4620 *Chem. Mater.* **2009,** *21,* 4620–4630
DOI:10.1021/cm901678q

CHEMISTRY OF MATERIALS
Article

Terminal Chains as a Tool To Modulate the Properties of Bent-Core Liquid Crystals

Nélida Gimeno, Joaquín Barberá, José Luis Serrano, and M. Blanca Ros*

Química Orgánica, Facultad de Ciencias, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

M. Rosario de la Fuente

Departamento de Física Aplicada II, Facultad de Ciencias y Tecnología, Universidad del País Vasco, Apdo. 644, Bilbao, Spain

Ibon Alonso and César L. Folcia

Departamento de Física de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644, Bilbao, Spain

Received June 17, 2009. Revised Manuscript Received July 29, 2009

Two series of bent-shaped liquid crystals derived from 4,4′-diphenylmethane and 3,4′-biphenylene moieties have been prepared and studied. The research, focused on the effect of the terminal chains on the mesogenic properties of bent-core compounds, demonstrates that they can be used as a tool to control their liquid crystal behavior. Together with achiral and chiral alkoxy tails, thioalkoxy chains and unusual terminal structures on bent-core mesogens such as oxyethylene moieties or unsaturated tails of different lengths have been investigated. Mesomorphism as well as dielectric responses of the new materials are reported and discussed in light of structural considerations. Interesting results concerning lowering of transition temperatures, mesophase vitrification, or columnar−lamellar sequences have been achieved by the incorporation of these terminal chains.

Since 1996, when Niori et al.[1] reported for the first time on ferroelectricity in a liquid crystalline phase formed by an achiral banana-shaped compound, these molecules have become a prime topic in the field of liquid crystals.[2] These compounds have given rise to a novel and very rich family of mesophases. Generally speaking, these liquid crystalline phases have either a lamellar or a columnar nature (Figure 1), although many variants of both types of structures (different types of undulated smectic, tilted and nontilted columnar, etc.) have been extensively reported.[2e,f] Furthermore, even when some peculiar optical and electro-optical features were considered to characterize some of the different phase variants, the allocation of a given material to one of them is ambiguous unless a complete structural analysis is performed.[2j] In any case, the so-called SmCP phase is the best known and studied one. This phase is characterized by its tilted lamellar and polar packing. Depending on the direction of polarization in adjacent layers, the mesophase can have either a ferro- or antiferroelectric ground state. On the other hand, depending on the tilt sense of the molecules in adjacent layers this soft phase could be homochiral (SmC_sP_F or SmC_aP_A phases) or racemic (SmC_aP_F or SmC_sP_A phases). Along with these unusual characteristics, this mesophase exhibits very attractive properties such as ferro- and antiferroelectric switching, significant NLO activity or piezoelectric response,[2k] and so forth.

The unusual physical properties and phenomena reported for these compounds and also the relationship between the molecular structure and the mesogenic properties of these materials have been of great interest in the last years.[2a,e,h] Thus, outstanding works where modifications on the different parts of the banana-shaped molecules, the angular core, the lateral core, and the terminal chains (Figure 1), have been analyzed and published.

Although the typically central core used is the benzene ring substituted in positions 1,3-, examples of

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*Corresponding author. Tel.: +34 976762277. E-mail: bros@unizar.es.

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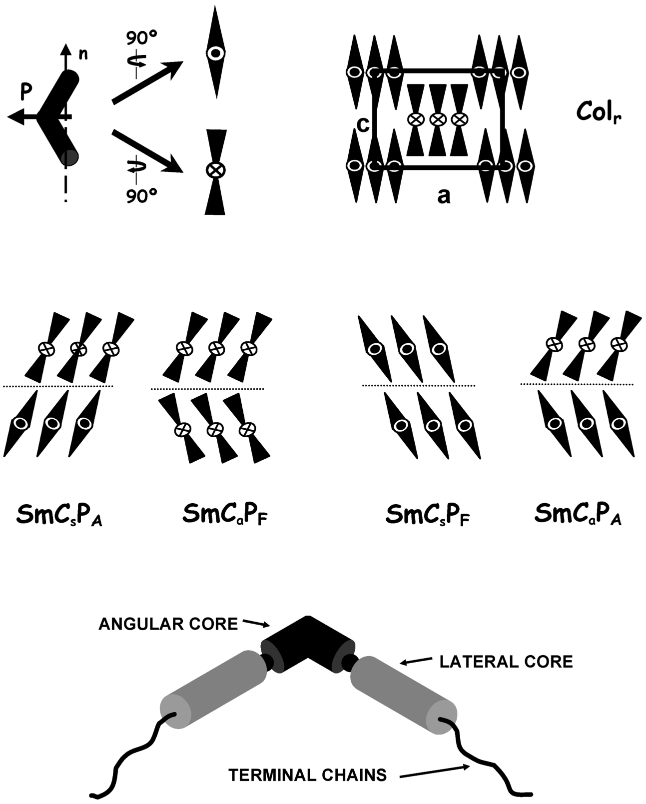

Figure 1. Schematic representations used for bent-shaped molecules (upper part/left) and one of the most accepted models for the columnar rectangular structure (Col$_r$) (see also ref 15c). The different arrangements proposed for some of the arrangements in the SmCP, which are distinguished by the relative tilt sense and the polar order in the smectic layers packing, are shown below. Here, s and a denote sinclinic or an anticlinic tilt and F and A behind P refer to a ferro- or antiferroelectricelectric polar order. General molecular structure of a bent-shaped molecule (bottom).

2,7-naphtalene[2a,e,3] or 3,4′-biphenyl central units[4] and an increasing variety of everywhere substituted central cores have been reported.[2a,e,h,i]· The lateral structures have also been widely modified.[2a,e,4e,5] In this case, the nature and sense of the links between the lateral aromatic rings have been probed to be useful tools to control the supramolecular packing. Furthermore, the variations of the number of lateral aromatic rings and the incorporation of substitutions in these aromatic rings (especially halides) have also become a very attractive target for researchers.[6]

However, few studies have been done on modifications of the terminal chains. Although several structure-mesomorphic properties relationship studies have been reported, where the length of the terminal chains is modified, namely, alkyl or alkoxy chains with 2 up to 22 carbons,[2e,7] scarce examples of systematic modifications of the nature of these chains have been reported so far.

Among these few and singular studies, those that are of special interest are those involving chiral chains.[8] They have allowed knowing the effect of introducing stereogenic centers in this type of phases. Also remarkable is the use of bulky silicon-containing groups to end the molecules.[9] In both cases these terminal tails could be used to control the ferro/antiferroelectric ground arrangement of this type of material. Also of interest are results dealing with the incorporation of polymerizable groups,[10] especially because this has opened ways to prepare high molecular weight materials presenting bent core-type phases. Finally, a few interesting examples of thioalkyl,[11] semifluorinated,[4a,12] or carbon−carbon multiple linked chains[13] with different effects on the type of the mesophase induced are mentioned.

