Ferroelectric Liquid-Crystalline Compounds Containing a Sulfinyl Group as Unique Source of Chirality: Asymmetric Synthesis and Mesomorphic Properties

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Received April 29, 1994. Revised Manuscript Received August 1, 1994[⊗]

The synthesis and mesomorphism of a series of new ferroelectric liquid crystals containing a sulfinyl group as the unique chiral center are described. This chiral center was introduced in the optically active form into the mesogenic molecules via the asymmetric synthesis of sulfinamide, sulfoxide, and sulfinate functional groups, directly connected to the aromatic rigid core. The role of the sulfinyl group nature, of the aromatic rigid core structure, of the chiral center position and of the alkyl chain length on the liquid-crystalline behavior have been investigated systematically. A central rigid core limited to two benzene rings only, and the presence of a pyramidal atom within the rigid core are not in favor of the occurrence of the mesomorphic character. On the contrary, sulfinates at the end of the core give a smectic C* phase, stable within a reasonable temperature range. On the other hand, the only change of the sulfinyl group has large effects on the thermal stability of the mesophases, on the transition temperatures and more deeply on the polymorphic nature. This change leads to thermal instability with the sulfoxide compounds and with some sulfinamide ones, whereas the sulfinate mesogens are perfectly stable from both optical and thermal points of view. Thermal smectic C* and A phases have been systematically studied as a function of aliphatic chain lengths. The alkyl chain of the sulfinate group plays a predominant role. Smectic A phases are favored when this chain is short, whereas smectic C* phases are favored for long chains. The thermal stability of the smectic C* mesophase is strongly correlated to the tilt angle of the molecules inside the smectic layers.

Introduction

Since the discovery of ferroelectricity in liquid crystalline S_C^* phases,[1] considerable interest in that new class of materials has emerged from both fundamental and practical points of view. Different types of electrooptical devices have been proposed since the discovery of the "surface stabilized ferroelectric liquid crystals" (SSFLC),[2] in which the S_C^* phase can exhibit a fast response time to an applied electric field. Taking into account that the response time τ is inversely proportional to the spontaneous polarization Ps ($\tau \sim \eta/Ps \cdot E$, η being the rotational viscosity and E the applied electric field), the synthesis of new liquid-crystalline ferroelectric materials suitable for applications in electrooptical devices[3] is currently focused on obtaining a large spontaneous polarization. To obtain a high value of Ps, a rigid steric coupling between the asymmetric center and a strong dipole moment (such as C=O, C—Hal, C—CN⋯) is generally assumed to be advantageous.[4] In addition, it has been demonstrated that the synthesis of molecules bearing at least one chiral center close to the rigid core leads to a large spontaneous polarization by damping the molecular rotation in the S_C^* phase.[4] During the past few years, the efforts of chemists have led to a range of S_C^* molecules bearing interesting chiral sources such as oxiranes,[5] thiiranes,[6] cyanohydrins,[7] β-chlorohydrins,[8] and some chiral δ- and γ-lactone derivatives.[9] Heteroatoms can represent an interesting chiral center for S_C^* molecules because they can also bear a strong dipole moment. For example, the sulfur atom is chiral in its fourth oxidized state $S^{(IV)}$ such as in sulfinyl groups for which the dipole moment S=O can reach 4–5 D.[10–12] To date, the use of heteroatom chirality in S_C^* compounds is rather limited. In the case

[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1994.

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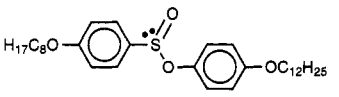
Table 1. Molecular Structures of Chiral Mesogenic Compounds Synthesized and Their Abbreviated Names: (BT for (Benzenecarbonyl)oxytolane; ST for (Benzenesulfonyl)oxytolane; T for Tolane; S for Sulfinyl; Me for Methyl; *m* and *n* for the Number of Carbon Atoms in the Alkyl Chains; Men for Menthyl; P for Pyrrolidinyl



4-(dodecyloxy)phenyl 4-(octyloxy)benzenesulfinate

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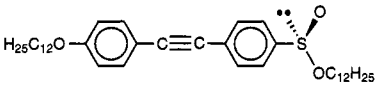

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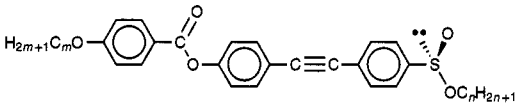
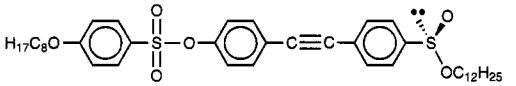
12-TS-O12



1-[(*S*)-(−)-4-(alkoxysulfinyl)phenyl]-2-[4-((4-alkoxyphenyl)carbonyloxy)phenyl]ethyne

m*-BTS-O*n



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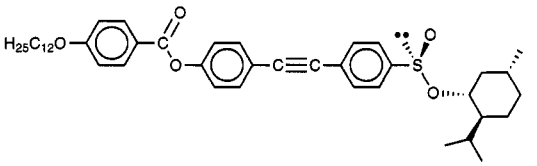
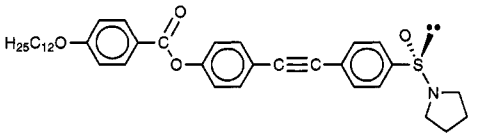
8-STS-O12



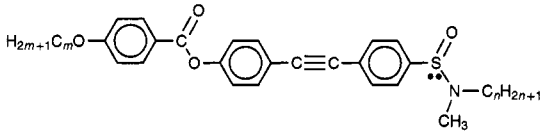
1-[(*S*)-(−)-4-(((1*R*,2*S*,5*R*)-(−)-menthyloxy)sulfinyl)phenyl]-2-[4-(4-dodecyloxy)phenylcarbonyloxy)phenyl]ethyne

12-BTS-OMen



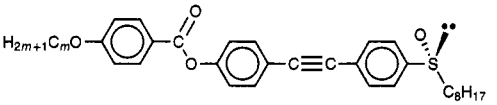
1-[(*S*)-(+)-4-((1-pyrrolidinyl)sulfinyl)phenyl]-2-[4-(4-(dodecyloxy)phenylcarbonyloxy)phenyl]ethyne

12-BTS-NP



1-[(−)-4-((*N*-alkyl-*N*-methyl)sulfinyl)phenyl]-2-[4-(4-alkoxyphenyl)carbonyloxy)phenyl]ethyne

m*-BTS-N(Me)-*n



1-[(*R*)-(+)-4-(octylsulfinyl)phenyl]-2-[4-((4-alkoxyphenyl)carbonyloxy)phenyl]ethyne

***m*-BTS-8**

of sulfinyl groups only two reports appeared in the literature. One of these papers deals with the synthesis and properties of a number of chiral sulfoxides,[11] but the materials did not exhibit stable S_C^* phases and the electrooptical properties were measured only with mixtures containing the optically active sulfoxides as dopants. The other concerns the synthesis and properties of mesogens which contain an optically active sulfinate functional group and a second chiral center (asymmetric carbon);[12] contrary to the case of sulfoxides, one of the two pure sulfinate diastereomers synthesized did exhibit a S_C^* phase, but it has not been possible to measure the electrooptical properties of the optically pure chiral material.

The S_C^* mesogenicity of the materials presented above can be considered as a promising starting point in the search of high spontaneous polarization in ferroelectric liquid crystals. On the basis of these results, we decided to carry out the synthesis of mesogens bearing a sulfinyl group as unique chiral center. The compounds synthesized are listed in Table 1. For the large majority of them, a diphenylethyne group (tolane) was used as the principal unit in the aromatic

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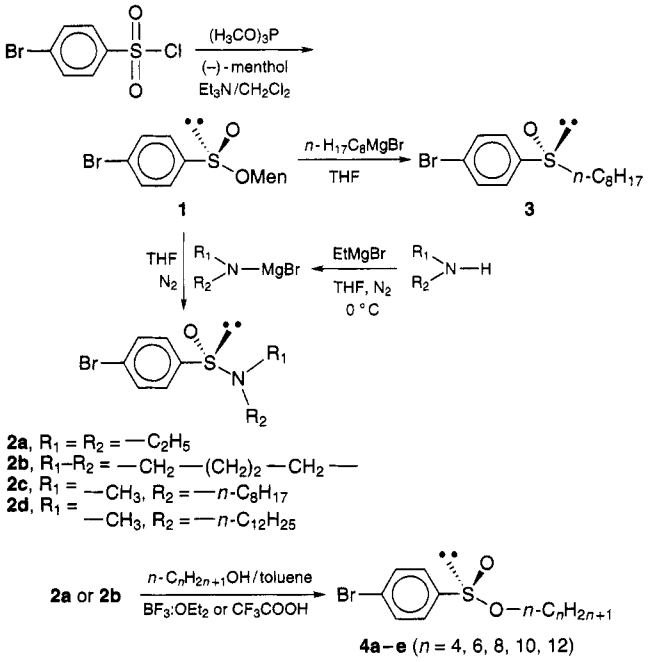
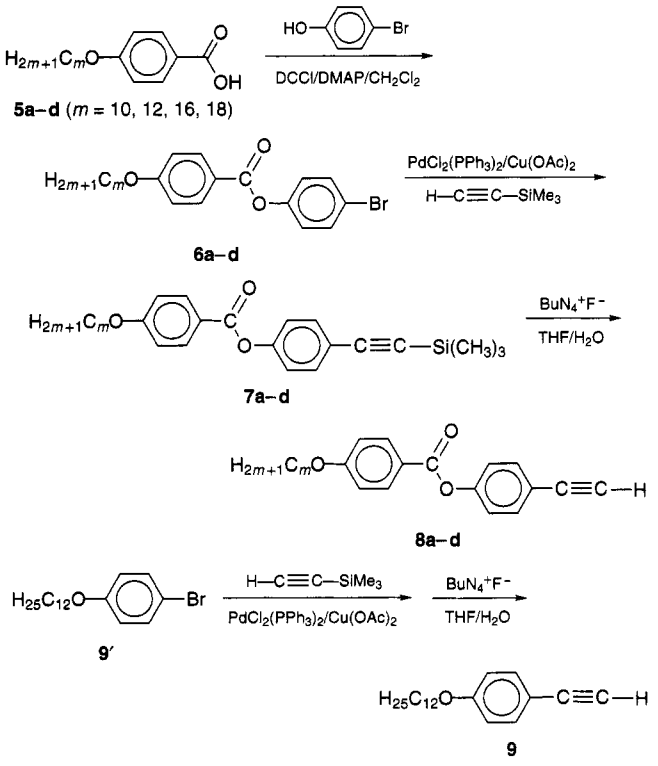
Scheme 1

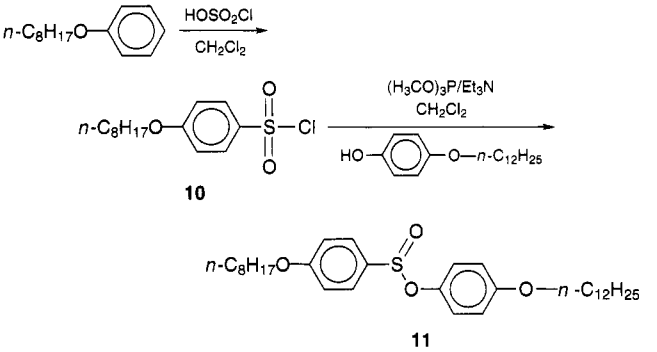


Scheme 2



core because of its good rigidity and of its global linearity. The chiral center was introduced through the sulfinamide, sulfinate, or sulfoxide functional groups directly connected to one peripheral position of the tolane group, while the other was substituted with an alkoxy, a (4-alkoxyphenyl)carbonyloxy or a (4-alkoxyphenyl)sulfonyloxy group (Schemes 1 and 2). In addition, a phenyl benzenesulfinate derivative was synthesized as an example of a compound having the chiral center incorporated inside the rigid core (Scheme 3). The mesomorphic behavior of the different compounds synthesized is then analyzed in detail in relation with the molecular architecture.

