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Ferroelectric Liquid Crystals with a Tolane Rigid Core and an Optically Active Alkyl Sulfinate Group: Synthesis, Characterization, Molecular Modeling, and Stereochemical Investigations

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The synthesis and the properties of new ferroelectric liquid-crystalline compounds with a tolane rigid core and an optically active alkyl sulfinate group are reported. These compounds contain two chiral centers: a sulfinate group and a branched aliphatic chain. The diastereomers having opposite configuration at the sulfur center and the same configuration at carbon have been isolated; one exhibits smectic C* and A phases, the other only a smectic A phase. This behavior confirms the role of sulfur configuration in determining the thermotropic properties. Molecular modeling has shown that the sign of the transverse dipole moment is directly related to the sulfur configuration. By correlation of the sign of the spontaneous polarization with the sign of the calculated transverse dipole component, it has been possible to deduce sulfur's absolute configuration for each diastereomer; this appears as a new method to determine the absolute configuration of an asymmetric sulfur in chiral mesogenic molecules leading to ferroelectric liquid crystals.

Introduction

Since the electrooptical properties (fast switching, bistability) of ferroelectric smectic C* liquid crystals were reported by Clark and Lagerwall in 1980,[1] there has been a considerable interest in the synthesis of new smectic C* materials exhibiting a large spontaneous polarization and a fast response to an applied electric field.[2] To obtain a ferroelectric liquid crystal with a fast switching time, the compound has to present the smectic C mesophase (because of its lower rotational viscosity) and a strong transverse dipole moment, normal to the tilt plane and close to the chiral center. To obtain a strong spontaneous polarization, it is considered that the transverse dipole moment has to be near the aromatic core to dampen the dipole rotation.[3] A variety of structures containing polar bonds, such as ether, ester, and halogenated[4] or else epoxy groups,[5] have been proved to enlarge the dipole moment. Kusumoto et al. placed the chiral center bearing the strong polar cyano group close to the rigid part without obtaining mesomorphic behavior.[6] To have a strong dipole near an aromatic core without breaking mesogeneicity, the new compound has to possess a molecular structure close to that of smectogenic C molecules. Many of the molecules exhibiting the smectic C mesophase are benzoates or Schiff bases.[7] In fact, empirical considerations design such molecules with a relatively long core (more than two rings), two tails relatively long (more than four atoms) and alkoxy or acyloxy groups for the link between tails and core.[8] These linkages act as the "outboard dipoles" in McMillan's theory.[9] If the sulfur atom is substituted to the carbon atom of a carboxy group, the sulfinate group so obtained presents chirality: a chiral center with a dipole moment is then joined to the rigid part. The corresponding two absolute configurations are shown in Figure 1.[10] A further advantage of introducing a sulfinate group in a molecule is the hope to lower the transition temperatures, since several sulfinate compounds are known to be oils at room temperature.[10] In the attempt to draw a sulfinate molecule which can have liquid-crystalline ferroelectric properties, computer molecular modeling was used in connection with

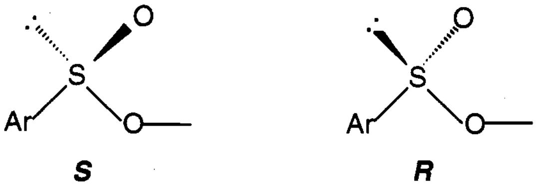

Figure 1. The two absolute configurations of sulfur in the sulfinyl group.

[●] Abstract published in *Advance ACS Abstracts,* April 1, 1994.

(1) Clark, N. A.; Lagerwall, S. T. *Appl. Phys. Lett.* **1980,** *36,* 899.

(2) For a review: Lagerwall, S. T.; Wahl, J.; Clark, N. A. *IEEE* **1985,** *2239-2,* 213.

(3) (a) Goodby, J. W.; Patel, J. S.; Chin, E. *J. Am. Chem. Soc.* **1986,** *108,* 4729. (b) Goodby, J. W.; Leslie, T. M. *Mol. Cryst. Liq. Cryst.* **1984,** *110,* 175. (c) Yoshino, K.; Ozaki, M.; Sakurai, T.; Sakamoto, K.; Honma, M. *Jpn. J. Appl. Phys.* **1984,** *23,* L175.

(4) (a) Nohira, H.; Nakamura, S.; Kamei, M. *Mol. Cryst. Liq. Cryst.* **1990,** *180B,* 379. (b) Yoshino, K.; Ozaki, M.; Taniguchi, H.; Ito, M.; Satoh, K.; Yamasaki, N.; Kitazume, T. *Jpn. J. Appl. Phys.* **1987,** *26,* L77.

(5) Walba, D. M.; Razavi, H. A.; Clark, N. A.; Parmar, D. S. *J. Am. Chem. Soc.* **1988,** *110,* 8686.

(6) Kusumoto, T.; Hanamoto, T.; Hiyama, T.; Takehara, S.; Shoji, S.; Osawa, M.; Kurijama, T.; Nakamura, K.; Fujisawa, T. *Chem. Lett.* **1990,** 1615.

(7) (a) *Handbook of Liquid Crystal;* Kelker, H., Hatz, H., Eds.; Verlag Chemie: Basel, 1980. (b) Demus, D.; Zaschke, H. *Flüssige Kristalle in Tabellen;* VEB Deutscher Verlag für Grundstoffindustrie: Leipzig, 1984.

(8) Poetsch, E. *Kontakte (MERCK)* **1989,** *9,* 421.

(9) McMillan, W. L. *Phys. Rev. A* **1973,** *8,* 1921.

(10) Pataï, S. *The Chemistry of Sulfinic Acids, Esters and Their Derivatives;* John Wiley & Sons: New York, 1990.

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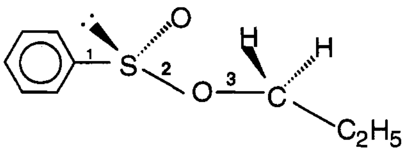


Figure 2. Alkyl phenylsulfinate molecule for the modeling process.

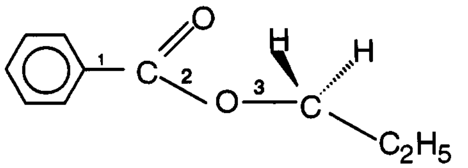


Figure 3. Propyl benzoate molecule for modeling process.

preexisting models such as the "zigzag" model[11] and the Boulder model.[12]

In this paper, we present the design, the synthesis and the physical properties of such ferroelectric sulfinate derivatives. In addition, we show that molecular modeling associated with spontaneous polarization measurements can be used to determine the absolute configuration of the chiral sulfur center.