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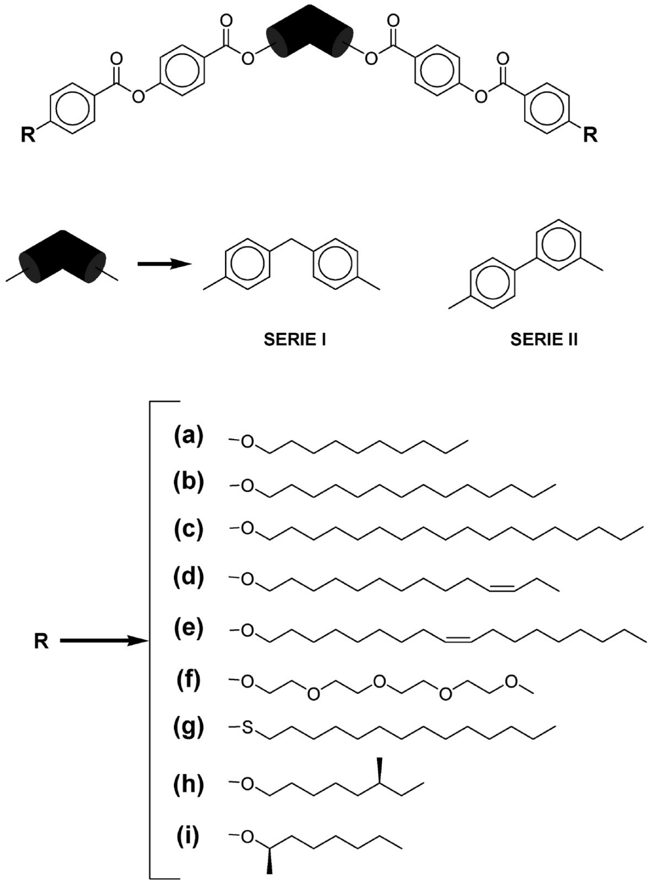
Chart 1. Molecular Structure of the Compounds Studied



Herein, we report a systematic study concerning the possibilities that the terminal tails could offer to modulate the properties of bent-core liquid crystals. We enclose the synthesis as well as the mesomorphic and dielectric characterization of two new series of banana-shaped liquid crystals bearing different terminal chains (Chart 1). Series I derives from a symmetric central core, the 4,4′-diphenylmethane, where an unusual sp^3 moiety derived from methylene is located in the center of the banana-shaped molecule. Only isolated examples of liquid crystals with this core have been reported previously.[14] On the contrary, the more common 3,4′-biphenyl moiety has been selected as a second central core to make comparisons. In both cases, an aromatic diester has been chosen as the lateral structure.

Up to nine different terminal chains have been proposed for this study. On one hand, we have incorporated alkoxy terminal chains of different lengths to know the effect of introducing a large number of methylenic groups, 10, 14, and 18, on the mesomorphic packing promoted by these two bent-cores. Alternatively, we have selected more unusual chains with different objectives. To decrease the transition temperatures and ultimately to obtain bent-core mesophases at room temperature, we have investigated the role of oxyethylenic long structures or less linear chains by incorporating double bonds. Thioalkoxy chains, which seem to favor the attractive B_7 phase[2] and chiral tails to analyze the antiferro-/ferroelectric balance were our last choices.

Compounds **Ib**, **IIg**, and **IIb** were initially prepared for this study, but some singular properties detected for them have been previously published by us elsewhere.[15] On the other hand, compounds **IIa** and **IIb** previously reported[4a] have been synthesized by an alternative route and included in this study for comparisons.

Results and Discussion

1. Synthesis. The general synthetic procedure to prepare all the banana-shaped compounds is outlined in Scheme 1. Compounds **Ia-Ig** and **IIa-IIi** were prepared by esterification of the corresponding benzoic acids (**1a**−**1i**) with appropriate diphenols, **6** and **7**, using the carbodiimide method. Diphenols **6** and **7** were prepared by esterification of 3,4′-dihydroxybiphenyl[10f] and the commercial 4,4′-bis(hydroxyphenylmethane) with *p*-hydroxybenzoic acid protected as tetrahydropyrane derivatives which were transformed to the bis-phenols by removing the protective group using *p*-TSA and ethanol as solvent. The syntheses of the acids **1a**−**1i** were accomplished by using either Mitsunobu or Williamson etherifications to introduce the different terminal chains to the benzoic esters. Subsequent hydrolisis of methyl ester yielded the corresponding benzoic acids.

2. Liquid Crystalline Properties of Series I and Series II. The mesomorphic properties of the compounds were investigated by polarized light optical microscopy (POM) on a hot stage and by differential scanning calorimetry (DSC) and X-ray diffraction (XRD) studies at variable temperature. The transition temperatures and corresponding enthalpy values of the products are summarized in Table 1, and for comparative purposes they are graphically represented in Figure 2.

a. Alkoxy Terminal Chains and the Effect of Changing Their Length (*Compounds* ***Ia***−***c*** *and* ***IIa***−***c***). Three long alkoxylic chains of different lengths, with 10, 14, and 18 carbon atoms, have been selected for this study.

All the compounds studied showed bent-core phases. Columnar mesophases were detected in compounds with the shortest length while the lamellar mesophases were observed for those bearing the longest ones. The columnar phase was proposed for **Ia** based on the mosaic texture observed by POM and by XRD through the

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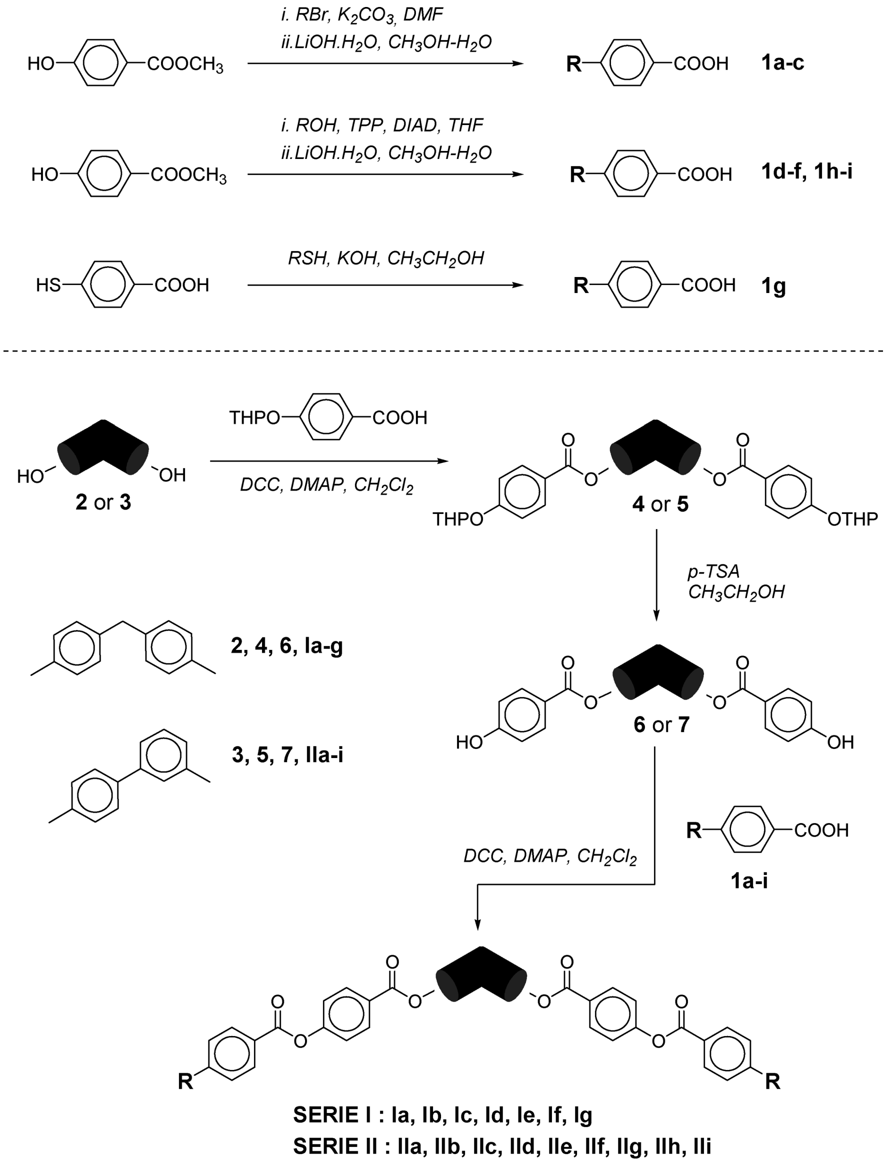
Scheme 1. Synthetic Routes Followed To Prepare the Bent-Core Compounds of Series I and Series II