Scheme 3



Experimental Section

NMR spectra were recorded on a Bruker AC 200 spectrometer. IR spectra were recorded on a Perkin-Elmer 930 spectrometer. Optical rotatory powers were measured on a Perkin-Elmer 241 MC polarimeter. Enantiomeric excesses were determined by ^{1}H NMR with addition of Eu(hfc)$_3$ as chiral shift reagent from a preoptimized spectrum of the racemic compound. A 20−30% molar equivalent of shift reagent generally gave satisfactory peak separation. DSC analyses were carried out with a Perkin-Elmer DSC7 calorimeter, using heating rates of 10 K min^{-1}. Observations by optical microscopy were carried out using a Leitz-Orthoplan microscope equipped with a Mettler FP 82 hot stage. X-ray diffraction patterns were recorded photographically using a Guinier focusing camera equipped with a bent quartz monochromator (Cu Kα_1 radiation from Phillips PW-1009 generator) and an electric oven.

Typical preparations of the new materials are described below. Yields, chemical data, and characterizations are collected in Tables 2−11.

(1*R*,2*S*,5*R*)-(−)-Menthyl (*S*)-4-Bromobenzenesulfinate (1, Scheme 1). A solution of 4-bromobenzensulfonyl chloride (20 g, 78.3 mmol), (−)-menthol (10.20 g, 65.3 mmol), trimethyl phosphite (11.6 mL, 98 mmol), and dry CH_2Cl_2 (300 mL) was vigorously stirred under a nitrogen atmosphere for 5−10 min at 40 °C. Triethylamine (7.92 g, 78.3 mmol) was added and the reaction mixture was heated to reflux for 4 h. The mixture was allowed to cool to room temperature, washed with HCl 5% (80 mL), saturated $NaHCO_3$ (80 mL), and saturated NaCl (3 × 60 mL), dried over Na_2SO_4, and concentrated to obtain a yellow oil (28.35 g). This oil was dissolved in acetone, and the mixture was allowed to cool to −30 °C to get 21 g of white crystals which contain 72% of the diastereomer having the *S* configuration at sulfur. The white solid so separated was recrystallized five times from acetone to give 10.83 g (yield 38.5%) of pure (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-4-bromobenzenesulfinate **1**; mp 119−120 °C; $[\alpha]_D^{22}$ 167° (*c* 2.9, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.67 {dd; J^3 8.6 Hz, J^4 = 1.25 Hz; 2H H−Ar}, 7.58 {dd; J^3 = 8.6 Hz, J^4 = 1.25 Hz; 2H, H−Ar}, 4.19 {td; J^3 = 10 Hz, J^4 = 4.5 Hz; 1H, C*H*−O}, 2.32 {mc; 1H, H−Men}, 2.15 {mc; 1H, H−Men}, 1.75 {mc; 2H, H−Men}, 1.6−1.1 {m; 5H, H−Men}, 1.02 {d; J^3 = 6.42 Hz; 3 H, CH_3(*i*Pr)}, 0.93 {d; J^3 = 7 Hz; 3H, CH_3(*i*Pr)}, 0.78 {d; J^3 = 6.9 Hz; 3H, CH_3−Men)}. Analysis: Found (calcd) for $C_{16}H_{23}BrO_2S$ (M_w = 356.06 g) %C 53.63 (53.62), %H 6.46 (6.47), %O 8.93 (9.20), %S 8.93 (8.79).

Synthesis of Optically Active *N,N*′-Dialkyl 4-Bromobenzenesulfinamide (2a−d, Scheme 1). *General procedure*: To a stirred suspension of magnesium (100 mmol) in dry THF (10 mL) was slowly added a dry solution of ethyl bromide (130 mmol) in THF (30 mL) at room temperature and under nitrogen. After complete reaction of the metal, the amine (130 mmol) was added slowly to the reaction mixture, cooled at 0 °C. The reaction mixture was kept at 0 °C for 15−20 min and then added dropwise under nitrogen to a stirred solution of (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-4-bromobenzenesulfinate (**1**, 33.3 mmol) in THF (60 mL) at temperatures shown in Table 2. After total disappearance of the starting material (checked by TLC on silica plates, eluant Et_2O/pentane 2/1) the mixture was quenched with saturated aqueous ammonium chloride; the

Table 2. Characterization of Chiral Sulfinamides 2a–d

product time (min) T(°C)	yield (%) aspect	anal. found (calcd)	^{1}H NMR ($CDCl_3$) (δ ppm)	ee (%) $[\alpha]_D$ c; EtOH
2a	91; 92	%C 43.80 (43.60)	7.64 {dd; J^3 = 8.64 Hz; 2H, H–Ar}, H–Ar}, 7.53 {dd;	75; 94
360	oil	%H 5.31 (5.11)	J^3 = 8.64 Hz; 2H, H–Ar}, 3.13 {q; J^3 = 7.2 Hz; 4H,	+65°; +80°
−30; −76		%N 5.05 (5.07)	CH_3CH_2N}, 1.13 {t; J^3 = 7.2 Hz;6H, CH_3CH_2N}	0.86; 0.66
		%S 11.75 (11.61)		
2b	96	%C 44.08 (43.81)	7.64 {dd; J^3 = 8.74 Hz; 2H, H–Ar}, 7.54 {dd; J^3 = 8.74 Hz;	92
240	solid (mp 37 °C)	%H 4.48 (4.41)	2H, H–Ar}, 3.34 {m; 2H, $-CH_2-N$}, 2.97 {m; 2H, CH_2-N},	+167°
−30		%N 5.04 (5.11)	1.88 {mc; 4H, $-CH_2-CH_2-N$}	0.51
		%S 11.69 (11.70)		
2c	48	%C 52.02 (52.27)	7.65 {dd; J^3 = 8.9 Hz; 2H, H–Ar}, 7.51 {dd; J^3 = 8.9 Hz;	–
1440	oil	%H 6.98 (7.15)	2H, H–Ar}, 3.12 {mc; 2H, $-CH_2-N$}, 2.52 {s; 3H, $N-CH_3$},	−7°
room		%N 4.29 (4.11)	1.65 {m; 2H, $-CH_2-CH_2-N$}, 1.28 {m; 10H, $-CH_2$ (octyl)},	1.09
		%S 9.26 (9.02)	0.89 {t; 3H, $-CH_3$ (octyl)	
2d	55	%C 54.16 (53.96)		–
1440	oil	%H 8.41 (8.52)	1.28 {m; 18H, $-CH_2$ (dodecyl)}	−15°
room		%N 3.87 (3.70)		0.65
		%S 8.55 (8.47)		

Table 3. Characterization of Chiral Sulfinates 4a–e

sulfinate (yield, %)	anal. found (calcd)	^{1}H NMR ($CDCl_3$) (δ, ppm)
4a (94)	$C_{10}H_{13}BrO_2S$	7.69 {d, J^3 = 8.12 Hz; 2H, H–Ar}, 7.62 {d, J^3 = 8.12 Hz; 2H, H–Ar},
	%C = 43.42(43.33)	4.05 {dt (ABX_2), J^2 = 9.62, J^3 = 6.42 Hz; 1H, $-SOO-CH_2$},
	%H = 4.76(4.73)	3.63 {dt (ABX_2), J^2 = 9.62, J^3 = 6.42 Hz; 1H, $-SOO-CH_2-$},
	%O = 11.48(11.54)	1.62 {mc; 2H, $-SOO-CH_2-CH_2-$}, 1.35 {m; 2H, $-CH_2-CH_3$},
	%S = 11.51(11.57)	0.90 {t, J^3 = 6.35 Hz; 3H, CH_3-CH_2}
4b (89)	$C_{12}H_{17}BrO_2S$	
	%C = 47.31(47.22)	1.64 {mc; 2H, $-SOO-CH_2-CH_2-$}, 1.27 {m; 6H, aliphatic ($-CH_2-$)},
	%H = 5.66(5.61)	0.90 {t, J^3 = 6.35 Hz; 3H, CH_3-CH_2}
	%O = 10.44(10.48)	
	%S = 10.47(10.50)	
4c (89)	$C_{14}H_{21}BrO_2S$	
	%C = 50.58(50.45)	1.62 {mc; 2H, $-SOO-CH_2-CH_2-$}, 1.25 {m; 10H, aliphatic ($-CH_2-$)},
	%H = 6.41(6.35)	0.88 {t, J^3 = 6.33 Hz; 3H, CH_3-CH_2}
	%O = 9.55(9.60)	
	%S = 9.57(9.62)	
4d (91)	$C_{16}H_{25}BrO_2S$	
	%C = 53.31(53.18)	1.60 {mc; 2H, $-SOO-CH_2-CH_2-$}, 1.24 {m; 14H, aliphatic ($-CH_2-$)},
	%H = 7.05(6.97)	0.86 {t, J^3 = 6.30 Hz; 3H, CH_3-CH_2}
	%O = 8.73(8.86)	
	%S = 8.79(8.87)	
4e (93)	$C_{18}H_{29}BrO_2S$	
	%C = 55.66(55.52)	1.62 {mc; 2H, $-SOO-CH_2-CH_2-$}, 1.25 {m; 18H, aliphatic ($-CH_2-$)},
	%H = 7.58(7.51)	0.86 {t, J^3 = 6.31 Hz; 3H, CH_3-CH_2}
	%O = 8.08(8.22)	
	%S = 8.13(8.23)	

aqueous phase was then extracted with diethyl ether, and the combined organic extracts were washed with saturated aqueous NaCl, dried over Na_2SO_4, and evaporated under reduced pressure. Each crude product was chromatographed on silica column (eluant Et_2O/pentane 2/1). Details and data are listed in Table 2.

(*R*)-(+)-4-Bromophenyl Octyl Sulfoxide (3, Scheme 1). Sulfoxide **3** was prepared by nucleophilic substitution on (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-4-bromobenzenesulfinate ***1*** (4.20 mmol) by octylmagnesium bromide (12.6 mmol) at −76 °C as described above for the synthesis of sulfinamide **2a**. The reaction time was 45 min, and the sulfoxide **3** as white solid was obtained optically pure ($[\alpha]_D^{22}$ + 126°; *c* 1.60, ethanol); yield 92%; mp 44–45 °C. ^{1}H NMR ($CDCl_3$) δ (ppm) 7.67 {d, J^3 = 8.56 Hz; 2H, H–Ar}, 7.50 {d, J^3 = 8.56 Hz; 2H, H–Ar}, 2.77 {t, J^3 = 7.65 Hz; 2H, $-CH_2-SO$}, 1.70 {mc; 2H, $-CH_2-CH_2-SO-$}, 1.25 {m; 10H, aliphatic ($-CH_2-$)}, 0.86 {t, J^3 = 6.72 Hz; 3H, CH_3-CH_2}. Analysis: Found (calcd) for $C_{14}H_{21}BrOS$ (M_w = 317.3 g): %C 52.97 (53.00), %H 6.74 (6.67), %S 9.90 (10.10).