Molecular Modeling

Molecular modeling has already been used to study the relationship between chemical structure and ferroelectric properties in ferroelectric liquid crystals.[13] Modeling an isolated molecule consists in finding its conformation of minimum energy. This was done in two principal steps. The first one was to find the most probable conformation by rotating suitable bonds. The second step has consisted in minimizing the local energy of this conformer (Sybyl 5.2 molecular modeling software from Tripos) using the Tripos Force Field.[14] To model the sulfinate group, a simple alkyl phenylsulfinate molecule was drawn (Figure 2): the benzene acts as the rigid part, and the alkyl chain contain only three carbons. The rotatable bonds are indexed by numbers. The energy of the most stable conformer after minimization was found to be 2.6 kcal/mol. The resulting structure presents an important angle of 52.2° between the phenyl plane and the S=O bond, which suggests an important transverse dipole moment. For comparison, the same study was done with *n*-propyl benzoate molecule presented in Figure 3. The energy found is 4.8 kcal/mol. The difference of 2.2 kcal/mol between the two esters is not significant, the computations being done at 0 K, without any influence of the neighborhood. The difference in the molecular structure is more significant. The angle between the C=O bond and phenyl group is very small (a few degrees), in conformity with the 9.8° angle crystal data found in literature for the phenyl benzoate molecules.[15]

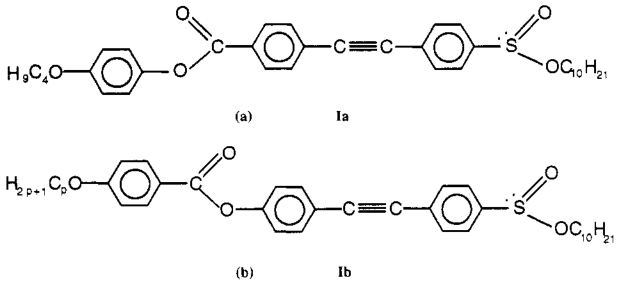
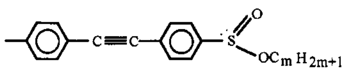
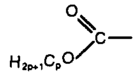


Figure 4. (a, top) The first sulfinate compound (**Ia**) exhibiting an enantiotropic smectic A mesophase. (b, bottom) The first sulfinate compounds (**Ib**) family exhibiting an enantiotropic smectic C mesophase.

Table 1. Nonmesogenic Sulfinate Compounds

terminal chains	rigid core
$H_{2p+1}C_p$—	
$H_{2p+1}C_pO$—	
NC—	
	

From these studies, the sulfinate chain presents an important "elbow" regarding the benzene ring which is not present in carboxylate chains. To compensate for this structural particularity, we decided to increase the linearity and planarity of the rigid part. This could be done by attaching a 1,2-diphenylacetylene (or tolane) group to the sulfinate. Experiments showed that the tolane core alone is not sufficient to lead to mesogenic molecules (Table 1 lists the different compounds we have synthesized for which no mesomorphic behavior has been observed). A benzoate group was then attached to the tolane core, knowing that some advantages come from the presence of the phenyl benzoate group in a core of a molecule,[16] such as chemical stability, more frequent smectic C mesophase in polymorphism sequence, and low viscosity. From the two kinds of relevant molecules shown in Figure 4, only molecules **Ib** are of interest for this paper because of the occurrence of the smectic C mesophase in their polymorphism when molecules **Ia** show only a smectic A mesophase.

Ib being able to obtain a smectic C mesophase, ferroelectricity had to be obtained. Two main possibilities with molecules represented in Figure 4b exist. First was the preparation of optically pure enantiomers by asymmetric synthesis or any kind of optical resolution; second was the addition of a second chiral center having a known configuration to obtain a pair of optically pure diastereomers, theoretically separable by classical methods. In addition, the presence of a second chiral center in the molecule near the aromatic core would probably dampen further the molecular rotation. So, the latter possibility was first chosen, and the molecules having an asymmetric carbon atom with the *S* configuration as second chiral center are presented in Figure 5 (**II** and **II′** corresponding to the two possible diastereomers).

The major problem to represent a molecule of a smectic C phase is to template it into the three axes: *z* is the normal to the layer, *y* is the transverse axis, (*xz*) is the tilt phase (Figure 6a). The first representation of such a molecule is to consider it as a rodlike molecule (Figure 6b). This was proved nonsatisfactory when Bartolino et al. compared the values of the tilt angle measured by

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(11) Bartolino, R.; Doucet, J.; Durand, G. *Ann. Phys.* **1978,** *3,* 389.

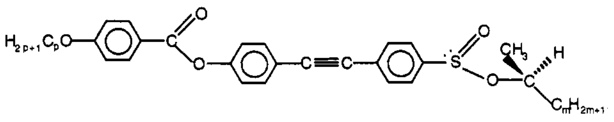
(12) Walba, D. M.; Vohra, R. T.; Clark, N. A.; Handschy, M. A.; Xue, J.; Parmar, D. S.; Lagerwall, S. T.; Skarp, K. *J. Am. Chem. Soc.* **1986,** *108,* 7424.

(13) (a) Sierra, T.; Serrano, J. L.; Ros, M. B.; Escurra, A.; Zubia, J. *J. Am. Chem. Soc.* **1992,** *114,* 7645. (b) Sierra, T.; Ros, M. B.; Omenat, A.; Serrano, J. L. *J. Chem. Mater.* **1993,** *5,* 938.

(14) Clark, J. W.; Cramer, R. D.; Van Opdenbosch, N. *J. Comput. Chem.* **1989,** *10,* 982.

(15) Adams, J. M.; Morsi, S. E. *Acta Crystallogr.* **1976,** *B32,* 1345.

(16) Alstermark, C.; Nilsson, M.; Otterholm, B. *Mol. Cryst. Liq. Cryst.* **1987,** *150,* 277.



II + II'

Figure 5. The first sulfinate compounds family exhibiting a chiral smectic C mesophase.

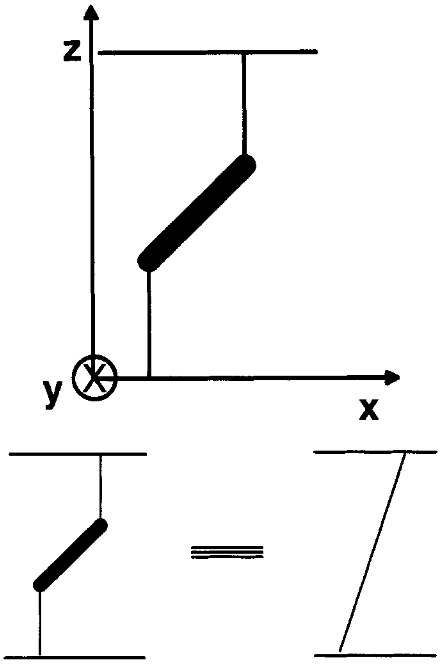


Figure 6. (a, top) Schematic representation of molecule in the smectic C tilt plane. (b, bottom) Representation of molecule in smectic C mesophase.

different techniques (optical, X-rays).[11] They proposed the "zigzag" model in which the molecules of the smectic C phase present their rigid parts more tilted than the aliphatic chains. Recently, Walba et al. proposed considering the polarization as a manifestation of a form of molecular recognition.[12,17,18] And starting from a biochemistry concept, they introduced a binding site, i.e., a surface of constant molecular mean field. They found a bent cylinder for the binding site shape of molecules in smectic C phase. This model is in fact in concordance with the "zigzag" model. The spontaneous polarization can then be written in terms of a summation over the possible conformations i (eq 1):[12,17,18]

$$P = \sum_i D_i P_i \tag{1}$$

where P is the spontaneous polarization, D_i is the number density of the ith conformation present in the phase, and P_i is the contribution to the polarization of the ith conformation.

$$P_i = d_{yi}\mathrm{ROF}_i \tag{2}$$

where d_{yi} is the component of the molecular dipole moment normal to the tilt plane of the ith conformation, and ROF_i is the rotation orientation factor (number between 0 and 1).

