-methylhexyl-(4-*n*-alkoxybenzilidene)], ($\underline{R}$)-(-)-4′-[2-methylhexyl-(4-*n*-alkoxybenzoyloxy)benzilidene] and ($\underline{R}$)-(-)-4′-[2-methylhexyl-(4-*n*-alkoxycinnamoyloxy)benzilidene]anilines, or series **1**, **2** and **3**, respectively, derived from (*S*)-(-)-ethyllactate. Series **1** did not show liquid crystal phase behavior and series **2** and **3** show chiral smectic C and smectic A phase over a wide range of temperatures, and a cholesteric phase as well. The phase transition behavior is described and for the series **1**, AM1 semiempirical calculations are presented.

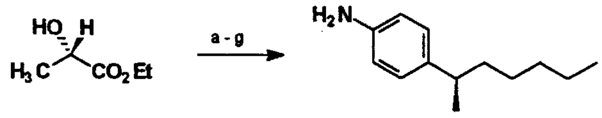
Keywords: (*S*)-(-)-ethyllactate; ferroelectric; chiral imines; synthesis; phase behavior

1. INTRODUCTION

The development of synthesis methodologies from chiral building blocks to Ferroelectric Liquid Crystals (FLCs) constitutes a fascinating branch of synthetic organic chemistry. In fact, many of the asymmetric synthesis methods applied to the construction of molecules with biological and pharmaceutical [1] interest are now available tools for chemists to design new materials with distinct properties, for example, FLCs [2].

Since 1975, when R. B. Meyer and coworkers [3] discovered the phenomenon of ferroelectricity in chiral SmC mesophases and, later, Clark and Largerwall [4] found a new eletrooptic effect-Surface Stabilized Ferroelectric-Liquid Crystals, the academic and technological research has increased enormously, due to practical applications of FLCs in displays, and organic synthetic methods have been used to construct chiral molecules with specific properties.

Recently we have reported new FLCs from (*S*)-(-)-2-methyl-1-butanol [5] and using of Piccolo's Method [6, 7], we have synthesized (*R*)-(-)-4-(2-methylhexyl) aniline [8], which is a key intermediate the synthesis of FLCs from (*S*)-(-)-ethyllactate. The synthesis is shown in Scheme I.



a) TsCl, py (55%); b) C_6H_8, $AlCl_3$ (60%); c) $AlLiH_4$, Et_2O, (89%); d) TsCl, py (95%); e) *n*-BuLi, CuI, Et_2O (73%); f) HNO_3 / H_2SO_4 (42%); g) H_2, Pd/C 10% (64%).

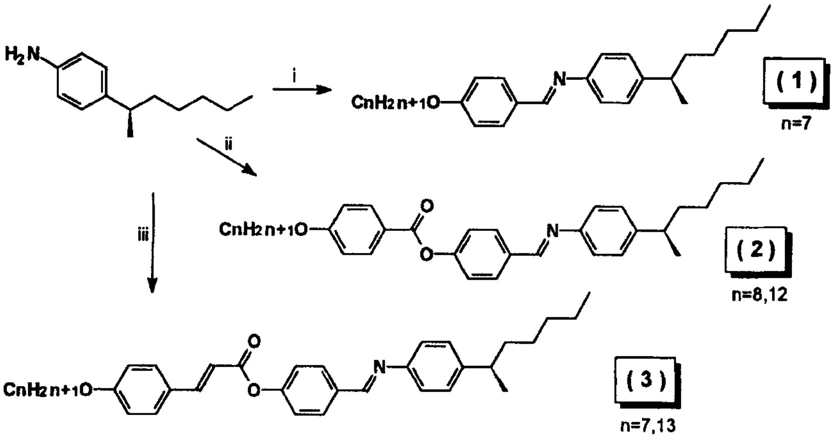
SCHEME I

In this paper we report the synthesis of Ferroelectric Chiral Imines derived from (*S*)-(-)-ethyllactate. The compounds investigated are members of the series (*R*)-(-)-4′-[2-methylhexyl-(4-*n*-alkoxybenzilidene)], (*R*)-(-)-4′-[2-methylhexyl-(4-*n*-alkoxybenzoyloxy)benzilidene] and (*R*)-(-)-4′-[2-methylhexyl-(4-*n*-alkoxycinnamoyloxy)benzilidene]anilines, or series **1**, **2** and **3**, respectively.

2. SYNTHESIS

The chiral starting material for the three series is (*R*)-(-)-4-[2-methylhexyl) aniline. The synthesis is outlined in Scheme II. The homologous series were prepared via well-known synthetic processes, using ethyl *p*-hydroxybenzoate, malonic acid and *p*-hydroxybenzaldehyde as starting materials. Condensation of the aldehydes with (*R*)-(-)-4-(2-methylhexyl/aniline) in ethanol furnished the target imines **1**, **2** and **3**, respectively.

We have prepared one member of series **1**, two members of series **2** and **3**, respectively.



i) CnH2n+1 OPhCHO, EtOH; ii) CnH 2n+1 OPhCO$_2$PhCHO, EtOH; iii) CnH 2n+1 OPhCH=CHCO$_2$PhCH, EtOH

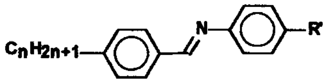
SCHEME II

3. PHASE BEHAVIOR OF THE LIQUID CRYSTALS

The sequence of phases and the corresponding transition temperatures for representatives of series **1**, **2** and **3** are shown in the Tables I, II and III, respectively. As a second member of series **1**; 4′-*n*-hexyl-(4-*n*-heptyloxybenzilidene)aniline [9] has been chosen.