Synthesis of Alkyl 4-Bromobenzenesulfinates (4a–e, Scheme 1). *General procedure*: To a solution of sulfinamide **2a** or **2b** (*n* mmol) and primary alcohol n-$C_nH_{2n+1}OH$ (4–6*n* mmol) in toluene (1.5 mL/mmol of **2a**) was added dropwise a solution of the acid catalyst (1.5*n* mmol of boron trifluoride etherate BF_3:OEt_2 or 2*n* mmol of trifluoroacetic acid) in toluene under temperature conditions shown in Table 3 and under nitrogen. The mixture was stirred at the same temperature until the starting material was consumed (about 2 h), then quenched with saturated aqueous $NaHCO_3$, and extracted with diethyl ether. The combined organic extracts were washed with saturated aqueous NaCl, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude yellow oil was purified by column chromatography on silica (diethyl ether/pentane: 1/1) to give the (*S*)-(−)-sulfinates **4a–e** as colorless oils. Details and data are given in Tables 3 and 4.

4-(Bromophenyl)-4-alkoxybenzoates (6a–d, Scheme 2). They were prepared by a classical esterification reaction between the selected acids **5** (*n* mmol) and 4-bromophenol (1.2*n* mmol) in absolute dry CH_2Cl_2 as solvent in the presence of dicyclohexylcarbodiimide (DCCI; 1.2*n* mmol) and (dimethylamino)pyridine (DMAP; 0.05*n* mmol) as basic catalyst. The reaction time was 2 h, and the esters obtained were purified by chromatography on a silica column (CH_2Cl_2/hexane 1/1) then recrystallized from methanol. White crystalline products were obtained in 90–94% yields. Spectral data are listed in Table 5.

Synthesis of 4-((Trimethylsilyl)ethynyl)phenyl 4′-*n*-Alkyloxybenzoate (7a–d, Scheme 2). Ester **6** (*m* = 10, 12, 16, 18; 46.20 mmol) and (trimethylsilyl)acetylene (TMSA, 92.30 mmol) were dissolved in triethylamine/toluene mixture (100 mL/30 mL) under a nitrogen atmosphere. Copper(II) acetate monohydrate (0.5 mmol), triphenylphosphine (4.6 mmol), and palladium chloride (0.90 mmol) were added to the stirred solution, and the mixture was heated at 60 °C for 4 h. After cooling, the precipitate of triethylammonium bromide was

Table 4. Characterization of Optically Active Sulfinates 4a–e Obtained from Chiral Sulfinamides 2a,b

sulfinamide (ee, %)	acid alcohol	T (°C)	sulfinate (yield, %)	$[\alpha]_D^{22}$ c; EtOH	ee (%)	stereoselectivity (%)
2a	BF_3:OEt_2	−30	**4a**	−84°	75	100
75	C_4H_9OH		94	2.12		
2a	BF_3:OEt_2	−76	**4b**	−99°	88	94
94	$C_6H_{13}OH$		89	1.34		
2b	CF_3COOH	−30	**4c**	−98°	88	95.7
92	$C_8H_{17}OH$		89	1.84		
2a	BF_3:OEt_2	−76	**4d**	−95°	85	90
94	$C_{10}H_{21}OH$		91	2.27		
2a	BF_3:OEt_2	−76	**4e**	−90°	81	86
94	$C_{12}H_{25}OH$		93	1.85		

Table 5. Characterization of Esters 6a–d

ester 6 *m* (yield, %)	mp (°C)	^{1}H NMR (200 MHz, $CDCl_3$) (δ, ppm)	anal. calcd (found)
6a		8.13 {d; J^3 = 8.94 Hz; 2H, H–Ar}, 7.54 {d; J^3 = 8.86 Hz; 2H, H–Ar},	$C_{23}H_{29}BrO_3$
10	83–84	7.10 {d; J^3 = 8.86 Hz; 2H, H–Ar}, 6.97 {d; J^3 = 8.94 Hz; 2H, H–Ar},	%C 63.76(63.69)
(94)		4.05 {t; J^3 = 6.5 Hz; 2H, CH_2–O}, 1.82 {mc; 2H, CH_2–CH_2–O},	%H 6.75(6.72)
		1.34 {m; 14H, aliphatic (CH_2)}, 0.88 {t; J^3 = 6.5 Hz; 3H, CH_3–(CH_2)}	%O 11.08(11.17)
6b			$C_{25}H_{33}BrO_3$
12	81–82	1.33 {m; 14H; aliphatic(CH_2)}	%C 65.08(65.12)
(92)			%H 7.21(7.17)
			%O 10.40(10.58)
6c			$C_{27}H_{77}BrO_3$
16	84–85	1.33 {m; 26H; aliphatic(CH_2)}	%C 67.31(67.42)
(90)			%H 7.99(7.91)
			%O 9.28(9.42)
6d			$C_{29}H_{41}BrO_3$
18	85–86	1.32 {m; 30H; aliphatic(CH_2)}	%C 68.26(68.33)
(91)			%H 8.32(8.29)
			%O 8.80(8.93)

Table 6. Characterization of Compounds 7a–d

7a–d *m* (yield, %)	mp (°C)	^{1}H NMR (200 MHz, $CDCl_3$) (δ, ppm)	anal. calcd (found)
7a	88–89	8.10 {d; J^3 = 8.95 Hz; 2H, H–Ar}, 7.50 {d; J^3 = 8.76 Hz; 2H, H–Ar},	$C_{28}H_{38}O_3Si$
10		7.16 {d; J^3 = 8.76 Hz; 2H, H–Ar}, 6.98 {d; J^3 = 8.95 Hz; 2H, H–Ar},	%C 74.63(74.71)
(91)		4.02 {t; J^3 = 6.5 Hz; 2H, CH_2–O}, 1.83 {mc; 2H, CH_2–CH_2–O},	%H 8.50(8.42)
		1.34 {m; 14H, aliphatic (CH_2)}, 0.90 {t; J^3 = 6.5 Hz; 3H, CH_3–CH_2–},	%O 10.65(10.82)
		0.25 {s; 9H, (CH_3)$_3$–Si	
7b	85–86	1.33 {m; 14H; aliphatic(CH_2)}	$C_{30}H_{42}O_3Si$
12			%C 75.28(75.36)
(90)			%H 8.84(8.78)
			%O 10.03(10.11)
7c	78–79	1.33 {m; 26H; aliphatic(CH_2)}	$C_{34}H_{50}O_3Si$
16			%C 76.36(76.44)
(87)			%H 9.42(9.35)
			%O 8.98(9.13)
7d	76–77	1.32 {m; 30H; aliphatic(CH_2)}	$C_{36}H_{54}O_3Si$
18			%C 76.83(76.91)
(83)			%H 9.67(9.62)
			%O 8.53(8.66)

filtered off and washed with 40 mL of toluene. The combined filtrates were quenched with HCl 5% (60 mL) and then extracted with methylene chloride (300 mL). The organic phases were washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting crude solid was chromatographed on a column of silica (CH_2Cl_2/hexane 3/2) and recrystallized from pentane to give esters **7a–d** as white crystals. Details and spectral data are listed in Table 6.

Synthesis of 4-Ethynylphenyl 4-*n*-alkyloxybenzoate (8a–d, Scheme 2). To a stirred solution of ester **7a–d** (33.3 mmol) in aqueous THF (THF/H_2O 200 mL/15 mL) was added dropwise a 1 M solution of tetrabutylammonium fluoride (16.8 mmol) in THF at 0 °C. The mixture was kept at 0 °C for 10–15 min and then treated with 150 mL of 5% HCl. The resulting mixture was extracted twice with 280 mL of methylene chloride. The combined extracts were washed with water (2 × 180 mL), dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting crude solid was chromatographed on a column of silica (CH_2Cl_2/hexane 1/1) and recrystallized from pentane/ethanol 70/30 to give pure compounds **8** as white crystals. Details and spectral data are listed in Table 7.

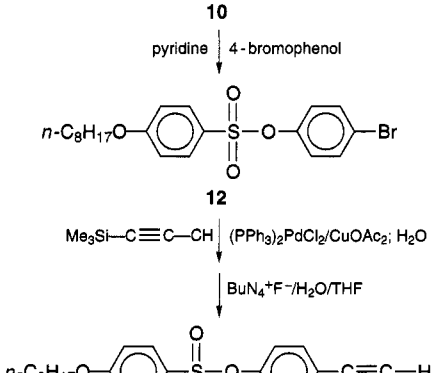
Synthesis of ((4-Dodecyloxy)phenyl)acetylene (9, Scheme 2). Compound **9** was prepared by the coupling reaction of 1-bromo-4-(octyloxy)benzene (**9′**) with (trimethylsilyl)acetylene, followed by deprotection of the triple bond with tetrabutylammonium fluoride as described above for acetylenic compounds **8**; mp 29–30 °C.

Synthesis of 4-(Octyloxy)benzenesulfonyl Chloride (10, Scheme 3). To a solution of (*n*-octyloxy)benzene (30 g, 145.4 mmol) in chloroform (100 mL) cooled at −30 °C was added dropwise chlorosulfonic acid (33.9 g, 290.8 mmol). After complete addition of the acid (about 10 min), the mixture was continuously stirred at room temperature for 45 min, then poured into cold water, and extracted with 2 × 200 mL of chloroform. The combined extracts were washed with water, dried over Na_2SO_4, and then concentrated under reduced pressure. The resulting crude product (31 g) was dissolved in hot hexane that gives upon cooling 3.5 g of a white solid

Table 7. Characterization of Compounds 8a–d

8a–d *m* (yield, %)	mp (°C)	^{1}H NMR, 200 MHz, $CDCl_3$, δ (ppm)	anal. calcd (found)
8a 10 (91)	73–74	8.12 {d; J^3 = 8.90 Hz; 2H, H–Ar}, 7.55 {d; J^3 = 8.78 Hz; 2H, H–Ar}, 7.20 {d; J^3 = 8.78 Hz; 2H, H–Ar}, 6.95 {d; J^3 = 8.90 Hz; 2H, H–Ar}, 4.05 {t; J^3 = 6.5 Hz; 2H, CH_2–O}, 3.09 {s; 1H, H-ethynyl}, 1.83 {mc; 2H, CH_2–CH_2–O}, 1.34 {m; 14H, aliphatic(CH_2)}, 0.90 {t; J^3 = 6.5 Hz; 3H, CH_3–CH_2–}	%C = 79.36(79.44) %H = 7.93(7.89) %O = 12.70(12.87)
8b 12 (87)	83–84	1.32 {m; 14H; aliphatic(CH_2)}	%C = 79.80(79.93 %H = 8.37(8.23) %O = 11.80(11.92)
8c 16 (83)	86–87	1.35 {m; 26H; aliphatic(CH_2)}	%C = 80.52(80.11) %H = 9.09(9.19) %O = 10.39(10.16)
8d (18) (84)	85–86	1.34 {m; 30H; aliphatic(CH_2)}	%C = 80.81(80.63) %H = 9.39(9.27) %O = 9.79(9.92)

Scheme 4



consisting of bis(4-(*n*-octyloxy)phenyl) sulfone, mp 196 °C. The sulfone was removed out by filtration, then the filtrate was concentrated under reduced pressure to give a crude oil that was distilled under vacuum. Pure 4-(*n*-octyloxy)benzenesulfonyl chloride ***10*** (27 g; yield 61%) was thus obtained as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.85 {d; J^3 = 8.95 Hz; 2H, H–Ar}, 7.00 {d; J^3 = 8.95 Hz; 2H, H–(Ar)}, 4.05 {t; J^3 = 6.20 Hz, 2H, CH_2–O}, 1.86 {mc; 2H, CH_2–CH_2–O}, 1.25–1.55 {m; 10H, aliphatic (CH_2)}, 0.90 {t; J^3 = 6.5 Hz; 3H, CH_3-CH_2-}. Analysis: Found (calcd) for $C_{14}H_{21}ClO_3S$ (M = 304.8 g): %C 54.98 (55.16); %H 6.86 (6.94); %O 15.82 (15.75); %S 10.48 (10.52).