appearance of the 101 and 002 reflections, which could be indexed to a rectangular cell (Table 2). The same behavior, a rectangular columnar mesophase, had been observed by Tschierske et al.[4a] for the biphenylene analogue **IIa**.

On lengthening the chains, a SmCP mesophase occurs for compounds **Ib**, **Ic**, and **IIc** that join to the one reported for **IIb**. The X-ray diffraction patterns of these compounds showed up to three reflections at periodic distances in the small-angle region in addition to a diffuse wide angle scattering (Table 2). On cooling from the isotropic liquid, typical textures reported for this lamellar phase are observed for most of these materials. Only in the case of **Ib** was an isotropic texture with dark conglomerates detected and fully characterized.[15]

Compound **Ic**, which incorporates the methylene central core and an *n*-octadecyloxy chain, exhibits mesophase polymorphism. On cooling down the compound from the isotropic liquid within untreated glass cells a mesophase appears showing small circular domains which coalesced into a focal-conic texture (Figure 3a). On further cooling, stripes appeared in the focal-conic domains indicating a mesophase transition (Figure 3b). This transition is also detected by DSC through a peak involving 1.3 kJ mol^{-1}. Both mesophases were investigated by XRD. The high temperature mesophase showed five reflections in the small-angle region besides the diffuse wide-angle scattering. These reflections were indexed on the basis of a two-dimensional rectangular cell, with the parameters $a = 100$ Å and $c = 58$ Å. At the low temperature mesophase, the diffraction patterns showed four reflections at periodic distances indicating a lamellar structure, with a layer spacing of 50 Å. These phases were identified as Col$_r$ and SmCP, respectively.

The relation between the parameter c at the Col$_r$ high temperature phase and the smectic spacing of the low temperature one is in agreement with the tilt occurring at the phase transition, according to the models depicted in Figure 2. Another feature that arises from the obtained X-ray diagrams is that the (101) reflection of the Col$_r$

phase and the (001) peak of the lamellar one are at almost the same Bragg angle and have a similar intensity (in both cases the strongest one). This fact occurs for all the columnar phases studied here (see Table 2) and could, in principle, suggest that the layer fragments of the rectangular columnar structure are oriented along the (101) direction, in which case the $(\bar{1}01)$ and the (101) reflections should present different intensities in accordance with a monoclinic structure. Unfortunately, this cannot be checked in our powder diagrams as far as both reflections are superimposed due to the rectangular translation lattice. Consequently, our interpretation of the X-ray diagrams is the simplest one in view of the limitation of the technique.

Table 1. Transition Temperatures (*T*, °C) and Enthalpies [ΔH, kJ mol^{-1}] for Compounds of Series I, Ia−g, and of Series II, IIa−i

compound	phase transitions (°C) [kJ/mol][a,b]
Ia	Cr 120.7 [19.6] Col$_r$ 169.6 [24.0] I
Ib	Cr 123.9 [60.5] SmC$_a$P$_A$ 161.6 [28.0] I
Ic	Cr 125.3 [69.9] SmC$_a$P$_A$ 161.8 [27.1] Col$_r$-I[c]
	I 160.8 [24.3] Col$_r$ 147.3 [1.3] SmC$_a$P$_A$ 114.4 [44.6] Cr
Id	Cr 108.6 [36.7] M 149.4 [25.0] I
	I 149.0 [25.1] M 99.2 [22.7] Cr
Ie	Cr 101.1 [28.7] SmC$_a$P$_A$ 137[d] Col$_r$ 142.9[e] [24.7] I
	I 141.5 [20.5] Col$_r$ 100[d] SmC$_a$P$_A$ 78.8 [29.1] Cr
If	Cr 60.2 [8.2] Col$_r$ 88.5[e] [12.3] I
Ig	Cr150.1 [28.5] Col$_r$ 166.6 [25.8] I
IIa	Cr 119 [37.7] Col$_r$ 166 [20.4] I[f]
IIb	Cr 74.2 [21.4] SmC$_a$P$_A$ 156.9 [27.9] I
IIc	Cr 84.8 [30.8] SmC$_a$P$_A$ 158.1 [23.3] I
IId	Cr 68.5 [31.8] SmC$_a$P$_A$ 146.3 [22.9] I
	I 145.5 [22.5] SmC$_a$P$_A$ 34.2 g
IIe	Cr 70.8 [2.6] SmC$_a$P$_A$ 138.3 [22.0] I
	I 134.3 [18.3] SmC$_a$P$_A$ 30.4 g
IIf	C 30.5 [1.5] SmC$_a$P$_A$ 56.8 [4.8] I
	I 50.6 [4.7] SmC$_a$P$_A$ 14.7 g
IIg	Cr 99.9 [6.8] SmC$_a$P$_A$ 138.5 [0.9] Col$_r$ 157.8[e] [20.5] I
	I 157.4 [21.9] Col$_r$ 121.6 [0.5] SmC$_a$P$_A$ 83.2 [14.5] Cr
IIh	Cr 133.1[41.0] Col$_r$ 157.5[d] [29.7] I
IIi	Cr 100.6 [33.0] I

[a] Data determined by DSC, from second scans at a scanning rate of 10 °C/min. [b] Cr: crystal, Col$_r$: columnar rectangular mesophase, SmC$_a$P$_A$: smectic C anticlinic polar antiferroelectric mesophase, M: coexistence of lamellar and columnar mesophases, I: isotropic liquid, g: glassy mesophase. [c] Joined enthalpy of the Colr-I transition. [d] Optical microscopic data. DSC peak was not detected. [e] Broad peak, data corresponding to the maximum of a DSC peak. [f] Data in agreement with the one reported in the literature (ref 4a).

Small angle X-ray diffraction diagrams present, however, some peculiarities for this material. Here, the 2θ interval is 0.5−4.0° and the SmCP phase is identified by the strong (001) reflection together with a small peak corresponding to the (002) one. On the other hand, apart from the strong (101) peak, the Col$_r$ structure shows two weak anomalies for 28.9 Å and 25.1 Å spacing (see Table 2). We performed various heating and cooling runs with different samples. Since we can reduce the time required to perform a diagram to less than half an hour, it can be considered that the thermal behavior that the material would show in a continuous run is not altered to a large extent. The diagram always shows a SmCP phase on heating from room temperature, which normally remains up to the clearing point. In a few heating runs, however, the Col$_r$ structure was observed before the isotropic phase. On the other hand, the sequence Isotropic−Col$_r$−SmCP was always observed on cooling, although, in some of the runs, the weak reflections characterizing the Col$_r$ structure and the (002) peak of the SmCP phase were not so well-defined or even were absent. It seems, therefore, that the existence of the Col$_r$ phase (and, perhaps, the degree of order of the Col$_r$ and SmCP structures) depends on the thermal history of the sample. This trend is also observed in the dielectric measurements as we shall mention later.