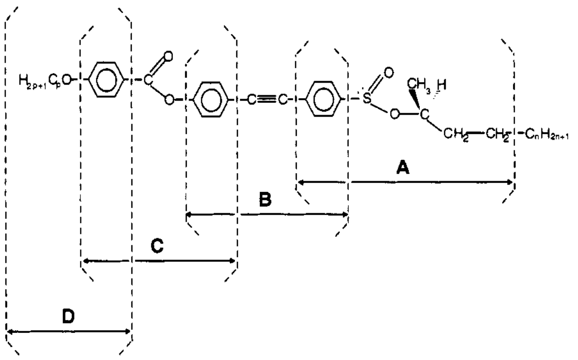


Figure 7. Fragmented sulfinate smectogen molecule for modeling.

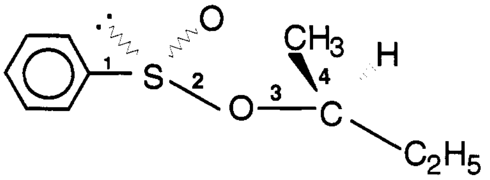


Figure 8. Ramified alkyl phenylsulfinate molecule for modeling process.

Table 2. Energy, S═O/Phenyl Angle, and Dipole Moment of the Two Sulfinate Diastereomers

compound	energy (kcal/mol)	SO/Ph angle (deg)	dipole (D)
sulfi-*R*,*S*	2.46	54.4	6.0
sulfi-*S*,*S*	2.40	41.6	5.8

Table 3. Modeling and Contribution to the Total Dipole Moment of Fragments of Molecule Presented in Figure 7

fragments of ramified sulfinate	geometry	transverse dipole contribution
part A	"elbow" at the sulfur level (modeling)	important
part B	planar and rigid	insignificant
part C	the two phenyl rings are perpendicular (according to refs 12, 17, 18)	insignificant (by symmetry consideration)
part D	alkoxy chain lies in the same plane as benzene ring (according to refs 12, 17, 18	insignificant (by symmetry consideration)

To achieve our modeling study, it was then necessary to check if the sulfinate smectic C molecule represented in Figure 5 can adequately fit in a bent cylinder. For that purpose, the molecule was subdivided in four parts (Figure 7). The junction between each part was made by a benzene ring that allows one to consider each element independently from one another. Part A, containing two chiral centers (carbon atom of *S* configuration and sulfur atom with the two possible *R* and *S* configurations), can lead, in fact, to two different molecules (called sulfi-*R*,*S* and sulfi-*S*,*S* in Tables 2 and 4), depending on the sulfur configuration, which were modeled separately by computer. As was found for the alkyl phenylsulfinate molecule, the sulfinyl group shows an "elbow" in both cases. Figure 8 indicates the suitable rotatable bonds, and Table 2 indicates, for the two diastereomers, the different values obtained by modeling process. One can notice a significant difference between the two diastereomers relative to the angle between the S═O bond and the phenyl group, which suggests a difference in the value of the transverse dipole moment. The modeling and the contribution of each part to the total dipole moment are summarized in Table 3.

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[17] Walba, D. M.; Clark, N. A. *Ferroelectrics* **1988**, *84*, 65.

[18] For a review: Walba, D. M. *Adv. Synth. React. Solids* **1991**, *1*, 173.

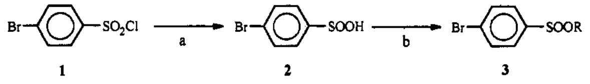
Modeling shows that the volumic representation of the sulfinate smectic C* molecule can be considered as a bent cylinder. Among the three axes represented, the y axis corresponds to the transverse axis; the transverse dipole moment can then be projected upon this axis and calculated. The differentiation between the two sulfur absolute configurations can be done.

As can be seen from Table 3, the major dipole contribution is brought by part A. The calculation of electrostatic charges in this element was done by using the semiempiric program MOPAC (AM1 parameters). Table 4 shows the values of the dipole moment components according to the sulfinate molecule registered in a bent cylinder for each diastereomer. From symmetry considerations,[19] only the d_{yp} dipole component is of interest for our purpose, and it is clear that its value is large enough to expect a compound with a relatively high spontaneous polarization (*Ps*). In fact, the most important feature arising from our molecular modeling study is the sign of this transverse dipole moment which depends upon the absolute configuration of the sulfur atom. For the conformation where the molecule fits quite well a bent cylinder, D_i from eq 1 can have a high value, and ROF$_i$ from eq 2 can be close to unity; so d_{yp} has the most important influence on *P*: this can then lead to the prediction of a sign change of *Ps* with inversion of configuration at the sulfur atom, and a high value of *Ps*.

Synthesis and Polymorphism

Synthesis and Polymorphism of Racemic Sulfinate Liquid–Crystalline Molecules. *Synthesis.* The synthetic route to racemic sulfinate liquid crystal is made in three steps as follows:

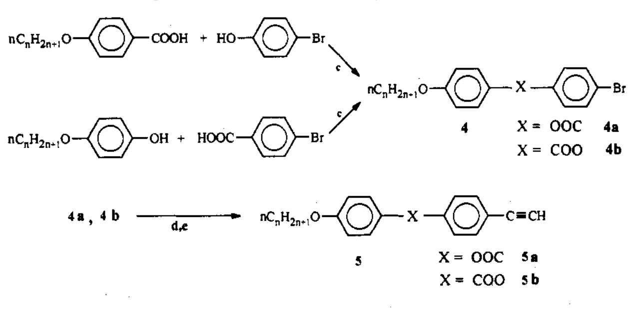
First step: Obtaining the sulfinate part:



(a) Na_2SO_3/H_2O; (b) *n*-alcohol (ROH), 2-chloro-*N*-methylpyridinium iodide.