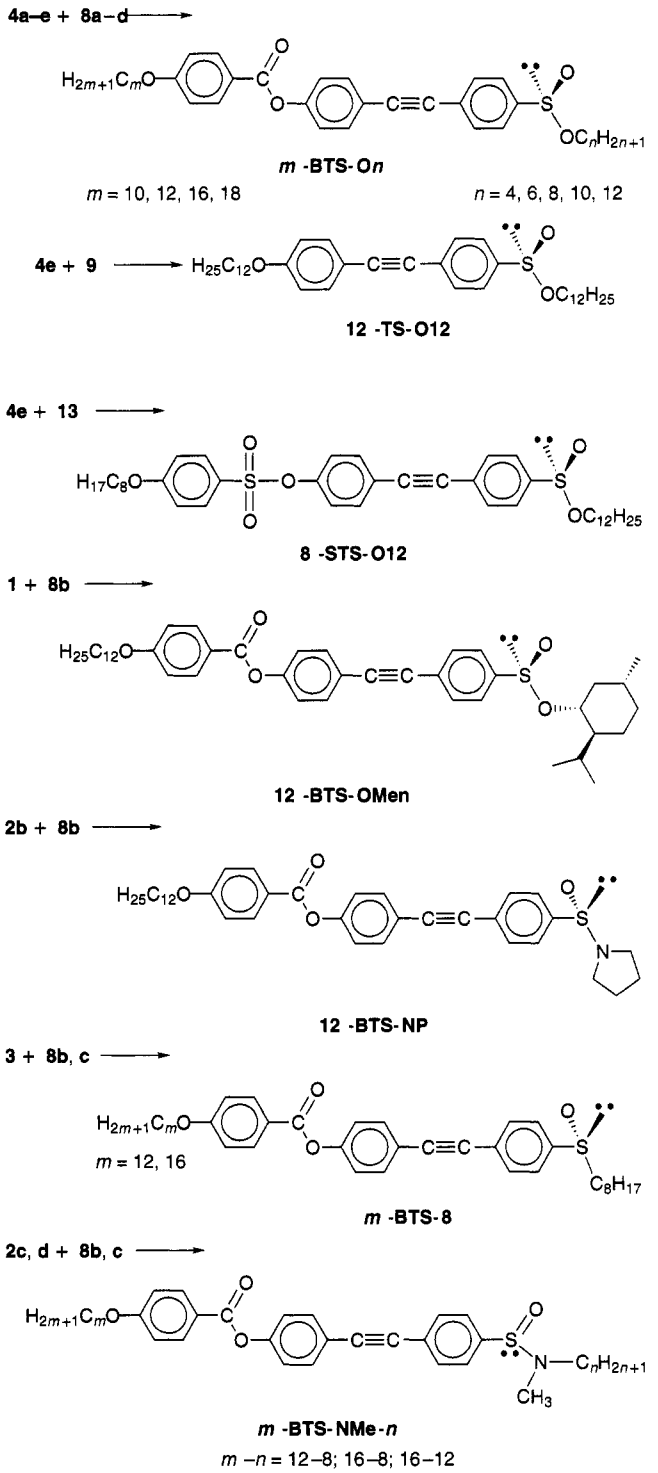
Synthesis of 4-Bromophenyl 4-(Octyloxy)benzenesulfonate (12, Scheme 4). A solution of 4-(octyloxy)benzenesulfonyl chloride **10** (10 g, 32.8 mmol), and of 4-bromophenol (8.5 g, 49.2 mmol) in pyridine (50 mL) was stirred at 0 °C for 1 h. The white precipitate formed during the reaction, consisting of pyridinium chloride, was removed out by filtration and washed with 200 mL of diethyl ether. The filtrate was washed with 2 × 60 mL of HCl 5% and 2 × 60 mL of water. The organic phase was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude oil was chromatographed on a column of silica (CH_2Cl_2) to give **12** (12.4 g, 85%) as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.72 {d; J^3 = 8.90 Hz; 2H, H–($ArSO_3$–)}, 7.45 {d; J^3 = 8.70 Hz; 2H, H–($ArOSO_2$)}, 7.10 {d; J^3 = 8.70 Hz; 2H, H–($ArOSO_2$)}, 7.00 {d; J^3 = 8.90 Hz; 2H, H–($ArSO_3$–)}, 4.05 {t; J^3 = 6.20 Hz, 2H, CH_2-O}, 1.85 {mc; 2H, CH_2–CH_2–O}, 1.25–1.55 {m; 10H, aliphatic (CH_2)}, 0.90 {t; J^3 = 6.5 Hz; 3H, CH_3–CH_2–}. Analysis: Found (calcd) for $C_{20}H_{25}BrO_4S$, M_w 441.4 g): %C 54.68 (54.42), %H 5.80 (5.71), %O 14.36 (14.50); %S 7.13 (7.26).

Synthesis of 4-(Ethynylphenyl) 4-(Octyloxy)benzenesulfonate (13, Scheme 4). 4-Bromophenyl 4-(octyloxy)-benzenesulfonate **12** (10 g, 22.7 mmol) and (trimethylsilyl)-acetylene (4.46 g, 45.40 mmol) were dissolved in dry triethylamine (50 mL) under N_2. Copper(II) acetate monohydrate (0.04 g, 0.20 mmol), triphenylphosphine (0.52 g, 2 mmol), and palladium chloride (0.09 g, 0.5 mmol) were added to the stirred solution. The mixture was heated to reflux for 2 h, cooled to room temperature, and filtered on a short column of neutral alumina. The filtrate was concentrated under reduced pressure to give a brown liquor. This liquor was dissolved in THF/H_2O 40 mL/10 mL stirred at room temperature followed by dropwise addition of a solution of 1 M tetrabutylammonium fluoride (2.63 g, 10 mmol) in THF. After 30 min of continuous stirring, the resulting mixture was filtered on a short column of silica (CH_2Cl_2), and the filtrate was concentrated under reduced pressure. The resulting residue was chromatographed on a column of silica (CH_2Cl_2/hexane 1/1) to yield 7.6 g of pure **13** as a yellow liquor. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.80 {d; J^3 = 8.95 Hz; 2H, H–($ArSO_3$–)}, 7.50 {d; J^3 = 8.70 Hz; 2H, H–($ArOSO_2$)}, 7.02 {d; J^3 = 8.70 Hz; 2H, H–($ArOSO_2$)}, 6.95 {d; J^3 = 8.95 Hz; 2H, H–($ArSO_3$–)}, 4.05 {t; J^3 = 6.20 Hz, 2H, CH_2–O}, 3.10 {s; 1H, H-ethynyl}, 1.86 {mc; 2H, CH_2–CH_2–O}, 1.25–1.55 {m; 10H, aliphatic (CH_2)}, 0.90 {t; J^3 = 6.5 Hz; 3H, CH_3–CH_2}. Analysis: Found (calcd) for $C_{22}H_{26}O_4S$ (M_w = 386.5 g): %C 68.55 (68.37), %H 6.82 (6.78), %O 16.48 (16.56), %S 8.17 (8.29).

Synthesis of 4-(Dodecyloxy)phenyl 4-(Octyloxy)benzenesulfinate (11, Scheme 3). Sulfinate **11** was prepared by in situ reduction of 4-(octyloxy)benzenesulfonyl chloride **10** (0.3 g, 0.98 mmol) by trimethyl phosphite (0.15 g, 1.18 mmol) in CH_2Cl_2 (20 mL) in the presence of 4-(dodecyloxy)phenol (0.32 g, 1.1 mmol) and triethylamine (0.1 g, 1 mmol) as described above for **1**. The reaction time was 4 h and the sulfinate **11** was obtained as white crystals (0.3 g; yield 58%); mp 27–28 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.71 {dd, J^3 = 8.85 Hz, 2H, H–Ar}, 6.94 {dd, J^3 = 8.85 Hz, 2H, H–Ar}, 6.87 {dd, J^3 = 8.9 Hz, 2 H, HAr}, 6.76 {dd, J^3 = 8.9 Hz, 2H, H-3}, 4.07 {t, J^3 = 5.5 Hz; 2H, –OSO–PH–O–CH_2–}, 3.90 {t, J^3 = 5.5 Hz; 2H, –SOO–PH–O–CH_2–}, 1.76 {mc; 2H, O–CH_2–CH_2–}, 1.2–1.6 {m; 6H, aliphatic (–CH_2–)} 0.93 {t, J^3 = 5 Hz; 3H, CH_3–CH_2–}. Analysis: Found (calcd) for $C_{32}H_{50}O_4S$ (M_w = 530.8 g): %C 72.64 (72.41), %H 9.29 (9.49), %O 12.23 (12.06), %S 5.89 (6.04).

Chiral Mesogenic Sulfinates *m*-BTS-O*n*. *General procedure (Scheme 5)*: Terminal acetylenic compounds **8a–d** (1.2*n* mmol) was dissolved in a mixture of triethylamine and toluene (3/2) at 50 °C. This solution was then degassed and kept at the same temperature under N_2. Copper(II) acetate monohydrate (0.005*n* mmol), triphenylphosphine (0.1*n* mmol), and palladium chloride (0.02*n* mmol) were added to the stirred solution, and the mixture was heated at 70 °C for 5 min. (*S*)-(–)-*n*-Alkyl 4-bromobenzenesulfinate **4a–e** (*n* mmol) was then added and the reaction mixture was stirred at 70 °C for 1 h. After cooling, the precipitate of triethylammonium bromide was filtered off and washed with CH_2Cl_2. The combined filtrates were washed with HCl 5% and water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting crude solid was chromatographed on a column of silica (CH_2Cl_2/Et_2O: 4/1) and recrystallized from acetone to give chiral sulfinates *m-BTSO-n* as white crystals. The other chiral sulfinates, sulfinamides and sulfoxides were prepared following the same procedure (Scheme 5). Details and spectral data are listed in Tables 8–11.

Scheme 5



Results and Discussion

Synthesis. The preparation of the chiral mesogens reported in Schemes 1–5 involves an asymmetric synthesis of the chiral sulfinyl group.[13] Stereospecific nucleophilic substitutions on the sulfinyl group is one of the best efficient methods which have been reported for asymmetric chemistry of sulfur atoms.[13,14] In our case, it was the most convenient synthetic route because of its high stereospecificity and of its good chemical yields, and it offers the possibility of preparing optically active sulfoxides, sulfinates, and sulfinamides from the same starting chiral compound[13,14] (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-4-bromobenzenesulfinate **1**, directly obtained from 4-bromobenzenesulfonyl chloride (Scheme 1) according to the Sharpless's procedure.[15] The *S* configuration of the sulfur atom of this pure crystalline diastereomer was deduced from its X-ray crystal structure, which will be reported in a separate paper.[16] Optically active sulfoxide and sulfinamides **3**, **2c**, and **2d** were prepared from **1** and nucleophilic reagents $H_{17}C_8MgBr$, $H_{17}C_8N(CH_3)MgBr$, and $H_{25}C_{12}N(CH_3)$-MgBr, respectively (Scheme 1). To enhance the chemical yields of these nucleophilic substitutions, it was necessary to use at least 2.5 mol equiv of nucleophilic reagent, because only moderate yields were obtained when 1 mol equiv was used. To avoid racemization at sulfur under the conditions reported above, it was necessary to work at low temperature (for example, sulfoxide **3** is obtained optically pure by setting the temperature at − 76 °C). In the case of sulfinamides **2c** and **2d**, even on increasing the reaction temperature to room temperature, only moderate yields were obtained (48% and 55% for **2c** and **2d**, respectively).