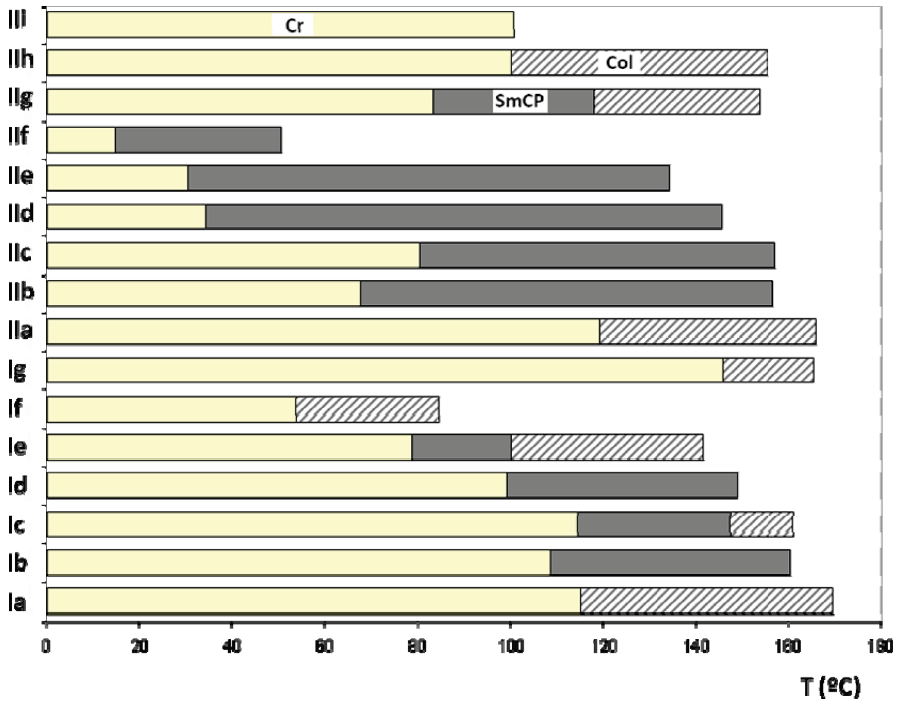


Figure 2. Graphical representation of the transition temperatures of compounds of series I and II on the cooling process.

Table 2. X-ray Diffraction Data for the Mesophases of the Compounds Ia−g and IIb−h

compound	phase	d_{obs} (Å)	Miller indices (*hkl*)	lattice parameters (Å)
Ia	Col_r	32.3	101	a = 42.7
		24.7	002	c = 49.4
Ib	SmCP	46.2	001	
		23.1	002	c = 46.2
		15.4	003	
Ic	Col_r	50.2	101, 200	
		28.9	301, 002	a = 100
		25.1	400, 202	c = 58
		18.9	501, 402, 103	
		16.7	600, 303	
	SmCP	48.7	001	
		25.4	002	c = 49.9
		16.7	003	
		12.5	004	
Id	Col_r	41.6	101	a = 66
		26.8	002	c = 53.5
		20.5	202, 301	
		17.2	103	
	SmCP	44.3	001	c = 45
		22.4	002	
		14.9	003	
Ie	Col_r	49.5	101, 200	a = 99
		28.6	301, 002	c = 57.2
		24.8	400, 202	
		18.7	501, 402, 103	
		16.5	600, 303	
	SmCP	49.7	001	c = 49.7
		24.9	002	
		16.5	003	
If	Col_r	35.3	101	a = 48.7
		24.4	002	c = 51.1
Ig	Col_r	50.5	101	
		33.6	301	a = 128
		26.9	002	c = 54.5
		18.1	103	
IIa[4a]	SmCP	37.2	001	c = 37.2
IIb	SmCP	42.8	001	c = 42.5
		21.2	002	
		14.1	003	
IIc	SmCP	46.4	001	c = 46.2
		15.4	003	
IId	SmCP	46.4	001	c = 46.2
		15.4	003	
IIe	SmCP	46.3	001	c = 46.5
		15.5	003	
		11.7	004	
IIf	SmCP	33.9	001	c = 32.4
		15.4	002	
IIg	Col_r	46.2	101	a = 82
		28.0	002	c = 56
		23.1	202	
	SmCP	47.2	001	c = 47
		23.4	002	
IIh	Col_r	28.3	101	a = 36.2
		22.7	002	c = 45.5

The phase sequence Col−SmCP is uncommon, and indeed, there are very few examples reported in the literature.[4a,9d,9f,9g,16] Additionally, the columnar phase has been described mostly for shorter components of the mesogenic series. However, in this case, the phase is recovered on increasing the molecular length, as appears for a terminal chain longer than the one presented in the previous component of the series, namely, **Ib** (*n*: 14), that does not exhibit this phase.

This is not the case for Series II; on lengthening the chain for the biphenyl derivatives, this columnar phase is not detected. The SmCP mesophase is the only one observed for both **IIb** and **IIc**. On cooling from the isotropic liquid a highly striped focal conic texture is obtained, typical for this lamellar phase. Likewise, the X-ray patterns of these compounds in the mesophase showed up to three reflections at periodic distances in the small-angle region in addition to a diffuse wide angle scattering (Table 2).

Layer spacings, in the range of 42−50 Å, were measured experimentally for the compounds at the SmCP phase for series I and II. When comparing experimental values with the ones determined theoretically using stereomodels (considering extended conformation of the terminal chains), it was possible to calculate tilting angles around 48°, accordingly to previous values reported for this mesophase in bent-core compounds. For those materials showing polymorphism, differences around 8−9 Å could be detected for the *c* parameter going from the lamellar to the columnar arrangement.

If we compare the properties of the two series it can be seen that both angular cores stabilize the liquid crystalline order in a similar way but in a range of temperatures in the case of the methylene core narrower than the biphenylene one. On the other hand, the methylene core allows both columnar and lamellar packing when very long flexible tails are present, probably related with the conformational freedom due the sp^3 C present in the central core.

b. Alkenes, Oxyethylenes, and Alkylthio Structures as Terminal Chains (*Compunds **Id−g** and **IId−g***). In 1993, Kelly[17] carried out a vast study where terminal chains bearing double bonds with cis and trans configurations were linked to pro-mesogenic cores. This work concluded that trans double bonds at an odd position with respect to the core increased the transition temperatures, whereas a cis double bond in an even position provoked an opposite effect. A second study, performed by Dyer and Walba,[18] also on calamitic liquid crystals, showed that it was possible to obtain room temperature liquid crystals by incorporating terminal chain derivates from alcohols coming from fatty acids with an even number of C-atoms, such as oleic acid.

With this purpose, we selected two different cis-unsaturated terminal chains, which were incorporated to both angular cores through the alcohols with 14 and 18 carbon atoms for comparisons. All the compounds prepared, **Id, Ie, IId**, and **IIe**, exhibit liquid crystalline properties. A decrease of both the melting and the clearing temperatures around 10−20 °C is afforded on changing to the unsaturated tails in both series, but far from room temperature. However, some differences depending on the nature of the central core can be pointed out.