4-Bromobenzenesulfonyl chloride (1) is reduced with aqueous sodium sulfite to the corresponding sulfinic acid (2)[20] and then esterified to sulfinate with *n*-alcohol according to Furukawa's procedure, using 2-chloro-*N*-methylpyridinium iodide as the activating reagent.[21]

Second step: Obtaining the mesogenic part:



(c) DCC, DMAP/CH_2Cl_2; (d) H—C≡C—TMS, $PdCl_2$-$Cu(OAc)_2 \cdot H_2O/PPh_3/(i\text{-}Pr)_2NH$; (e) $(n\text{-}Bu)_4N^+F^-$/THF.

Table 4. Dipole Moment Components (in debye) of Ramified Sulfinate Molecules Registered in a Bent Cylinder, According to the Sulfur Absolute Configuration

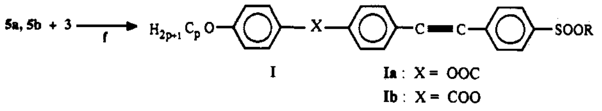
diastereomer	sulfur configuration	dx_P	dy_P	dz_P
sulfi-*R*,*S*	*R*	−3.38	−4.08	+0.84
sulfi-*S*,*S*	*S*	−4.61	+3.31	+0.45

Table 5. Polymorphism of Two Linear Sulfinate Molecules Exhibiting Smectic A Phase Only

compound	polymorphism	dS_A, Å
C4O–OCO–C10	$K \xrightarrow{108\,°C} S_A \xrightarrow{124\,°C} I$	
C7O–OCO–C10	$K \xrightarrow{106\,°C} S_A \xrightarrow{122\,°C} I$	39.2

Benzoate compounds **4a** and **4b** were prepared by classical esterification between phenol and carboxylic acid, using dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) in dichloromethane.[22] Terminal acetylenes **5a** and **5b** were prepared by a coupling reaction of aryl bromides **4a** and **4b** with (trimethylsilyl)acetylene using a palladium catalyst,[23] followed by deprotection of the acetylenic moiety, according to Hagihara's procedure.[24] Desilylation to the ethynyl compounds proved to be more efficient by using tetra-*n*-butylammonium fluoride in THF, rather than the classical method using aqueous methanolic potassium hydroxide.[25]

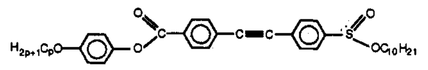
Third step: Obtaining the final compound:



(f) $PdCl_2$–$Cu(OAc)_2 \cdot H_2O$–$PPh_3/(i\text{-}Pr)_2NH$.

Sulfinate liquid-crystalline molecules (**I**) were finally obtained in good yields by coupling the aromatic acetylene **5a** and **5b** with alkyl 4-(bromophenyl)sulfinate (**3**) by using the same catalytic coupling as above.[23,26] Purification was done by column chromatography followed by crystallization in acetone.

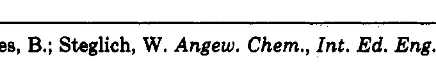
*Polymorphism of sulfinate smectic A molecules (**Ia**):*



Ia

The temperatures reported in Table 5 are determined by DSC from the second heating run. The textures shown by the sample are classical of a smectic A mesophase: batonnet textures; homeotropic areas.[27]

*Polymorphism of sulfinate smectic C molecules (**Ib**):*



Ib

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[19] Meyer, R. B.; Liebert, L.; Strzelecki, L.; Keller, P. *J. Phys. Lett.* **1975**, *36*, L69.

[20] (a) Kulka, M. *J. Am. Chem. Soc.* **1950**, *72*, 1215. (b) *Org. Synth. Coll. Vol. IV*, 674.

[21] (a) Furukawa, M.; Ohkawara, T.; Noguchi, Y.; Nishikawa, M.; Tomimatsu, M. *Synthesis* **1978**, 441. (b) Furukawa, M.; Ohkawara, T.; Noguchi, Y.; Nishikawa, M.; Tomimatsu, M. *Chem. Pharm. Bull., Tokyo* **1980**, *28*, 134.

[22] Neises, B.; Steglich, W. *Angew. Chem., Int. Ed. Eng.* **1978**, *17*, 522.

[23] (a) Dieck, H. A.; Heck, F. R. *J. Organomet. Chem.* **1975**, *93*, 259. (b) Heck, F. R. *Palladium reagents in organic synthesis*; Academic Press: London, 1985. (c) Cassar, L. *J. Organomet. Chem.* **1962**, *93*, 253. (d) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467.

[24] Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

[25] Harris, R. L. N.; Huppatz, J. L.; Philipps, J. N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 707.

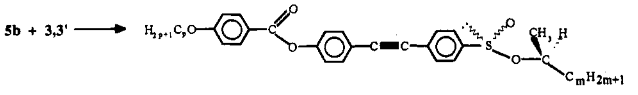
[26] Carpita, A.; Lessi, A.; Rossi, R. *Synthesis* **1984**, 571.

Table 6. Polymorphism of Two Linear Sulfinate Smectic C Molecules

compound	polymorphism	dS_A, Å
C12O–C10	$K \xrightarrow{68\,°C} S_C \xrightarrow{102\,°C} S_A \xrightarrow{111\,°C} I$	41.3
C16O–C10	$K \xrightarrow{79\,°C} S_C \xrightarrow{108\,°C} S_A \xrightarrow{111\,°C} I$	45.1

The transition temperatures, as determined by DSC and optical microscopy observations, are shown in Table 6. The optical textures present focal conics which are classical for disordered smectic mesophases. Thanks to silane treatment of glasses, homeotropic textures for smectic A mesophase and schlieren textures for smectic C permit one to detect transitions very easily. The smectic A and C nature of smectic phases is then confirmed by X-ray diffraction.

Synthesis and Polymorphism of Optically Active Sulfinate Liquid-Crystalline Molecules. *Synthesis.* The synthetic route is the same as described for previous sulfinate molecules. The only difference is the presence of two diastereomers. During the first step, 4-bromobenzenesulfonyl chloride (1) was reduced to the corresponding sulfinic acid 2 and then esterified to a mixture of diastereomeric sulfinates 3 and 3′ using (*S*)-(+)-2-octanol, (*S*)-(+)-2-heptanol, or (*S*)-(+)-2-hexanol[28] according to Furukawa's procedure.[21] Attempts to isolate the pure diastereomers 3 and 3′ from the viscous oily mixture led to an isohypsic reaction as in as previously noted for the (*S*)-2-octyl (4-bromophenyl)sulfinate synthesis. The second step concerning the core synthesis does not change. The third step to obtain the diastereomeric sulfinates is shown in the following scheme:



II and II'

(f) $PdCl_2–Cu(OAc)_2·H_2O–PPh_3/(i\text{-}Pr)_2NH$

The number of carbon atoms is changed on each side of the core. For a better understanding, we choose the nomenclature $C_nO–R$ for compounds **II** and **II′** in the following text, where *n* is the number of carbon atoms in the alkoxy chain (8, 10, 12, 16) and R corresponds to the diminutive of the ramified chain attached to the sulfinyl groups:

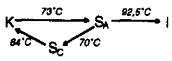
R = 2Oct when $m = 6$

R = 2Hept when $m = 5$

R = 2Hex when $m = 4$

The mixture 3 and 3′ was previously obtained by Furukawa's procedure.[21] Attempts to isolate the pure diastereomers from the viscous oily mixture led to substantial isomerization to the isomeric sulfone; so the mixture was used for the third step without separation. The compounds **II** and **II′** were obtained in good yields by coupling the aromatic acetylene **5b** with the mixture 3 and 3′ using a palladium catalyst in a dialkylamine solvent.[23,24] The absolute configuration of sulfur is not known at this level. It is the reason why the symbolisms **II** and **II′** are used. The first eluted product by column chromatography over silica gel affords the pure diastereomer called **II**. The other diastereomer **II′** was obtained as pure material from the residue by preparative TLC when possible due to the small difference in R_f for the two compounds. Only compounds C16O–2Oct, **II** and **II′**, and C16O–2Hept, **II** and **II′**, so obtained are considered to be free of contamination by the other diastereomer, as shown by ^1H and ^{13}C NMR spectra (several NMR signals of **II** and **II′** are highly differentiated). Each of them showed satisfactory microanalysis and a good thermal stability. As for the optical purity of each chemically pure diastereomer, it was not yet checked quantitatively, but given the synthetic route followed, it is supposed to be at least the same as the starting commercial (*S*)-(+)-2-octanol or (*S*)-(+)-2-heptanol.[28]

Table 7. Polymorphism of Ramified Sulfinate Molecules

compound	polymorphism	dS_A, Å	remarks
C8O–2Oct (**II**)	$K \xleftrightarrow{73°C} S_A \xleftrightarrow{\sim 102°C} I$	38.9	unstable
C8O–2Oct (**II′**)	/		not separated
C10O–2Oct (**II**)	$K \xleftrightarrow{71°C} S_A \xleftrightarrow{\sim 99°C} I$	40.4	unstable
C10O–2Oct (**II′**)	/		not separated
C12O–2Oct (**II**)	$K \xleftrightarrow{69°C} S_A \xleftrightarrow{97°C} I$	42.9	stable
C12CO–2Oct (**II′**)	$K \xleftrightarrow{48°C} S_C \xleftrightarrow{\quad} S_A \xleftrightarrow{96°C} I$	42.9	presence of **I**
C16O–2Oct (**II**)		44.5	stable
C16O–2Oct (**II′**)	$K \xleftarrow{53°C} S_C \xleftarrow{80°C} S_A \xleftarrow{95°C} I$	44.5	stable

Polymorphism of CnO–2Oct Compounds. The temperature transitions are determined with DSC by cooling the sample from the isotropic phase. The determination of the structure has been done using polarized optical microscopy and X-ray diffraction. The presence of conic focals in optical textures is indicative of the smectic A nature of the mesophase. The X-ray diffraction patterns permit one to determine the interlamellar distances, dS_A. The existence of striations in conic focals reveals the presence of a chirality in the smectic C mesophase. Table 7 indicates the polymorphism, the interlamellar distances and the thermal stability for the CnO–2Oct compounds (n = 8, 10, 12, 16). It shows that the number of carbon atoms in the alkoxy chain has an influence in the thermal stability of sulfinate molecules: 12 carbons are necessary to obtain a good stability and to obtain the pure **II** diastereomer. In this family, only the compound C16O–2Oct shows satisfactory results, as was reported in a preliminary communication.[29]

To see the influence of the number of carbon atoms in the sulfinate thermal stability, molecules C16O–2Hept and C16O–2Hex were synthesized with the same procedure described above, and their polymorphisms are reported below.

Polymorphism of C16O–2Hept: By cooling compound C16O–2Hept (**II′**) from the isotropic phase, DSC and optical microscopy show two main transitions, one at 98.5 °C corresponding to the transition from the isotropic phase to a mesomorphic phase, and another one at 72 °C corresponding to the occurrence of another smectic phase, which can be kept supercooled down to 55 °C before the crystallization of the compound.

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[27] Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals (Textures and Structures)*; Leonard Hill: Glasgow, 1984.

[28] (*S*)-(+)-2-Octanol($[\alpha]^{20}$ = +9.5° (neat)) and (*S*)-(+)-2-heptanol ($[\alpha]^{24}$ = +10° (neat)) were supplied by Aldrich.

[29] Soldera, A.; Nicoud, J. F.; Galerne, Y.; Skoulios, A.; Guillon, D. *Liquid Cryst.* **1992**, *12*, 347.

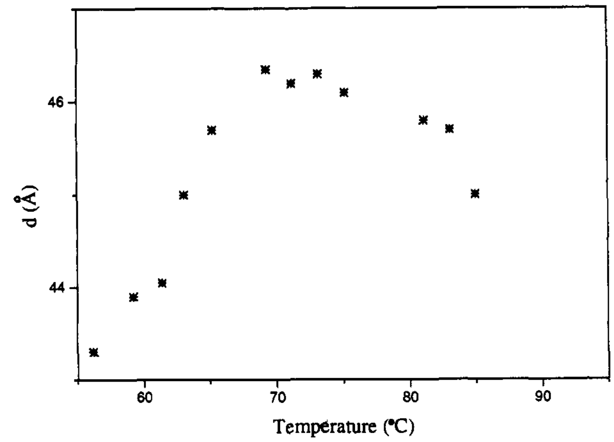

Figure 9. $C_{16}O$–2Hept interlamellar distance as a function of temperature.

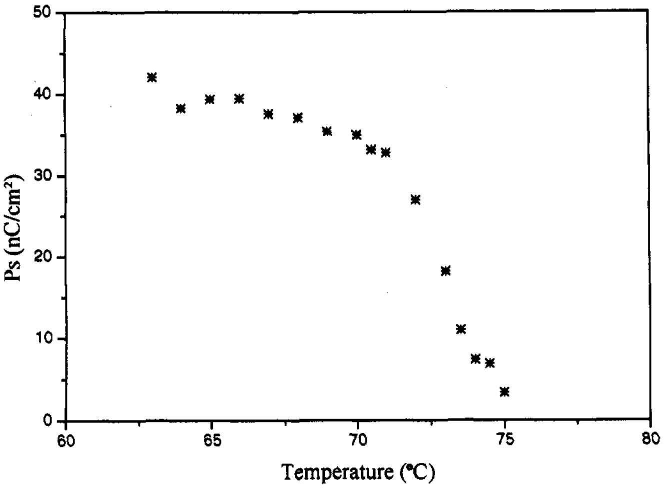

Figure 10. Spontaneous polarization of mixture A as a function of temperature.