Optically active sulfinates with a long alkyl chain at the sulfur atom **4a–e** (n = 4, 6, 8, 10, 12) were prepared from (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-4-bromobenzenesulfinate **1** via an alcoholysis reaction of sulfinamide **2a** or **2b** by primary alcohols $H_{2n+1}C_nOH$ (n = 4, 6, 8, 10, 12) using trifluoroacetic acid[17] or boron trifluoride etherate [18] as catalysts (Scheme 1). However, it was found that the alcoholysis reaction of the sulfinamide **2a** or **2b** was much faster than that reported for the *p*-tolyl derivative,[17–19] and it was also found that the stereoselectivity was strongly dependent upon the reaction rate. Low rates, obtained by decreasing the temperature to less than −30 °C, were found to give the highest enantiomeric excesses.[16]

Terminal ethynyl compounds **8a–d**, **9**, and **13** were prepared by the coupling reaction of aryl bromides **6**, **9′**, and **12** with (trimethylsilyl)acetylene (TMSA) using a palladium catalyst,[20,21] followed by desilylation of the ethynyl group with tetrabutylammonium fluoride in aqueous tetrahydrofuran (Schemes 2 and 4).[22]

To complete the synthesis of the tolane mesogens, a coupling reaction of chiral aryl bromide and terminal ethynyl compounds **8a–d** using a palladium catalyst was used (Scheme 5). However, under the classical conditions previously published[20,21] for most catalytic reactions using a palladium catalyst and copper (I or II) as cocatalyst, the yield of the desired tolane was very poor (<10%) and the predominant compound was the diyne **D** (Table 12). To increase the yield of the catalytic coupling, the cases of the (*S*)-(−)-octyl 4-bromobenzenesulfinate **4c** (n = 8) and of the terminal ethynyl compound **8b** (m = 12) were studied under different

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Table 8. Characterization of Sulfinates *m*-BTS-O*n*

m-BTS-O*n* *m*−*n*	^{1}H NMR (200 MHz, $CDCl_3$) (δ, ppm)	anal. found (calcd)
10−4	8.15 {d; J^3 = 8.90 Hz; 2H, H−(ArCOO)}, 7.70 {s, 4H, H−(ArSOO)}, 7.61 {d; J^3 = 8.70 Hz; 2H, H−(ArOCO)}, 7.24 {d; J^3 = 8.70 Hz; 2H, H−(ArOCO)}, 6.98 {d; J^3 = 8.90 Hz; 2H, H−(ArCOO)}, 4.05 {mc; 3H; (2H, CH_2−O and 1H, SOO−CH_2−}, 3.62 {dt (ABX_2), J^2 = 9.62, J^3 = 6.42 Hz; 1H, −SOO−CH_2−}, 1.83 {mc; 2H, CH_2−CH_2−O−Ph}, 1.65 {mc; 2H, −SOO−CH_2−CH_2−}, 1.30−1.60 {m; 16H, aliphatic (CH_2)}, 0.90 {t; J^3 = 6.5 Hz; 6H, CH_3−CH_2−}	%C 73.18 (73.14) %H 7.40 (7.37) %O 13.88 (13.92) %S 5.66 (5.58)
10−6	1.30−1.60 {m; 20H, aliphatic (CH_2)}	%C 73.68 (73.71) %H 7.79 (7.69) %O 13.22 (13.27) %S 5.36 (5.32)
10−8	1.30−1.60 {m; 24H, aliphatic (CH_2)}	%C 74.28 (74.24) %H 8.00 (7.92) %O 12.59 (12.68) %S 5.14 (5.08)
10−10	1.30−1.60 {m; 28H, aliphatic (CH_2)}	%C 74.50 (74.72) %H 8.39 (8.26) %O 11.98 (12.14) %S 4.63 (4.86)
10−12	1.30−1.60 {m; 32H, aliphatic (CH_2)}	%C 75.15 (75.17) %H 8.57 (8.51) %O 11.60 (11.64) %S 4.57 (4.67)
12−4	1.30−1.60 {m; 20H, aliphatic(CH_2)}	%C 73.77 (73.71) %H 7.83 (7.69) %O 13.24 (13.27) %S 5.16 (5.32)
12−6	1.30−1.60 {m; 24H, aliphatic (CH_2)}	%C 74.28 (74.24) %H 8.07 (7.99) %O 12.59 (12.68) %S 5.01 (5.08)
12−8	1.30−1.60 {m; 28H, aliphatic (CH_2)}	%C 74.74 (74.72) %H 8.34 (8.26) %O 12.14 (12.14) %S 4.83 (4.86)
12−10	1.30−1.60 {m; 32H, aliphatic (CH_2)}	%C 75.22 (75.17) %H 8.60 (8.51) %O 11.55 (11.64) %S 4.51 (4.67)
12−12	1.30−1.60 {m; 36H, aliphatic (CH_2)}	%C 75.38 (75.58) %H 8.78 (8.74) %O 11.19 (11.19) %S 4.44 (4.48)
16−4	1.30−1.60 {m; 28H, aliphatic (CH_2)}	%C 74.76 (74.72) %H 8.31 (8.26) %O 12.09 (12.14) %S 4.82 (4.86)
16−6	1.30−1.60 {m; 32H, aliphatic (CH_2)}	%C 75.21 (75.17) %H 8.55 (8.51) %O 11.60 (11.64) %S 4.55 (4.67)
16−8	1.30−1.60 {m; 36H, aliphatic (CH_2)}	%C 75.72 (75.58) %H 8.82 (8.74) %O 11.22 (11.19) %S 4.42 (4.48)
16−10	1.30−1.60 {m; 40H, aliphatic (CH_2)}	%C 76.19 (75.96) %H 9.00 (8.95) %O 10.68 (10.76) %S 4.24 (4.31)
16−12	1.30−1.60 {m; 44H, aliphatic (CH_2)}	%C 76.37 (76.31) %H 9.21 (9.15) %O 10.29 (10.37) %S 4.08 (4.16)
18−4	1.30−1.60 {m; 32H, aliphatic (CH_2)}	%C 75.11 (75.17) %H 8.57 (8.51) %O 11.65 (11.64) %S 4.52 (4.67)
18−6	1.30−1.60 {m; 36H, aliphatic (CH_2)}	%C 75.69 (75.58) %H 8.84 (8.74) %O 11.09 (11.19) %S 4.48 (4.48)
18−8	1.30−1.60 {m; 40H, aliphatic (CH_2)}	%C 76.19 (75.96) %H 9.07 (8.95) %O 10.80 (10.76) %S 4.28 (4.31)
18−10	1.30−1.60 {m; 44H, aliphatic (CH_2)}	%C 76.37 (76.31) %H 9.18 (9.15) %O 10.40 (10.37) %S 4.09 (4.16)
18−12	1.30−1.60 {m; 48H, aliphatic (CH_2)}	%C 76.60 (76.64) %H 9.41 (9.33) %O 10.06 (10.01) %S 3.98 (4.01)

Table 9. Optical Activity and Enantiomeric Excess of Sulfinates *m*-BTS-On (*, Deduced from Sulfinates 4a–e)

m-BTS-O*n* *m*–*n*	$[\alpha]_D^{23}$	*c*; CH_2Cl_2	ee (%)
10–4	−42°	1.31	75*
10–6	−58°	1.53	89
10–8	−56°	1.42	88*
10–10	−54°	1.39	85
10–12	−44°	1.24	80
12–4	−39°	1.08	75*
12–6	−59°	1.48	90
12–8	−55°	1.22	86
12–8	+69°	1.77	99
12–10	−55°	1.99	86
12–12	−46°	1.35	80
16–4	−38°	1.14	75*
16–6	−56°	2.32	88*
16–8	−53°	1.79	89
16–10	−54°	1.56	86
16–12	−42°	2.07	81*
18–4	−37°	1.28	75*
18–6	−52°	1.33	89
18–8	−49°	0.96	88*
18–10	−50°	3.48	85
18–12	−38°	2.18	81*

conditions (Table 12). The results obtained showed a large variation of the yield and of the reaction rate upon changing the temperature and the molar ratio of palladium(II) to copper(II) in the catalytic mixture. When this ratio was less than 1, the desired tolane could not be isolated, and the reaction solely gave a good yield of the diyne derivative. In the extremely case when no Cu(II) catalyst was used, the reaction gave yields of 26% tolane and 5% diyne. However, when a Pd(II)/Cu(II) ratio between 10/1 and 4/1 was used, tolane was obtained with good yield (88–92%), and only a small amount of the diyne was observed. The other tolanes (sulfoxides and sulfinamides in Scheme 5) were isolated in lower yields (48–68%) than those obtained for the sulfinates. This may have been due either to their partial thermal degradation (it was necessary to hold the reaction at 80 °C because the sulfoxides and the sulfinamides were not isolated at 50 °C) or to the relative contamination of the palladium catalyst by the sulfur atom of the sulfinyl group which may inhibit the catalytic process.

It must be noticed that under the conditions used for the coupling reaction, the enantiomeric excesses of the starting bromoaryl sulfinyl compounds were proved to be almost totally conserved. The determination of the enantiomeric excess (ee) of most of the chiral sulfinyl compounds described above was performed by ^1H NMR using 20–30% of tris[3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III) [Eu(hfc)$_3$, Aldrich, 98%] as chiral shift reagent. The best resolved signals were observed for the ortho aromatic protons of the phenylsulfinyl group. To enhance the resolution, they were decoupled with the meta ones. The induced shift as determined from this resolution (see, for example, Figure 1 in the case of the chiral sulfinate **4c**, *n* = 8) allowed us a very accurate measurement.

Mesomorphism and Thermal Behavior. Phase identification was carried out by means of optical microscopy, the corresponding optical textures being easily identifiable for each mesophase. The crystal-to-mesophase transition temperatures were determined by means of DSC (heating runs).