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(16) (a) Amaranatha Reddy, R.; Sadashiva, B. K. *Liq. Cryst.* **2004**, *31*, 1069. (b) Pelz, K.; Findeisen, S.; Pelzl, G.; Diele, S.; Weissflog, W. *Liq. Cryst.* **2006**, *33*, 803. (c) Pelzl, G.; Tamba, M. G.; Findeisen-Tandel, S.; Schroeder, M. W.; Baumeister, U.; Diele, S.; Weissflog, W. *J. Mater. Chem.* **2008**, *18*, 3017.

(17) Kelly, S. M. *Liq. Cryst.* **1993**, *14*, 675.

(18) Dyer, D. J.; Walba, D. M. *Chem. Mater.* **1994**, *6*, 1096.

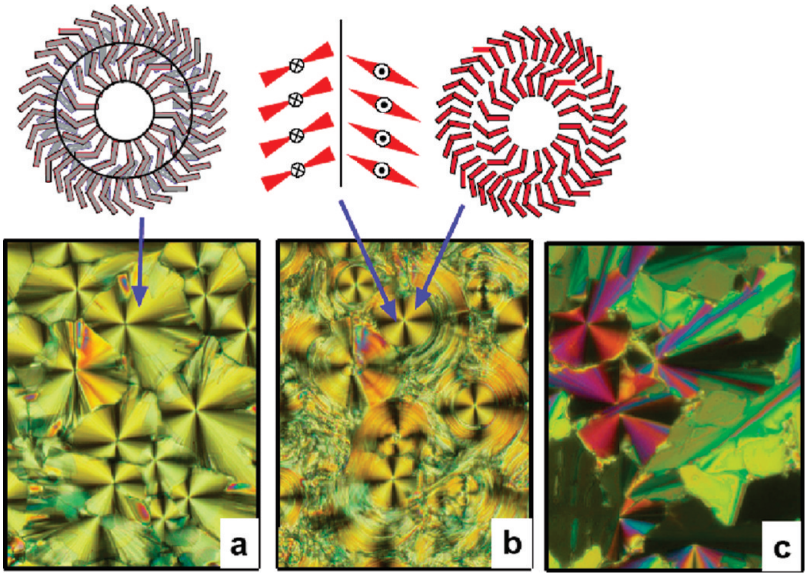

Figure 3. Microphotographs of the textures corresponding to the Colr (a) and SmCP (b) mesophase of compound **Ic**. The schematic molecular arrangement proposed for the circular domains of the Col_r structure is in agreement with the observed birefringence as explained in ref 15c. In the case of the SmCP structure, two different molecular arrangements are, in principle, possible if no electric field has been applied to the sample. Microphotograph of the texture corresponding to the Colr mesophase of compound **IIh** (c).

Regarding the mesogenic ranges, on the heating processes the alkene compounds form a mesophase within temperature ranges similar to the ones provided by the saturated analogues (**Id** and **Ie** vs **Ib** and **Ic**, respectively, and **IId** and **IIe** vs **IIb** and **IIc**). However, compounds **IId** and **IIe** incorporating the biphenyl moiety as the central core show upon cooling the vitrification of the mesophase ($T_g \sim 30$ °C) instead of its crystallization. Thus, in both cases the mesophase order, namely, SmCP, is frozen at room temperature, which increases the interest for these compounds. Moreover, compound **IIe** under triangular fields shows ferroelectric-like switching, as we shall mention later.

Second, compounds **IId** and **IIe** show the SmCP, as it was confirmed from their X-ray diffraction patterns and with a dark conglomerated texture in the case of **IIe**. However, the methylene analogues **Id** and **Ie** exhibit polymorphysm at the liquid crystalline state. Thus, a clear enantiotropic SmCP-Col_r transition was detected by means of wide and small-angle X-ray scattering in compound **Ie** with 18 C-atoms in the terminal tails. On the other hand, when a shorter alkene chain is present, as in compound **Id**, the small-angle X-ray diagrams, obtained for various cooling and heating runs in different samples, show a clear coexistence of lamellar and columnar arrangements. For each structure the observed spacing sequence corresponds with that presented in Table 2, and the volume relation between both phases depends strongly on the thermal history of the material. Again, like in the case of compound **Ic**, the relation between the parameter *c* at the Col_r structure and the layer spacing of the smetic phase indicates that the molecular arrangement becomes tilted at the phase transition, according to Figure 2.

Once again the combination of both long terminal tails and a sp^3 C based angular core lead to diverse molecular arrangement in the soft phase that could be attributed to the conformational possibilities of both the terminal and the central parts of the molecules.

Alternatively, a different approach to lower the transition temperatures was considered. Namely, the incorporation of oxyethylenic chains, a methodology broadly used in calamitic liquid crystals and mesogenic polymers.[19]

Two oxyethylenic compounds **If** and **IIf** were prepared, leading both to mesomorphic behavior. As it had been observed for most of the compounds of series **I**, a columnar phase was detected for compound **If**. A mosaic texture was observed under POM when cooling from the isotropic liquid, and up to two reflections in the X-ray diffraction pattern were detected, which could be indexed to a rectangular columnar cell which lattice parameters $a = 49$ Å and $c = 51$ Å. If we compare compounds **If** with the methylene analogue **Ib**, a remarkable decrease in the transition temperatures for compound **If** was observed as well as a change in the type of mesophase but within a shorter temperature range.

Similar effects were observed for compound **IIf**, but in this case a SmCP phase was confirmed by its grainy texture of on cooling from the isotropic liquid and by XRD studies. Interestingly, on cooling the lamellar phase is stable at room temperature, and furthermore, it vitrifies below room temperature.

Finally, when alkylthio terminal chains were used, neither **Ig** nor **IIg** afforded the expected B_7 phase.[19] In the case of compound **Ig**, with the methylene central core, a columnar mesophase was detected in a very narrow range of temperatures, in contrast to the lamellar one

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(19) (a) Haller, I.; Cox, R. J. *Liquid Crystals and Ordered Fluids*; Plenum Press: New York, 1970. (b) Chiang, Y. H.; Ames, A. M.; Guadiana, R. A.; Adams, T. G. *Mol. Cryst. Liq. Cryst.* **1991**, *208*, 85. (c) Kaminska, A.; Mieczkowski, J.; Pociecha, D.; Szyddlowska, J.; Gorecka, E. *J. Mater. Chem.* **2003**, *13*, 475.

induced by the alkoxy analogue (**Ib**). Indexation of the reflections observed for **Ig** by XRD revealed a rectangular cell with parameters *a*: = 128 Å and *c* = 55 Å (Table 2).

On the contrary, compound **IIg** affords a SmCP−Col phase sequence. This transition has been deeply studied by using by XRD measurements and calorimetry, and additionally, a field-induced columnar to lamellar transition has also proposed for this material. All these results were previously reported by us.[15a−h] Compound **Ic** shows a similar behavior as we shall show later.

c. Introducing Chirality through Stereogenic Centers. Even though the singular properties of the SmCP phase occur lacking molecular chirality, literature has also offered very attractive results working on chiral bent-core molecules, especially to control the ferro- vs antiferroelectric packing at the SmCP phase.[2e,8]

Taking this into account we also pursued the investigation of the effect of incorporating chiral alkoxy chains derived from both (*S*)-(+)-2-methylheptanol and (*S*)-(+)-6-methyl-1-octanol. On the basis of the low tendency of the methylene core to induce broad mesophase ranges, only the biphenylene derivatives were prepared for this study (**IIh**, **IIi**). In fact, compound **IIi**, where the stereogenic center is closer to the rigid core, does not form a mesophase. However, compound **IIh** shows an enantiotropic columnar mesophase. This result confirms that also for bent-core structures the closer the stereogenic center to the core, the worse the mesomorphism.