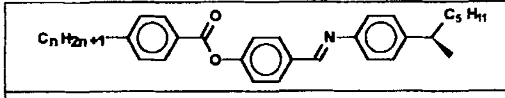
In Table I, we note that the replacement of the *n*-hexyl group by the 2-methylhexyl group leads to a dramatic change in the mesomorphic behavior: The mesophases disappear completely.

TABLE I Transition temperatures (°C) of the (R)-(-)-*p*-[2-methylhexyl-(4-*n*-heptyl oxybenzilidene)aniline (series **1**) and 4-*n*-hexyl-(4-*n*-heptyloxy-benzilidene)aniline

									
n	R'	K	SmG	SmF	SmB	SmC	SmA	N	I
7	C_7H_{15}*	· 40	· -	· -	· -	· -	· -	· -	·
7	n-hexyl	· 38	· 55	· -	· 66	· 70	· 81	· -	·

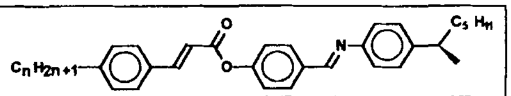
(*) assimetric carbon

TABLE II Transition temperatures (°C) of the series 2



n	K	SmC*	SmA	Ch	I
8	• 74,0	• -	• 127	• 130	•
12	• 54,0	• 117	• 124	• -	•

TABLE III Transition temperatures (°C) of the series 3



n	K	SmC*	SmA	Ch	I
7	• 89,0	• 123	• 163	• 166	•
13	• 72,0	• 148	• 154	• -	•

In order to investigate the origin of the different phase behavior in these compounds, we have performed AM1 semiempirical calculations [10] to obtain relations between the conformational properties of the molecule and its phase behavior. The relevant conformational characteristics for the phase transitions properties are the molecular linearity (here evaluated by the angle between in the iminic carbon and the two terminal carbon atoms of the alkylic chain) and the molecular dipole moment which are related to intermolecular interactions.

The more stable conformation of the isolated 4'-*n*-hexyl-(4-*n*-heptyloxy benzilidene)aniline has a low linearity (*n*-hexyl group is perpendicular to the benzene ring) and probably predominates in the isotropic phase. The other stable conformations have the central iminic system and the alkyl group almost in one plane. The energetic differences between these conformations are very small (lower than 1,0 kJ/mol) due to the large distance between the groups with different relative positions in each conformation. Thus the magnitude of the intermolecular interactions are large enough to compensate any internal disfavorable energetic contribution. Another important factor affecting the magnitude of the intermolecular interaction is the dipolar contribution. A large variation of the dipole moment, depending the relative orientation of the iminic and the alkoxy group, has been obtained for different conformations (0.7 to 2.7 D).

The modifications in the phase behavior of the (*R*)-(-)-4′-[2-methylhexyl-(4-*n*-heptyloxybenzilidene)aniline can be explained by conformational properties of the chiral center neighbored to the benzene ring. As in the previous case, the more stable and non-linear conformation shows the alkyl chain perpendicular to the benzene ring. Due to the presence of the methyl group at the carbon bridged to the aromatic ring, only conformations with the hydrogen atom in the same plane of the ring are stable. These conformations are highly non linear and, consequently, disfavor the formation of organized structures in the liquid crystalline phase. However, the dipoles moments are of the same magnitude.

From the data of Tables II and III, we can observe that these compounds of series **2** and **3** show chiral smectic C and smectic A phase over a wide range of temperatures, and cholesteric phases as well.

The smectic C thermal interval increases with increasing chain length accompanied by smaller ranges decreases of the smectic A phase. The higher smectic C thermal stability in the compounds of series III indicates an increased interaction between adjacent molecules in the smectic layers. These results show that the double bond in the cinnamate moiety has a stabilizing effect, that is, coplanarity in the central part of the molecule, favors smectic ordering in general.

We have attempted to measure the spontaneous polarization in these compounds, however is difficult due to several factors such as their low resistivity and poor alignability [11]. Preliminary measurement of the spontaneous polarization is in itself quite low and this fact, in combination with others, makes measurement difficult. The method used was the field reversal (square wave) current method [12].

4. EXPERIMENTAL

The purity of the compounds has been determined by thin layer chromatography (TLC) and elemental analysis. I. R. Spectra were recorded in KBr discs with a Perkin-Elmer model 283 spectrometer, and ^{1}H NMR were recorded at 60 MHz (Varian T-60). The 4-*n*-alkoxybenzoic acid was obtained from ethyl *p*-hydroxybenzoate under standard Williamson etherification conditions. The corresponding acid chlorides were prepared by treatment of the acid with freshly distilled thionyl chloride. The 4-(4′-*n*-alkoxybenzoyloxy) benzaldehydes and 4-(4′-*n*-alkoxycinnamoyloxy) benzaldehydes were prepared by methods of reference 13.

The target imines were prepared by standard methods and purified by chromatography on silica gel and recrystallized several times from ethanol or a mixture of hexane and benzene.

Spectroscopic data for serie **1**, ^{1}**H NMR** (CCl_4, TMS, 60 MHz, ppm): $\delta = 0{,}9$ (2t, 6H, J = 6Hz, $C\underline{H}_3$); 1,3 (d, 3H, J = 7Hz, $C\underline{H}_3CH$); 1,4 (m, 18H, $C\underline{H}_2$); 2,7 (sext. 1H, J = 7Hz, $CH_3C\underline{H}$); 4,10 (t, 2H, J = 6Hz, $C\underline{H}_2O$); 7,10 (d, 2H, J = 8Hz, Ar); 7,30–7,40 (m, 4H, Ar); 8,10 (d, 2H, J = 8Hz, Ar) and 8,60 (s, 1H, $C\underline{H} = N$). **I. R.** (KBr) νmáx: 2980, 2940, 2850, 1600, 1540, 1430, 1380, 1250, 1120 and 820 cm^{-1}.

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