Influence of the nature of the rigid core: To incorporate the chiral center in the rigid core and on the basis

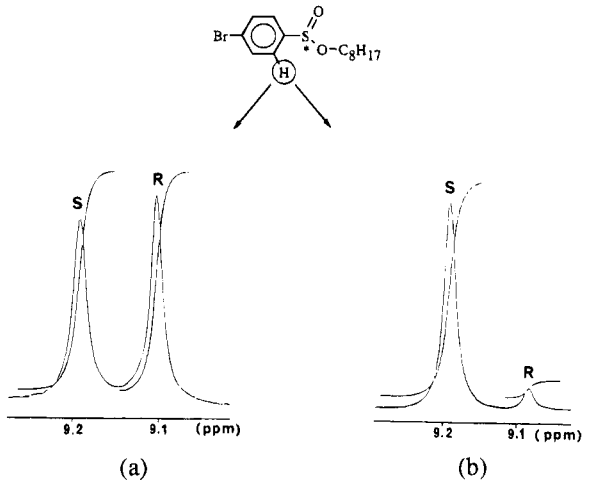
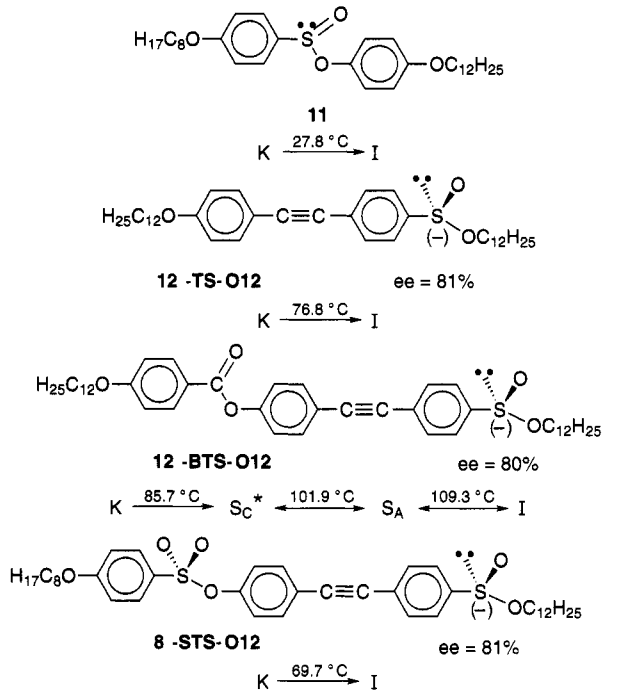


Figure 1. Proton NMR spectrum of the sulfinate **4c** in a $CDCl_3$ solution with Eu(hfc)$_3$. Signals of the ortho aromatic protons of the phenylsulfinyl group are decoupled with those of the meta ones: (a) in the case of the racemic compound; (b) in the case of the optically active one.

Scheme 6



of the results already reported for the phenyl carboxylate smectogens,[23] the homologous phenyl benzenesulfinate **11** was preapred. However, no mesophase was detected, and the compound melts directly from the crystal to the isotropic liquid at 27.8 °C (Scheme 6).

This may be due to the pyramidal structure of the sulfinyl group which causes the loss of the global linearity of the rigid core. To overcome this problem, the sulfinyl group was moved from the center to one peripheral position of the rigid core which was then restricted to a diphenylethyne moiety. However, the resulting **12-TS-O12** compound again did not present any mesophase (Scheme 6). Since the core length of the liquid-crystalline molecules has a strong influence on the thermal stability of the mesophase, the **12-TS-O12** core length was thought to be short, and we decided to

(23) Demus, D.; Zaschke, H. *Flüssige Kristalle in Tabellen*; VEB Deutscher Verlag für Grundstoffindustrie: Leipzig, 1974.

Table 10. Characterization of the Mesogenic Sulfoxide 12-BTS-8, of Mesogenic Sulfinamides 12-BTS-NP, *m*-BTS-N(Me)*n*, and of Nonmesogenic Sulfinates

compound	^{1}H NMR (200 MHz, $CDCl_3$) (δ, ppm)	anal. found (calcd)
12-BTS-8	8.10 {d; J = 8.75 Hz; 2H, H−(ArCOO)}, 7.71−7.58 {m; 6H, (4H−(ArSO) and 2H−(ArOCO)}, 7.26 {d; J^3 = 8.60 Hz; 2H, H−(ArOCO)}, 6.98 {d; J^3 = 8.75 Hz; 2H, H−(ArCOO)}, 4.05 {t; J^3 6.5 Hz, 2H; CH_2−O}, 2.80 {t, J^3 7.7 Hz; 2H, −CH_2−SO}, 1.83 {mc; 2H, CH_2−CH_2−O−Ph}, 1.65 {mc; 2H, −CH_2−CH_2−SO−}, 1.20−1.57 {m; 28H, aliphatic (CH_2)}, 0.88 {t; J^3 = 6.5 Hz; 6H, CH_3−CH_2−}	%C 76.42 (76.59) %H 10.06 (9.96) %O 9.54 (9.96) %S 4.82 (4.98)
12-BTS-NP	8.20 {d; J^3 = 8.75 Hz; 2H, H−(ArCOO)}, 7.66 {4H, H−(ArSO)}, 7.60 {d; J^3 = 8.65 Hz; 2H, H−(ArOCO)}, 7.28 {d; J^3 = 8.65 Hz; 2H, H−(ArOCO)}, 7.00 {d; J^3 = 8.75 Hz; 2H, H−(ArCOO)}, 4.10 {t; J^3 = 6.5 Hz, 2H; CH_2−O}, 3.42 {m; 2H, −CH_2−N}, 3.05 {m; 2H, CH_2−N}, 1.90 {mc; 6H, (2H; CH_2−CH_2−O−Ph; and 4H; CH_2−CH_2−N)}, 1.20−1.60 {m; 18H, aliphatic (CH_2)}, 0.90 {t; J^3 = 6.5 Hz; 3H, CH_3−CH_2−}	%C 74.25 (74.09) %H 7.63 (7.57) %N 2.29 (2.34) %S 5.19 (5.32)
12-BTS-NMe-8	8.20 {d; J^3 = 8.70 Hz; 2H, H−(ArCOO)}, 7.70 {4H, H−(ArSO)}, 7.60 {d; J^3 = 8.60 Hz; 2H, H−(ArOCO)}, 7.28 {d; J^3 = 8.60 Hz; 2H, H−(ArOCO)}, 6.96 {d; J^3 = 8.70 Hz; 2H, H−(ArCOO)}, 4.05 {t; J^3 = 6.5 Hz, 2H; CH_2−O} 3.12 {mc; 2H, −CH_2−N}, 2.58 {s; 3H, N−CH_3}, 1.85 {mc; 2H, CH_2−CH_2−O−Ph}, 1.60 {m; 2H, −CH_2−CH_2−N}, 1.15−1.55 {m; 28H, aliphatic (CH_2)}, 0.90 {t; J^3 = 6.5 Hz; 6H, CH_3−CH_2−}	%C 74.92 (75.07) %H 8.63 (8.56) %N 1.86 (2.09) %S 4.53 (4.76)
16-BTS-NMe-8	1.15−1.55 {m; 28H, aliphatic (CH_2)}	%C 75.64 (75.88) %H 9.20 (9.01) %N 1.58 (1.92) %S 4.14 (4.40)
16-BTS-NMe-12	1.15−1.55 {m; 44H, aliphatic (CH_2)}	%C 76.44 (76.58) %H 9.43 (9.39) %N 1.67 (1.79) %S 3.92 (4.08)
12-BTS-OMen	8.15 {d; J^3 = 8.70 Hz; 2H, H−(ArCOO)}, 7.68 {4H, H−(ArSOO)}, 7.60 {d; J^3 = 8.65 Hz; 2H, H−(ArOCO)}, 7.25 {d; J^3 = 8.65 Hz; 2H, H−(ArOCO)}, 6.95 (d; J^3 = 8.70 Hz; 2H, H−(ArCOO)}, 4.15 {td; J^3 = 10 Hz, J^4 = 4.5 Hz; 1H, CH−O−(Men)}, 4.05 {t; J^3 = 6.5 Hz, 2H; CH_2−O}, 2.28 {mc; 1H, H−Men}, 2.15 {mc; 1H, H−Men}, 1.86 {mc; 2H, CH_2−CH_2−O−Ph}, 1.75 {mc; 2H, H−Men}, 1.2−1.6 {m; 23H, (CH_2)aliph and H−Men}, 1.05 {d; J^3 = 6.42 Hz; 3H, CH_3 (i-Pr)}, 0.90 {m; 6H, CH_3−CH_2− and CH_3(i-Pr)}, 0.75 {d; J^3 = 6.9 Hz; 3H, CH_3−Men)}	%C 75.55 (75.40) %H 8.32 (8.25) %O 11.76 (11.69) %S 4.58 (4.67)
12-TS-O12	8.05 (d; J^3 = 8.7 Hz; 2H, H−(Ar)}, 7.72 {s, 4H, H−(ArSOO)}, 7.55 {d; J^3 = 8.7 Hz; 2H, H−(Ar)}, 4.35 {t; J^3 = 6.6 Hz, 2H, CH_2−O}, 4.06 {dt (ABX_2), J^3 = 9.6, J^3 = 6.45 Hz; 1H, −SOO−CH_2−}, 3.65 {dt (ABX_2), J^2 = 9.6, J^3 = 6.45 Hz; 1H, −SOO−CH_2−}, 1.80 {mc; 2H, CH_2−CH_2−O−Ph}, 1.65 {mc; 2H, −SOO−CH_2−CH_2−}, 1.30−1.55 {m; 36H, (CH_2) aliph}, 0.90 {t; J^3 = 6.5 Hz; 6H, CH_3−CH_2−}	%C 76.67 (76.71) %H 9.76 (9.83) %O 8.16 (8.07) %S 5.32 (5.38)
8-STS-O12	7.75 {d; J^3 = 8.90 Hz; 2H, H−($ArSO_3$−)}, 7.67 {4H, H−(ArSOO)}, 746 {d; J^3 = 8.70 Hz; 2H, H−($ArOSO_2$)}, 7.02 {d; J^3 = 8.70 Hz; 2H, H−($ArOSO_2$)}, 6.95 {d; J^3 = 8.90 Hz; 2H, H−($ArSO_3$−)}, 4.05 {mc; 3H; (2H, CH_2−O and 1H, SOO−CH_2−}, 3.63 {dt (ABX_2), J^2 = 9.6 Hz, J^3 = 6.4 Hz; 1H, −SOO−CH_2−}, 1.84 {mc; 2H, CH_2−CH_2−O−Ph}, 1.64 {mc; 2H, −SOO−CH_2−CH_2−}, 1.20−1.55 {m; 28H, (CH_2) aliph}, 0.90 {t; J^3 = 6.5 Hz; 6H, CH_3−CH_2}	%C 69.22 (69.13) %H 7.95 (7.83) %O 14.17 (13.82) %S 9.59 (9.59)

Table 11. Characterization of the Optical Purity of Mesogenic Sulfoxides *m*-BTS-8, of Mesogenic Sulfinamides 12-BTS-NP and *m*-BTS-N(Me)*n*, and of Nonmesogenic Sulfinates (*, Deduced from Sulfinamides 2b−d and Sulfoxide 3)

compound	$[\alpha]_D^{22}$	c; CH_2Cl_2	ee (%)(*)
12-BTS-8	+70°	2.35	100
16-BTS-8	+68°	1.24	100
12-BTS-NP	+75°	0.76	93
12-BTS-N(Me)-8	+9.3°	0.86	
16-BTS-N(Me)-8	+12.4°	0.92	
16-BTS-N(Me)-12	+17.3°	0.58	
12-BTS-OMen			100
12-TS-O12			81*
8-STS-O12			81*

increase it by adding a (phenylcarbonyl)oxy group. The resulting **12-BTS-O12** compound did exhibit the desired S_C* phase over a large temperature domain (Scheme 6). The mesogenic character is due not only to the increase of the core length from two to three aromatic rings but also to the polar effect and to the planar structure of the linking carbonyloxy group −COO−. This is demonstrated by the fact that if the carbonyloxy group is replaced by a pyramidal sulfonyloxy group (such as **8-STS-O12**, for example; Scheme 6), the mesomorphic character is lost.