On cooling down compound **IIh** from the isotropic state a mosaic texture occurs indicating a columnar mesophase (Figure 3c). X-ray diffraction patterns confirmed the nature of this mesophase as two incommensurate reflections in the small angle region were detected, which could be indexed to a columnar rectangular lattice with parameters a = 36 Å and c = 45.5 Å. Interestingly, this is a singular material as it offers molecular chirality within a columnar packing. However, no electro-optic switching was observed for it under electric field; additionally, orthogonal crossing defects were observed through the microscope. On the basis of this, a nonswitchable columnar rectangular mesophase was assigned for it.

3. Polarization and Dielectric Characterizations. Most of these compounds were studied under electric fields. As a general trend, those exhibiting a SmCP mesophase give rise to large polarization values in nonaligned samples (600−800 nC cm^{-2}), and based on MOP analysis, SmC$_a$P$_A$ phases were identified for them. Representative results from these studies will be discussed for compounds **Ic** and **IIe**.

*Compound **Ic***. As already mentioned, this compound shows a Col$_r$−SmCP mesomorphism. The dielectric properties and switching behavior of the columnar phase under strong electric fields are quite similar to the ones observed and previously reported for compound **IIg**.[15b] Thus, a rectangular nontilted structure with an antiferroelectric arrangement between adjacent columns, dipoles parallel to the columnar axis with some splay inside the columns, has been proposed for it (see Figure 1).

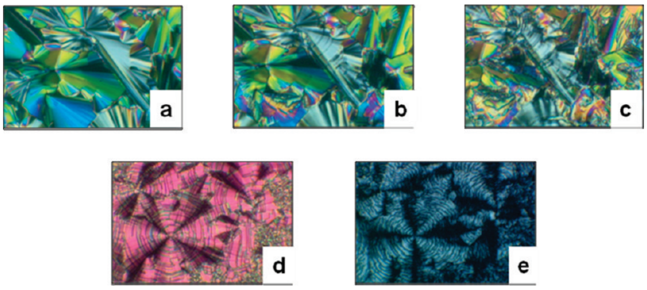


Figure 4. Microphotographs of the textures corresponding to compound **Ic**: in the Col$_r$ mesophase (a) at 160 °C and at 150 °C (b) and in the SmC$_a$P$_A$ at 140 °C (c), on applying E_{DC} = 10 V μm^{-1} (d), after removal of the DC field (e).

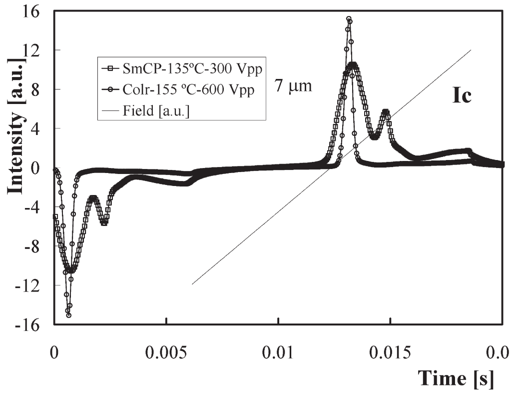


Figure 5. Polarization current in the lamellar and columnar phases for the **Ic** compound.

Cooling down the sample, the phase transition is clearly detected. Microphotographs in Figure 4 were taken upon cooling the compound from the isotropic phase in an EHC (7 μm thick) cell. The typical texture of the columnar phase (Figure 4a, at 160 °C) becomes broken when reaching the lamellar phase (Figure 4c, at 140 °C). Figure 4d,e shows respectively the SmCP texture observed under a dc field and after removing it at that temperature. As already mentioned, these textures suggest that the lamellar structure is SmC$_s$P$_F$ under field and SmC$_a$P$_A$ under no field.

Figure 5 (open squares) reveals a typical switching current under triangular voltage, 40 Hz, in this mesophase; compound **Ic** shows the antiferroelectric type polarization switching. The saturated spontaneous polarization reaches a value of 950 nC cm^{-2} with 300 Vpp in 7 μm. In the Col$_r$ order, the reversal of the spontaneous polarization could also be registered, but in this case, even at high temperatures close to the isotropic phase, a very high field is needed, 600 Vpp in 7 μm, as is shown in Figure 5 (open circles). The saturated spontaneous polarization reaches a value of 600 nC cm^{-2}. After switching-off this field, the texture becomes completely broken. Upon cooling until the lamellar phase, a square wave can afford a texture similar to that in Figure 4d. Probably the switching destroys the columnar arrangement.

Figure 6 is a three-dimensional plot of the dielectric losses vs frequency and temperature on cooling, when the 50 μm thick gold cell is used. Measurements in the range of 10^2-10^9 Hz have been made, but only the 10^2-10^7 Hz range is plotted. The different dielectric behavior of the columnar and lamellar phases is clearly visible. The dielectric spectrum is complicate and several relaxation modes are present although not clearly visible in the figure (see Supporting Information for more details).

After a fitting procedure, the strengths and frequencies of the most relevant modes are represented in Figure 7a,b vs temperature, respectively. The isotropic phase mode, frequency around 10 MHz, and dielectric strength around 1 should be attributed to the rotation around molecular long axis. This mode is also visible in the Col_r phase but with a larger frequency (open dots in the figures). In this mesophase exists also a much lower frequency and larger strength mode (open squares in the figures). In the lamellar phase this mode is also present but with decreasing strength (see also Supporing Information). Here the predominant mode has an intermediate frequency and a much larger strength, around 6 (open triangles in the figures). This mode is usually observed in SmCP mesophases, and we propose a collective antiphase-phason mode. Its strength depends significantly on the field treatment.[15b,g−i] The presence of the low frequency mode in the lamellar phase, similar to the one in the columnar phase, could be attributed to some phase coexistence. This dielectric behavior is very similar to the one shown by compound **IIg** and already published.[15b] In both compounds we observe that the predominant mode in the lamellar phase has lower frequency than in the columnar one. In ref 15j the reverse is predicted. We do not have a clear explanation about this fact and just note that the columnar phase in our compounds probably is quite “lamellar”; the phase transition to the lamellar phase is first order but with a very small enthalpy content, and then the structural change involved should be small. As already mentioned, the X-ray measurements show that after some thermal treatment several reflections disappear, indicating the instability of the columnar phase. This fact is also observed in the dielectric measurements; after some thermal runs with the same sample the low frequency mode disappears and the intermediate one appears just below the isotropic phase.