The X-ray diffraction patterns, registered as a function of temperature within the mesomorphic domain of compound C16O–2Hept (**II′**), contain one sharp reflection in the low-angle region and a diffuse ring in the wide-angle region, as is often the case for disordered smectic phases. The variation of the Bragg period as a function of temperature is reported in Figure 9. It shows clearly the existence of two distinct regimes within the temperature range of the mesomorphic domain: a low-temperature regime where the spacing increases regularly up to a temperature of 72 °C, and a high-temperature regime where the spacing decreases slightly. Although no harmonics of the Bragg reflection can be observed to confirm the lamellar nature of the mesophases, the first regime is typical of a smectic C* phase and the second one is typical of smectic A phase (the molecular spacing decreases because of the lateral expansion of the molten aliphatic chains). By taking the spacing at the smectic C*–smectic A transition (46.2 Å) as corresponding to the length of one molecule (the molecular length found by molecular modeling is 45.5 Å), the tilt angle, θ, of the molecules in the smectic C* phase is calculated through the relation $\cos(\theta) = d_{C*}/d_A$.[30] The maximal value found for θ, far from the transition, is 22° at 56 °C, very close to the "ideal" value of 22.5°.

As for compound C16O–2Hept (**II**), DSC measurements and optical microscopy observations show, by cooling, the existence of a mesomorphic domain between 102 and 73 °C. This mesomorphic range is characterized by the same optical textures than those already observed for compound C16O–2Hept (**II′**), but no plane textures were observed after stressing the upper glass. The X-ray diffraction patterns of compound C16O-2Hept (**II**) registered as a function of temperature within the liquid-crystalline domain are characteristic of disordered smectic phases, but in this case the layer spacing does not vary with temperature, and its value is close to the molecular length. It shows clearly that the mesomorphic domain corresponds in fact to one smectic A mesophase only.

Thus, the transition temperature diagrams of C16O–2Hept **II** and **II′** are the following:

$$\text{compound } \mathbf{II} \qquad K \overset{73\,°C}{\leftrightarrow} S_A \overset{102\,°C}{\leftrightarrow} I$$

$$\text{compound } \mathbf{II'} \qquad K \overset{68\,°C}{\rightarrow} S_C \overset{72\,°C}{\leftrightarrow} S_A \overset{98.5\,°C}{\leftrightarrow} I$$

As was shown previously,[29] the polymorphism of chiral sulfinate compounds depends on the absolute configuration of the sulfur atom. Only the C16O–2Hept (**II′**) compound presents the smectic C* mesophase and, therefore, possesses a spontaneous polarization. To determine the virtual spontaneous polarization of the C16O–2Hept (**II**) compound, mixtures of **II** and **II′** were investigated.

Polymorphism of C16O–2Hex. The presence of a mesophase for the mixture of the diastereomers has been revealed by polarized optical microscopy, but the thermal instability of these compounds does not permit one to pursue this study.

From all these polymorphic studies, it is clear that ramified sulfinic esters must possess long chains to be stable. It is C16O–2Hept compound which presents the smallest number of carbon atoms in its chains (16 for the linear alkoxy chain and 7 for the ramified sulfinate chain). The measurements of the spontaneous polarization were then investigated with this compound.

Spontaneous Polarization Measurements

The spontaneous polarization measurements were not carried out for the pure compounds because of the impossibility to orient the smectic planes perpendicular to the ITO covered glasses (see Experimental Section). However, mixtures of the two disastereomers were successfully oriented. Two mixtures corresponding to two diastereomeric excesses were investigated: mixture A with 16% **II**/84% **II′** (excess of diastereomer **II′**) and mixture B with 75% **II**/25% **II′** (excess of diastereomer **II**). Mixture A presents the expected smectic A–smectic C* transition. The spontaneous polarization as a function of the temperature is reported in Figure 10. The highest value of *Ps* is -42.1 nC/cm^2. The linear extrapolation gives a value of -50.1 nC/cm^2 for the pure compound **II′**. The value of *Ps* in mixture B at 60 °C was found to be equal to $+52.2$ nC/cm^2. By linear extrapolation, the virtual value of *Ps* for **II** compound is $+70$ nC/cm^2.

Indeed, the important feature arising from the measurements of the polarization is the change of the sign according to the mixture. This is in agreement with the

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[30] Guillon, D.; Skoulios, A. *J. Phys. (Paris)* 1977, *38*, 79.

predictions of our molecular modeling study reported above.

Discussion and Conclusion

With the help of molecular modeling, a new kind of molecules containing a sulfinate group as chiral center and exhibiting the smectic C mesophase has been drawn. The presence of an "elbow" in the sulfinate group does not lead a priori to mesogenic precursor. The adjunction of the 1,2-diphenylacetylene group balances this geometric particularity and forces the molecule to adopt a "zigzag" shape.[11] But for the molecule to fit in a bent cylinder as proposed in the Boulder model,[18] the rigid core has to be increased with a benzoate group, in agreement with previous experimental synthesis and predictions (core containing more than two rings). This addition leads to the first liquid-crystalline sulfinate molecules. In such molecules, however, the carboxy group can be bound in two opposite directions so that the COO dipole can point in the same direction as the sulfinate group or in the opposite sense. As it was mentioned in the literature, this direction plays an important role in the polymorphic sequence.[31,32] This was still verified in sulfinate molecules. The former sense gives the expected SmA–SmC sequence. In contrast, the chain of the carboxylic homologs of these sulfinate molecules must possess 12 carbon atoms to exhibit the expected smectic C mesophase.[33] The later sense of COO dipole leads the sulfinate molecules to present only a smectic A mesophase in a small temperature range. For carboxylic esters, it shows the smectic C mesophase readily.[34] This point is not cleared up yet. With a view to obtaining ferroelectric liquid crystals, only sulfinate molecules possessing carboxy dipole pointed to the sulfinic group were of good interest for this pupose because of the presence of the enantiotropic smectic C mesophase.

With the presence of a second chiral center, it has been possible to separate experimentally the two diastereomers with opposite absolute configuration of the sulfur atom. Two principal results came out from the polymorphic studies of these molecules. First, as mentioned in the preliminary communication,[29] the absolute configuration of the sulfur atom plays an important role in determining the thermotropic properties: only one diastereomer (**II′**) shows an enantiotropic smectic C mesophase; the other diastereomer shows a single smectic A mesophase. Second, the stability and the separation of the two diastereomers are influenced by the number of carbon atoms in the alkyl chains. The sulfinate molecule has to possess at least 16 carbon atoms in its alkoxy linear chain and 7 in its sulfinate ramified chain to be stable. This could run counter to the obtention of a fast switching time because of the important dependence of viscosity on the carbon chain length.