To dampen the molecular rotation in the S_C* phase, which is generally believed to decrease the value of the spontaneous polarization of ferroelectric mesogens bearing two alkyl chains, two compounds were synthesized (**12-BTS-OMen** and **12-BTS-NP**) bearing the menthyl and pyrrolidinyl group respectively as bulky substituents directly connected to the chiral center. For the menthylsulfinate **12-BTS-OMen**, no mesophase was observed (Scheme 7). But for the sulfinylpyrrolidine derivative **12-BTS-NP**, although no S_C* phase was observed, a very interesting mesomorphic sequence occurred. Indeed, a blue phase was detected between the isotropic liquid and the cholesteric phase within a relatively large stability domain (>2 °C, Scheme 7).

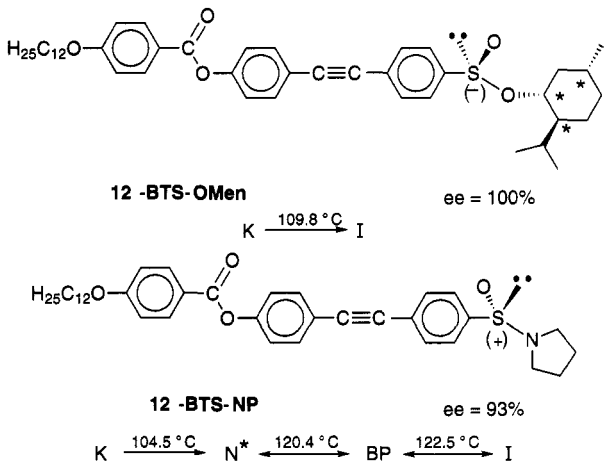
Role of the alkyl chain length: From the above examples, it is clear that, keeping the same aromatic core, the presence of two alkyl chains is necessary for the obtention of smectic phases. It was then interesting to study the influence of the number of carbon atoms in the alkyl chains upon the thermal stability of the S_C* phase for the ***m*-BTS-On** series. For that aim, a series of 20 ***m*-BTS-On** sulfinate derivatives were synthesized and analyzed systematically. They were not obtained with the same enantiomeric excess (Table 9); only the members with the same chiral center (the same alkyl chain on the sulfinyl group) had approximately the same enantiomeric excess. Thus, to avoid a possible effect of the enantiomeric excess, only the mesomorphic properties as a function of the number m of carbon atoms in the alkyl chain (in para position relatively to the carbonyloxy group) were compared quantitatively. The 20 ***m*-BTS-On** sulfinates were classified in the following five families: ***m*-BTS-O4**, ***m*-BTS-O6**, ***m*-BTS-O8**, ***m*-**

Table 12. Catalytic Coupling Reaction of Sulfinate 4c with Terminal Acetylenic Compound 8b by Varying the Pd/Cu Ratio in the Catalytic Mixture

$$\underset{\textbf{4c}}{Ar_1{-}Br} + \underset{\textbf{8b}}{Ar_2{-}C{\equiv}C{-}H} \xrightarrow[Et_3N/toluene]{(PPh_3)_2PdCl_2/Cu(OAc)_2} \underset{\textbf{12-BTS-08}}{Ar_1{-}C{\equiv}C{-}Ar_2} + \underset{\textbf{D}}{Ar_2{-}C{\equiv}C{-}C{\equiv}C{-}Ar_2}$$

n_{4c} (mol)	n_{8b} (mol)	n_{PPh_3} (mol)	$n_{Pd^{II}}$ (mol)	$n_{Cu^{II}}$ (mol)	T (°C)	yield of **12-BTS-O8**	yield of **D**	reaction duration
1	1.2	0.1	0.01	0.01	60	<10	50%	7 h
1	1.2	0.1	0.01	0.00	60	26	<5%	12 h
1	1.2	0.1	0.02	0.01	60	60	20%	4 h
1	1.2	0.1	0.02	0.005	80	92	<1%	45 min
1	1.2	0.1	0.04	0.005	50	90	<1%	2 h 30 min
1	1.2	0.1	0.01	0.02	80	0	75%	3 h
1	1.2	0.1	0.05	0.005	50	88	<1%	2 h

Scheme 7



BTS-O10, and ***m*-BTS-O12**. Their respective transition temperatures and enthalpies are shown in Table 13, and the transition temperatures reported as a function of peripheral alkyl chain length are shown in Figures 2–6.

The general thermotropic sequence observed for the compounds ***m*-BTS-On** is crystal (K), smectic C* (S_C*), smectic A (S_A), isotropic liquid (I). Mesophases were identified by comparison with textures reported in the literature[24] (focal-conic fan texture for S_A phases, and striated focal-conic fan texture for S_C* phases) and by X-ray diffraction experiments.

For the ***m*-BTS-O4** homologous series, with four carbon atoms on the sulfinyl group, only a S_A phase is observed for which the largest stability domain is obtained when $m = 12$ (Figure 2). However, with six carbon atoms in the sulfinyl chain, a S_C* phase occurs besides the S_A phase; it is monotropic for $m = 10$ and enantiotropic for the other members of the ***m*-BTS-O6** homologous series (Figure 3). The stability domain of the S_C* phase is the largest when $m = 12$ and decreases significantly in size by increasing the value of m. It has to be noticed that the highest thermal stability of the S_A mesophase is obtained from m = 10. In the case of the ***m*-BTS-O8** homologous series, all the members exhibit both stable S_C* and S_A phases (Figure 4). As for the ***m*-BTS-O6** series, the highest thermal stability of S_C* and S_A phases is still obtained for m = 12 and m = 10, respectively. This behavior is also observed for the two ***m*-BTS-O10** and ***m*-BTS-O12** series (Figures 5 and 6). However, increasing the value of m in these series causes a large reduction of the S_A stability domain while the S_C* stability domain is not greatly affected.

From the general observation of these phase diagrams (Figures 2–6), it is interesting to note that with a short alkyl chain on the sulfinyl group ($n = 4, 6$) the S_A phase is well stabilized. Increasing the *p*-carbonyloxy chain leads to a large reduction of the S_C* stability domain (case $n = 6$), while the S_A stability domain is not significantly affected. On the contrary, when n is equal to 10 or 12, the S_A stability domain decreases with increasing the *p*-carbonyloxy chain length, and the S_C* phase presents a good stability for all the members of the two series. The intermediate case is illustrated by the ***m*-BTS-O8** series.

Similar effects were deduced from X-ray measurements. The lamellar spacing in the S_C* phase for the ***m*-BTS-O6** homologous series (Figure 7) varies as a function of temperature from 34.9 to 38.3 Å for $m = 12$, while with increasing m, the amplitude of this variation is smaller (from 43.2 to 44.9 Å for $m = 16$ and from 47.1 to 48.8 Å for $m = 18$). The corresponding tilt angles Θ (Figure 8, calculated with the relation $\cos\Theta = d_{SC}{}^*/d_{S_A}$[25]) are smaller for $m = 16, 18$ than that for $m = 12$. This unusual effect showing the tendency for the tilt angle to be smaller as a function of increasing the chain length, can be correlated to the thermal stability domain of the S_C* phase which is larger for $m = 12$ than that for the higher terms of the series (Figure 3). On the contrary, for the ***m*-BTS-O10** and ***m*-BTS-O12** homologous series, where the S_A stability domain decreases with increasing the alkyl chain length m, the amplitude of variation of the lamellar spacing d from S_A to S_C* upon temperature is more important (Figures 9 and 10). This corresponds to a strong increase of the tilt angle for $m > 10$ (Figures 11 and 12). For the intermediate case of the ***m*-BTS-O8** series where the S_A phase exhibits the same stability as in the case of the ***12*-BTS-O8** and ***16*-BTS-O8** members (Figure 4), the corresponding tilt angles are equal at the same $T - T_{ac}$ (T_{ac} = S_C*–S_A transition temperature; Figure 13). Within this series, it is interesting to note that the highest stability domain of the S_A phase for ***10*-BTS-O8** corresponds to the smallest tilt angle far from the S_C*–S_A transition.

Thus, the above study suggests that the tilt angle of the ***m*-BTS-On** molecules within the S_C* layers is directly driven by the nature of the corresponding thermotropic sequence. In fact, as a function of increasing m, the tilt angles increase when the S_A thermal domain becomes smaller, besides a good stability of the S_C* domain.

The above variation of the stability of the S_A and S_C* phases observed inside the ***m*-BTS-On** sulfinate series

(24) Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals; Textures and Structures*; Leonard Hill; Heyden & Son: Philadelphia, 1984.

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

Table 13. Transition Temperatures (°C) and Transition Enthalpies (kJ mol^{-1}) of the *m*-BTS-O*n* Sulfinates

m-BTS-O*n* *m*−*n*	*T*(*K*−S_C*) (°C)	Δ*H*(K−S_C*) (kJ mol^{-1})	*T*(S_A−S_C*) (°C)	*T*(S_A−I) (°C)	Δ*H*(S_A−I) (kJ mol^{-1})
10−4	89.23 (K−S_A)	40.09		118.35	4.33
12−4	80.75 (K−S_A)	41.72		118.6	4.34
16−4	94.83 (K−S_A)	50.75		121.55	4.56
18−4	98.47 (K−S_A)	56.03		116.4	4.62
10−6	88.4	40.03	87.1 (monotropic)	117.9	3.27
12−6	86.86	43.87	98.9	116.5	4.88
16−6	94.72	58.65	100.7	114.6	5.67
18−6	93.64	65.94	95.4	113.5	5.47
10−8	77.90	42.57	88.9	114.9	4.54
12−8	81.51	45.06	100.6	113.1	5.11
16−8	88.99	50.31	102.7	113.8	3.58
18−8	87.35	52.83	101.75	115.2	3.37
10−10	81.40	40.90	93.5	111.9	4.47
12−10	84.04	46.93	102.25	112.9	5.50
16−10	92.32	59.83	106.5	111	6.18
18−10	95.70	66.65	106.4	108.1	7.20
10−12	81.84	44.30	91	111.25	5.51
12−12	85.70	48.74	102.95	108.5	5.66
16−12	93.42	59.13	107.7	108.2	7.43
18−12	93.43	64.53		107(S_c*−I)	7.00

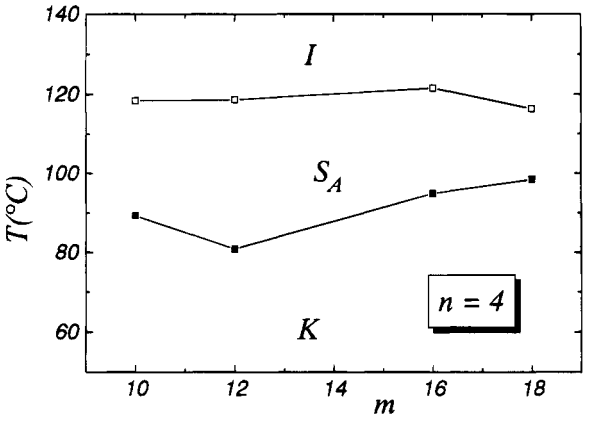


Figure 2. Transition temperatures as a function of *m* for the ***m*-BTS-O4** series.

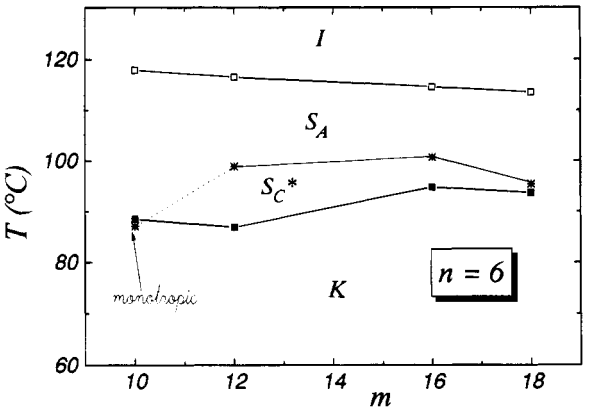


Figure 3. Transition temperatures as a function of *m* for the ***m*-BTS-O6** series.