Compounds **Id** and **Ie** show a quite similar behavior to compound **Ic**. For **Id** a switching behavior in the columnar phase similar to that shown in Figure 4 for **Ic** could be detected. Figure 8 shows textures of compound **Id** under a strong square wave and after its switching-off. It should

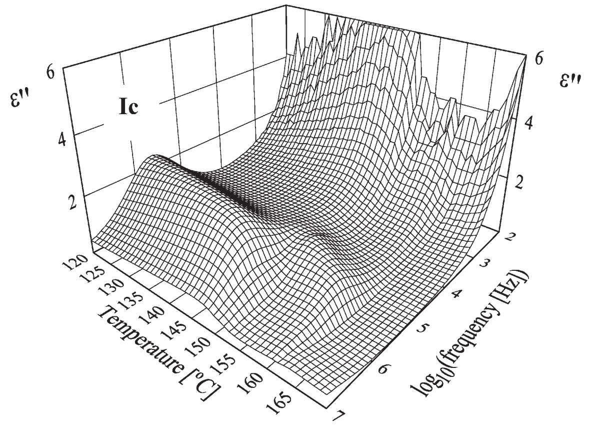


Figure 6. Three-dimensional plot of the dielectric losses vs temperature and frequency for **Ic** compound (gold cell 50 μm).

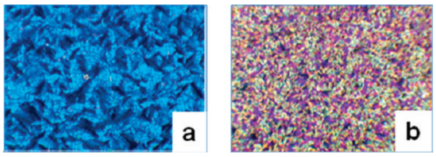


Figure 8. Microphotographs of the textures corresponding to compound Id in the Col phase, Linkam cell 5 μm: (a) under square wave 50 Hz, ± 12.5 V μm^{-1}; (b) after switching off the field suddenly.

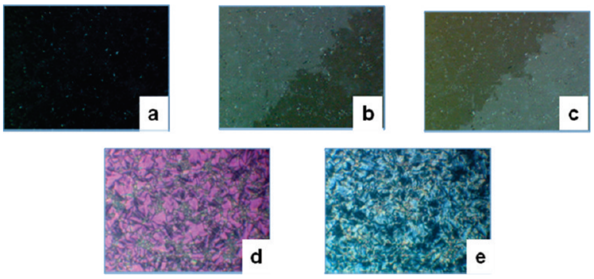
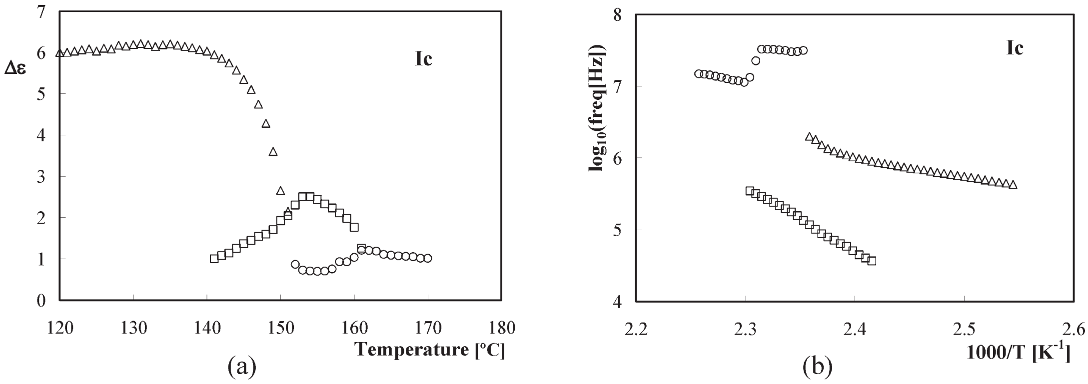


Figure 9. Compound **IIe**, EHC cell 7 μm. Dark texture obtained after switching-off gradually the field (square wave 50 Hz, ±10 V μm^{-1}): (a) crossed polarizers; (b and c) domains with opposite optical activity and slightly uncrossed polarizers; (d) birefringent texture when the field is on (square wave 50 Hz, ±10 V μm^{-1}); and (e) texture after switching off the field suddenly.



(a) (b)

Figure 7. Temperature dependence of the dielectric strengths (a) and frequencies (b) of the relaxation modes measured for compound **Ic**.

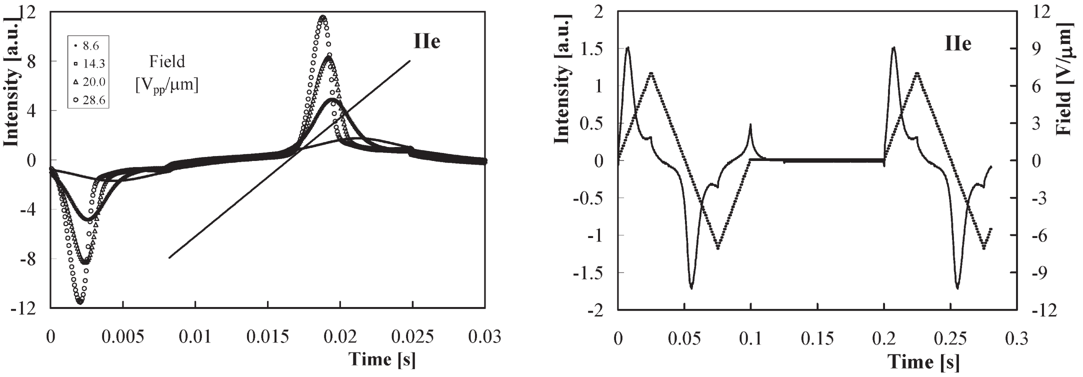


Figure 10. Polarization current for **IIe** compound at 100 °C under different electric field conditions: (a) triangular wave and (b) modified triangular wave.

be stressed that the initial texture (no field) was similar to Figure 4a and that although Figure 8b is similar to Figure 4d, in the case of compound **Ic** (Figure 4d) this corresponds to the lamellar phase.

Compound **IIe**. When a square wave, 50 Hz, ±10 V μm^{-1}, is on, compound **IIe** shows a birefringent and opaque texture with some circular domains with crosses at about 45° with the polarizers, indicating a tilt angle about 45°, compatible with a synclinic ferroelectric state with polarization along the electric field $\mathrm{SmC_sP_F}$ (Figure 9d). When the electric field is gradually removed, the lamellar phase of this compound forms a dark conglomerate phase (see Figure 9a). Domains of opposite chirality upon uncrossing analyzer and polarizer are clearly visible, as it is shown in Figure 9b,c. The nearly isotropic and clear texture is compatible with a $\mathrm{SmC_aP_A}$. However, if the electric field is switched off suddenly, the texture remains partially birefringent, as in Figure 9e. This effect has been also observed in other compounds,[16] and it could be related to the internal fields that build up due to the large polarization of the material, around 850 nC cm^{-2}.

Polarization studies have been also carried for compound **IIe**. Figure 10 shows the switching current under different field conditions, namely, for a triangular wave of 30 Hz in Figure 10a and in Figure 10b for a modified triangular wave. As it can be seen the molecular switching is ferroelectric-like with only one peak per half cycle, delayed with respect to the field sign change. We propose that although the ground structure is $\mathrm{SmC_aP_A}$, under certain conditions the ferroelectric state remains as a metastable state with no field.

Figure 11 shows a three-dimensional plot of the losses vs temperature and frequency in the range 10^2-10^7 Hz for compound **IIe**, measured in a gold cell (50 μm thick). A clear relaxation process whose strength increases and frequency decreases on cooling could be observed, starting around 1 MHz near the isotropic phase and 100 Hz at 60 °C, indicating a high thermal activation, faster than Arrhenius as is typical for glass-forming compounds.[20] Another low frequency process is also present, but it will not be discussed because it is partially out of the experimental window.