Molecules presenting a smectic C* mesophase in their polymorphism are expected to present a nonzero transverse dipole moment. Therefore, the design of the two sulfinate diastereomers according to the Boulder model makes possible the calculation of the transverse dipole moment even for diastereomer **II**, possessing only the smectic A mesophase in its polymorphism (in this case, it is considered virtually). It has been shown that the transverse dipole moment of the most stable conformation has the largest influence on the value of the spontaneous polarization.[18] Therefore, the transverse dipole moment found for the two diastereomers should lead to high spontaneous polarizations. However, *Ps* measurements could not be made for pure compounds because of the impossibility to orient the smectic planes perpendicular to the conducting glasses. This was also observed for carboxylic homologs by Nguyen *et al.*[33] The linear extrapolations of *Ps* measurements of the diastereomer mixtures give medium values (70–50 nC/cm^2). But recently, sulfinate molecules possessing the sulfur atom as the only chiral center have been prepared by asymmetric synthesis in our laboratory.[35] Their high values of spontaneous polarization (100–300 nC/cm^2) are in good agreement with the high values of transverse dipole moment found for such molecules by molecular modeling. It seems that the presence of the methyl group in the γ position of the phenyl could explain the impossibility to orientate the pure compounds. Studies are presently in progress in this direction.

Another important feature, revealed by molecular modeling, is the sign change of the transverse dipole moment according to the absolute configuration of sulfur atom. *Ps* measurements indicate effectively a sign change according to the diastereomer considered. The sign of the transverse dipole moment corresponding to the sign of *Ps*, it is possible to correlate molecular modeling and electrooptical experiments in order to deduce the sulfur absolute configuration of the diastereomers. Thus, compound **II′** presenting the smectic C mesophase in its polymorphism and showing a negative polarization must correspond to the diastereomer sulfinate with sulfur atom in the *R* absolute configuration, its transverse dipole moment being negative according to the Boulder model. Correspondingly, the sulfinate diastereomer **II** with the only smectic A mesophase in its polymorphism must have its sulfur atom in the *S* absolute configuration. This could be generalized, and molecular modeling associated with smectic C models appears as a new method of determination of the absolute configuration of an asymmetric sulfur in chiral mesogenic molecules forming ferroelectric liquid crystals, as it has been already reported for asymmetric carbon.[5]

Experimental Section

Optical Microscopy. Transmission optical observations were made using a Leitz polarizing microscope fitted with a Mettler FP 52 hot stage.

X-ray Diffraction. X-ray diffraction patterns of powder samples in Lindemann capillaries were recorded photographically using monochromatic Cu Kα_1 radiation and a Guinier focusing camera equipped with a bent quartz monochromator.

Differential Scanning Calorimetry. DSC measurements were performed using a Perkin-Elmer DSC-7 instrument. Contained in aluminium pans, the samples were heated or cooled in the temperature range from 300 to 480 K at a scanning rate of 5 K min^{-1}.

Polarization Measurements. The sample was placed between two indium–tin oxide (ITO)-coated conducting glass electrodes.

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(31) (a) Goodby, J. W.; Patel, J. S. *Mol. Cryst. Liq. Cryst.* **1984**, *110*, 175. (b) Coates, D. *Liquid Cryst.* **1987**, *2*, 63.

(32) (a) Kelly, S. M.; Bucheker, R.; Fromm, H. J.; Schadt, M. *Ferroelectrics* **1988**, *85*, 385. (b) Kelly, S. M.; Villiger, A. *Liquid Cryst.* **1988**, *3*, 1173.

(33) Nguyen, H. T.; Twieg, R. J.; Nator, M. F.; Isaert, N.; Destrade, C. *Ferroelectrics* **1991**, *121*, 187.

(34) Seto, K.; Shimojitosho, H.; Imazaki, H.; Matsubara, H.; Takahashi, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1020.

(35) Cherkaoui, M.; Nicoud, J. F.; Galerne, Y.; Skoulios, A.; Guillon, D., communication presented at the 14th International Liquid Crystal Conference, Pisa, 1992.

These glasses were previously treated with Teflon according to the Wittman and Smith method,[36] in order to obtain the molecules parallel to the plates (and the smectic planes perpendicular to them as it is in SSFLC cells). The optical observations were made using a Leitz microscope equipped with an INSTEC hot stage controlled by a computer. The spontaneous polarization measurements were then performed by applying a triangular voltage across the cell. The signal (current versus time) was recorded on a HP 54501A oscilloscope. Knowing the active area of the cell, the polarization measurements were investigated by integrating the characteristic peak of a polarization reversal. The optical observations permitted to measure and to determine the sign of the polarization: the algebric value of the tilt angle was determined from the rotation of the cell which restores extinction between cross polarizers.

Molecular Modeling. The molecular modeling was performed with a Micro VAX II VMS 5.2 minicomputer coupled with an Evans & Sutherland PS390 high-resolution screen, using the SYBYL software from Tripos Associates Inc. The energy was calculated by Tripos Force Field 5.2, and it was minimized by MM2 program. A quantum mechanic semiempirical software, MOPAC, was used to calculate charges.

Chemical Part. Instrumentation: ^{1}H nuclear magnetic resonance (NMR) spectral data were obtained on a Bruker AC 200 spectrometer; chemical shifts (δ in ppm) are reported downfield from TMS. Commercial starting materials were supplied by Aldrich.

*4-Bromobenzenesulfinic acid (**2**).*[20] To a vigorously stirred solution of sodium sulfite (57 g, 0.45 mol) in 200 mL of water warmed to 70 °C was added 4-bromobenzenesulfonyl chloride (25 g, 0.1 mol). The reaction mixture was kept at a temperature of 70–80 °C for 5 h, then heated to 100 °C for 7–8 min, strongly acidified with concentrated hydrochloric acid (pH 1.5–2), cooled, and filtered. The white precipitate was recrystallized twice from water yielding 4-bromobenzenesulfinic acid with 80% yield; mp 117 °C.

*Synthesis of Sulfinate **3**. Representative Procedure for Esterification of 4-Bromobenzenesulfinic Acid with Linear Primary Alcohol (1-Decanol).* To a nitrogen-flushed flask containing unstabilized dichloromethane (60 mL without ethanol) with 4.2 g (30 mmol) of 1-decanol and 6.65 g (30 mmol) of 4-bromobenzenesulfinic acid (**2**) were added with stirring 9.2 mg (36 mmol) of powdered 2-chloro-1-methylpyridinium iodide and 10 mL (72 mmol) of triethylamine. The solution was then refluxed with stirring for 5 h under nitrogen atmosphere. After cooling, the organic phase was extracted by ether, washed with 1% aqueous $NaHCO_3$ and H_2O, twice each, and then dried over Na_2SO_4. The solvent was evaporated yielding the *n*-decyl 4-bromobenzenesulfinate (**3**, yield 91%; oil at room temperature).

*Synthesis of Ramified Sulfinates (Diastereomeric Mixture **3** and **3′**). Representative Procedure for Esterification of 4-Bromobenzenesulfinic Acid (**2**) with Ramified Optically Active Secondary Alcohol.* The same procedure was done as for the esterification of 4-bromobenzenesulfinic acid with 2-octanol and 2-heptanol. The separation of the two diastereomers was not done at this step because of the substantial isohypsic reaction. The yields thus obtained by GLC were 79 and 75% for the 2-octanol and 2-heptanol derivatives, respectively.

*Synthesis of Ester **4a**. Representative Procedure for Esterification of Carboxylic Acid (4-Bromobenzoic Acid) with 4-(n-Heptyloxy)phenol.*[22] In a 100-mL monocol equipped with a calcium chloride drying tube was charged 2.6 g of 4-bromobenzoic acid (1 equiv), 5 g of 4-(*n*-heptyloxy)phenol (1.5 equiv) and 0.05 g (catalytic quantity) of DMAP in 20 mL of anhydrous CH_2Cl_2. DCC (4 g) was then added to the reaction mixture at 0 °C, which was stirred for 1 night at room temperature. The residue was taken up in CH_2Cl_2 and, if necessary, filtered free of any further precipitated urea. The filtrate was washed twice with 0.5 N HCl and with saturated $NaHCO_3$ solution. The organic phase was dried over Na_2SO_4 and then evaporated to dryness.

*Synthesis of Acetylenic Ester (**5a**). Representative Procedure for the Ethynation Reaction of 4-Bromo-4′-(n-octyloxy)phenyl Benzoate (**4a**).* To a nitrogen-flushed flask containing 7.4 g of 4-bromoaryl compound **4a** (1 equiv) and 5.3 mL of (trimethylsilyl)acetylene (2 equiv) in diisopropylamine (20 mL), were added 68 mg of $PdCl_2$ (2%), 75 mg of $Cu(OAc)_2$, and 492 mg of PPh_3 (10%). The reaction was stirred for 24 h at 45 °C. The reaction mixture was taken up with dichloromethane, and the ammonium salt residue was removed. The filtrate was then washed with 5% HCl solution and dried over Na_2SO_4, and then CH_2Cl_2 was removed under vacuum. The compound was mixed with THF and was treated with tetrabutylammonium fluoride in THF for 30 min at room temperature. The THF was then removed, and a first flash chromatography was made with 50% CH_2Cl_2/50% hexane as eluant (yield 58%).

The same procedures as above were used for compounds **4b** and **5b** (yield 46%); mp of **5b** 84 °C.

*Synthesis of Mesogenic Compounds. Representative Procedure for Acetylenic Substitution of (S)-2-Octyl-4-bromobenzenesulfinates **3** and **3′** with 4-Ethynylphenyl 4-(n-Hexadecyloxy)benzoate (**5b**).* To a nitrogen-flushed flask containing 1 g of diastereomeric mixture **3** and **3′** (1 equiv) and 1.25 g of **5b** (1 equiv) in a diisopropylamine were added 9.5 mg of $PdCl_2$ (2%), 11 mg of $Cu(OAc)_2$, and 73 mg of PPh_3 (10%). The reaction was stirred for 24 h at 40 °C. The amine solvent was evaporated, the residue was diluted with dichloromethane, and ammonium salt residue was removed; then the filtrate was washed with 5% HCl solution and dried over Na_2SO_4, and the solvent was evaporated. A first partial separation of the two diastereomers was made by flash chromatography over silica gel, with CH_2Cl_2 as eluant. The compound first eluted from the column (**II**) is obtained as pure material. The diastereomer eluted in the second (**II′**) is contaminated by the first one and must be purified by preparative TLC on a silica plate. Thus were obtained 1-[((4-(*n*-hexadecyloxy)phenyl)carbonyl)oxy)-4-phenyl]-2-[4-((2-(*S*)-octyloxy)sulfinyl)phenyl)]ethyne, **II**, and **II′** (Figure 5, $p = 16$, $m = 6$).

II: ^{1}H NMR (200 MHz, CD_3COCD_3, δ from TMS) 0.86 (6H, m, (2t)), 1.28 (34H, m), 1.37 (3H, d, $J = 6.2$ Hz), 1.5 (2H, m), 1.8 (2H, sext), 4.1 (2H, t, $J = 6.4$ Hz), 4.43 (1H, sext, $J = 6.1$ Hz), 7.1 (2H, d, $J = 8.9$ Hz), 7.34 (2H, d, $J = 8.7$ Hz), 7.68 (2H, d, $J = 8.7$ Hz), 7.78 (4H, s), 8.1 (2H, d, $J = 8.9$ Hz). Anal. Calcd for $C_{45}H_{62}O_5S$: C, 75.59; H, 8.74; O, 11.19. Found: C, 75.02; H, 8.75; O, 11.23.

II′: ^{1}H NMR (200 MHz, CD_3COCD_3, δ from TMS) 0.86 (6H, m, (2t)), 1.2 (3H, d, $J = 6.3$ Hz), 1.28 (34H, m), 1.6 (2H, m), 1.8 (2H, sext), 4.1 (2H, t, $J = 6.4$ Hz), 4.5 (1H, $J = 6.1$ Hz), 7.1 (2H, d, $J = 8.9$ Hz), 7.34 (2H, d, $J = 8.7$ Hz), 7.68 (2H, d, $J = 8.7$ Hz), 7.78 (4H, s), 8.1 (2H, d, $J = 8.9$ Hz).

By using the same procedure, we obtained 1-[((4-(*n*-hexadecyloxy)phenyl)carbonyl)oxy)-4-phenyl]-2-[4-(((2-(*S*)-heptyloxy)sulfinyl)phenyl)ethyne: **II** and **II′** (Figure 5, $p = 16$, $m = 5$), yield 61%.

II: ^{1}H NMR (200 MHz, CD_3COCD_3, δ from TMS) 0.86 (6H, m, (2t)), 1.26 (32H, m), 1.38 (3H, d, $J = 6.2$ Hz), 1.5 (2H, m), 1.8 (2H, sext), 4.05 (2H, t, $J = 6.4$ Hz), 4.43 (1H, sext, $J = 6.1$ Hz), 7.0 (2H, d, $J = 8.9$ Hz), 7.2 (2H, d, $J = 8.7$ Hz), 7.6 (2H, d, $J = 8.7$ Hz), 7.7 (4H, s), 8.1 (2H, d, $J = 8.9$ Hz).

II′: ^{1}H NMR (200 MHz, $CDCl_3$, δ from TMS) 0.89 (6H, m, (2t)), 1.25 (3H, d, $J = 6.2$ Hz), 1.27 (30H, m), 1.5 (2H, m), 1.8 (2H, sx), 4.05 (2H, t, $J = 6.4$ Hz), 4.5 (1H, sext, $J = 6.1$ Hz), 7.0 (2H, d, $J = 8.9$ Hz), 7.6 (2H, d, $J = 8.7$ Hz), 7.7 (2H, d, $J = 8.7$ Hz), 7.7 (4H, s), 8.1 (2H, d, $J = 8.9$ Hz). Anal. Calcd for $C_{44}H_{60}O_5S$: C, 75.39; H, 8.63; O, 11.41. Found: C, 75.63; H, 8.74; O, 11.57.

Acknowledgment. We would like to thank Miss L. Oswald for very helpful technical assistance.

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(36) Wittmann, J. C.; Smith, P. *Nature* 1991, *352*, 414.