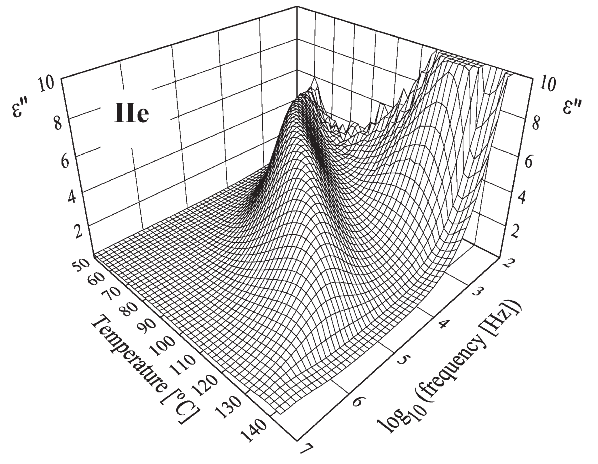


Figure 11. Three-dimensional plot of the dielectric losses vs temperature and frequency for **IIe** compound, gold cell 50 μm.

In Figure 12a the strength and frequency of the mentioned mode have been plotted vs temperature. Although the strength is quite high, 16 at 100 °C, it is not much higher than in other SmCP[15g,h,16] compounds with antiferroelectric mesophase. Its origin is the same as for compound **Ic**: a collective antiphase-phason mode. In ref 15i a model to describe the para-antiferroelectric SmA−$\mathrm{SmAP_A}$ phase transition is presented. The mode presented in the antiferroelectric phase is described as a collective antiphase−phason mode. When a bias field is on, this mode becomes enhanced; its strength increases while its frequency decreases. Above the threshold field that induces the ferroelectric state, the mode becomes quenched and the dielectric permittivity goes down. We have analyzed the field behavior of **Ic** measuring with an EHC cell 7 μm thick. The dielectric strength and the relaxation frequency of the above-mentioned mode at 100 °C, as a function of the dc applied voltage, for a virgin sample of **IIe** are plotted in Figure 12b. As it can be seen, both the strength and frequency just slightly decrease with field. However, after applying a strong electric field (triangular or square wave 50 Hz, ±10 Vμm^{-1}) and then switching off the field, the dielectric strength of the mode increases until 60; this value does not relax, and the frequency decreases. Further, we applied dc fields.

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(20) (a) González, Y.; Palacios, B.; Pérez Jubindo, M. A.; de la Fuente, M. R.; Serrano, J. L. *Phys. Rev. E* **1995**, 5764. (b) Palacios, B.; de la Fuente, M. R.; Pérez Jubindo, M. A.; Ros, M. B. *Liq. Cryst.* **1997**, *23*, 349.

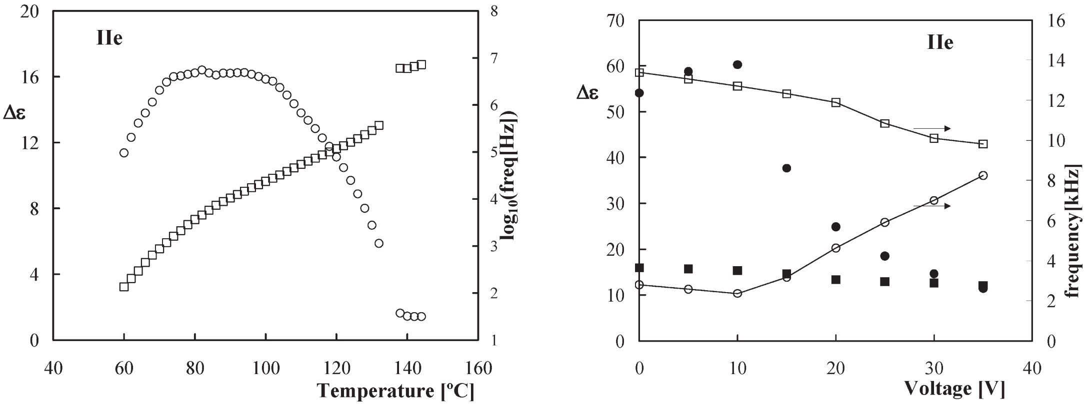

Figure 12. Compound **IIe**: (a) Temperature dependence of the strength and frequency of the dielectric relaxation mode, gold cell 50 μm. (b) Dielectric strength, full symbols, and relaxation frequency, empty symbols, vs bias dc field (100 °C, EHC cell 7 μm). Squares: virgin sample; dots: after switching-off a square wave 50 Hz ± 10 V μm^{-1}.

The strengths and frequencies are also plotted in Figure 12b. The strength first increases (while the frequency decreases), and for voltages larger than 10 V decreases (while the frequency increases) until almost the same value as in the other run. This field behavior is the same as predicted in ref 15i, but we also need to explain the difference of 16 (before the strong field was on) vs 60 (after switching off the strong field) when measuring at 0 V. We propose for this material a behavior similar to the one reported for the adamantine-based compound.[2k] Under a strong field the material was in a ferroelectric state ($\mathrm{SmC_sP_F}$) with polarization parallel to the field. On removing this field the ferroelectric order remains, but the polarization turns perpendicular to the previously applied field. In this situation the field has a great effect on the polarization, giving rise to a high permittivity value. On applying dc fields the polarization turns parallel to the field, the probe ac field has no torque on the polarization, and the permittivity decreases.

Conclusions

Novel bent-shaped molecules based on 4,4′-diphenylmethane and 3,4′-biphenyl moieties as bent cores and bearing different terminal chains have been synthesized and fully characterized. As a general conclusion, it can be said that by changing the terminal tails, the liquid crystalline properties of the bent-shaped molecules can be attractively modulated and a variety of effects can be induced.

When using long alkoxylic chains (from 10 to 18 carbon atoms), both columnar mesomorphism and $\mathrm{SmC_aP_A}$ phases can be promoted. Interestingly, bent-core mesophase polymorphism, as in compound **Ic**, can occur with the longest chain.

By using unsaturated chains, the supramolecular arrangement could also be modified with different effects depending on the central core selected. Thus, 3,4′-biphenyl derivates allows the vitrification of the SmCP mesophase around 30 °C, or appealingly, the ferroelectric order a SmCP mesophase can be stabilized, as it has been observed for **IIe**. In contrast, these tails on methylene-based structures leads to the mesophase sequence $\mathrm{Col_r}$−SmCP or their coexistence.

A room temperature SmCP mesophase was achieved by incorporating oxyethylene chains in the biphenyl derivatives, whereas it was not enough for the methylene derivative, even though a short range of columnar phases close to room temperature was obtained.

Sulfur-based tails have not induced any B7 phase; on the contray columnar self-assembling is favored. Thus, the $\mathrm{Col_r}$−SmCP polymorphism was once more detected for a sulfur-containing biphenyl derivative while the methylene core promotes a short-range columnar mesophase.

Finally, to induce bent-core liquid crystal order by using chiral tails, the incorporation of stereogenic centers far from the central core is recommended. Furthermore, a columnar mesophase could be also promoted by the appropriate selection of the bent core.

Acknowledgment. Research was supported by CICYT-FEDER of Spain-UE MAT2006-13571-C02, the Department of Ciencia, Tecnología y Universidad del Gobierno de Aragón-Fondo Social Europeo (project E04), and the Basque Country (Project No. IT-484-07) Government. N. G. acknowledges the Spanish Government for a Juan de la Cierva fellowship and I.A. is grateful to UPV for a grant.

Supporting Information Available: Additional experimental details, graphics, and description of techniques (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.