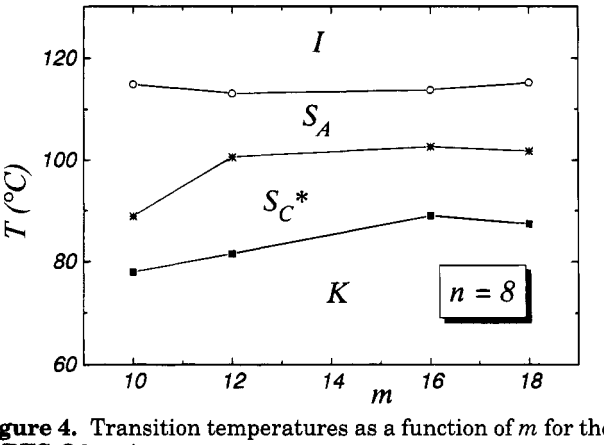


Figure 4. Transition temperatures as a function of *m* for the ***m*-BTS-O8** series.

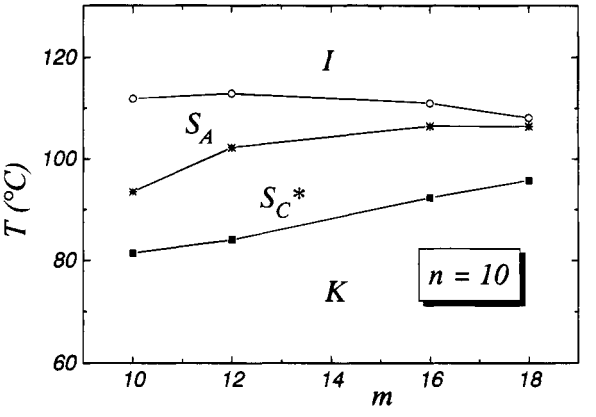


Figure 5. Transition temperatures as a function of *m* for the ***m*-BTS-O10** series.

may also be due to a conjugated effect between the two alkyl chains and their respective conformations. In fact, the values of transition enthalpies for the ***m*-BTS-O*n*** sulfinate homologs given in Table 13 are different for two compounds having globally the same number of carbon atoms. For example, the ***16*-BTS-O6** and ***12*-BTS-O10** compounds, both having 22 carbon atoms in their alkyl chains, exhibit crystal-to-mesophase transition enthalpies of 58.6 and 46.9 kJ mol^{-1}, respectively. This may indicate that the crystal-to-mesophase transition enthalpies, corresponding to the melting of the two alkyl chains, are not additive and suggest distinct effects from the two alkyl chains at the transition. We cannot exclude also the possibility of different crystalline structures with different energies, according to the homologue considered. However, we are not able to demonstrate these effects at a molecular scale since we don't know at this time the crystalline structure of the ***m*-BTS-O*n*** mesogens.

Effect of the nature of the sulfinyl group: As mentioned above, this work was also focused on the effect of the nature of the sulfinyl group, the unique source of chirality of the synthesized mesogens. Thus, with preserving the same molecular architecture as for the ***m*-BTS-O*n*** smectogen sulfinates, a number of sulfoxides and sulfinamides were synthesized, having two

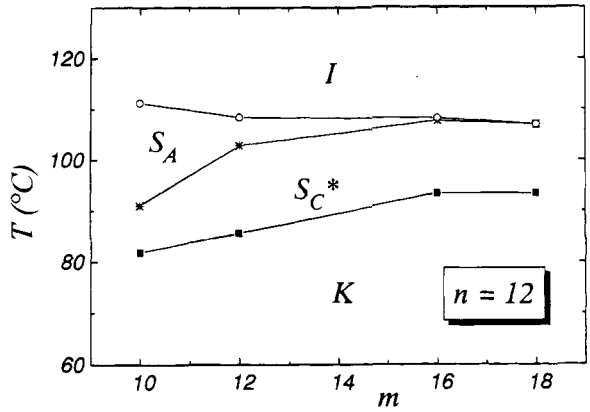


Figure 6. Transition temperatures as a function of m for the ***m*-BTS-O12** series.

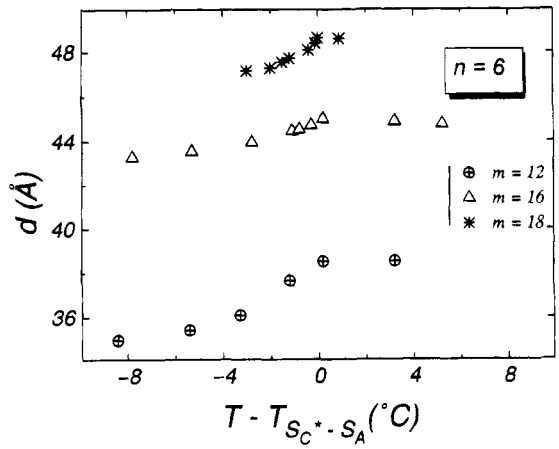


Figure 7. Smectic A layer spacing as a function of temperature for the members of the ***m*-BTS-O6** series.

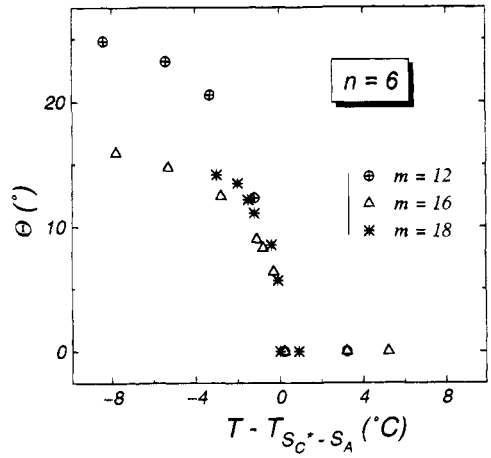


Figure 8. Temperature dependence of the tilt angle of the molecules in the S_C* phase for the members of the ***m*-BTS-O6** series.

peripheral alkyl chains linked to a (benzenecarbonyl)-oxy tolane rigid core.

The two synthesized sulfoxides (***m*-BTS-8**; m = 12, 16) exhibit the S_C* phase (Scheme 8). However, in comparison with the ***m*-BTS-On** sulfinates, the thermal stability domain of the S_C* phase is smaller, the K–S_C* transition temperature being higher than 120 °C and the two compounds undergoing degradation (in isotropic state for m = 12 and in the S_C* phase for m = 16).

Spectacular effects on the thermotropic sequence are observed when the sulfoxide group is changed with *N*-methyl sulfinamide. For the **12-BTS-N(Me)-8** sulfinamide, the crystal-to-mesophase transition temperature decreases strongly, the S_C* phase is not observed, and a S_B phase is detected and well characterized between the crytalline and the S_A phase (Scheme 9). Extending the *p*-carbonyloxy alkyl chain from 12 to 16 carbon atoms does not induce any S_C* phase and the same thermotropic sequence is obtained. However, the increase of the sulfinyl alkyl chain length from 8 to 12 carbon atoms leads finally to the occurrence of the S_C* phase (Scheme 9 and Table 14).

If the large diminution of the crystalline-to-mesophase transition temperature obtained when going from the

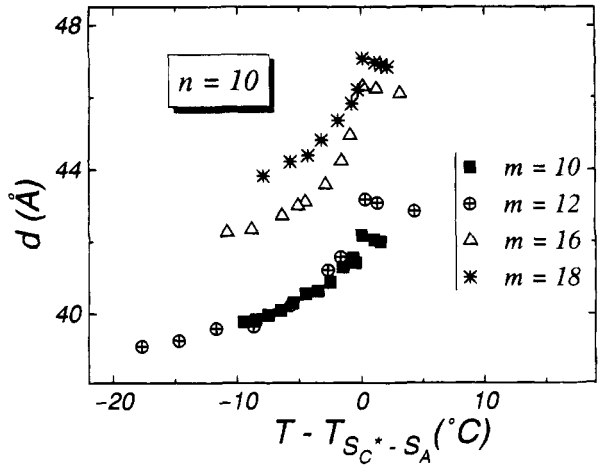


Figure 9. Smectic A layer spacing as a function of temperature for the members of the ***m*-BTS-O10** series.

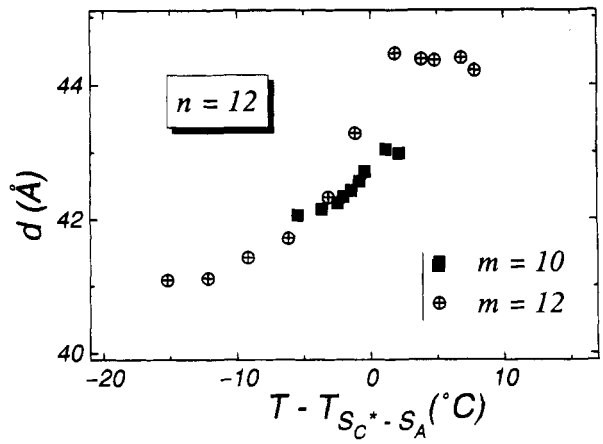


Figure 10. Smectic A layer spacing as a function of temperature for the members of the ***m*-BTS-O12** series.

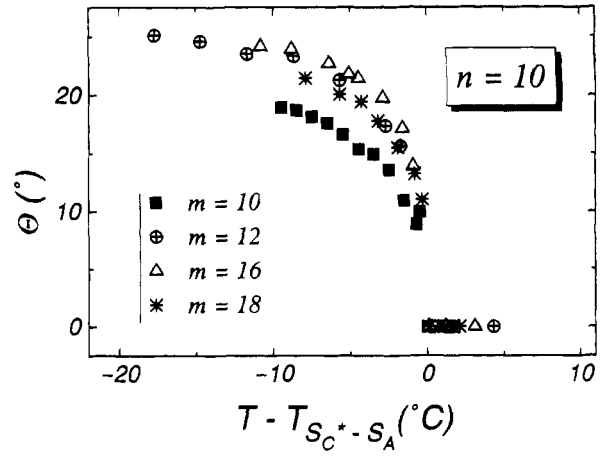


Figure 11. Temperature dependence of the tilt angle of the molecules in the S_C* phase for the members of the ***m*-BTS-O10** series.

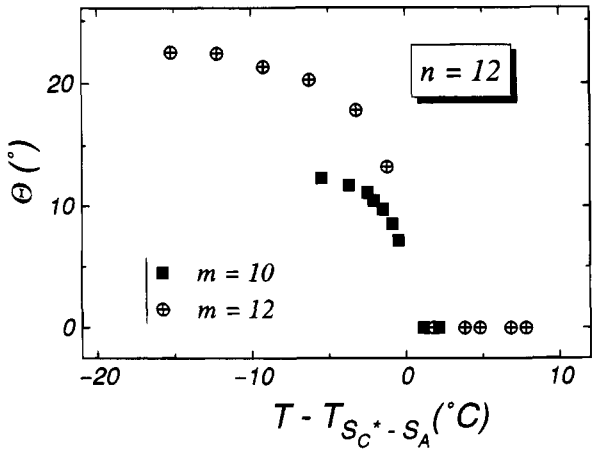


Figure 12. Temperature dependence of the tilt angle of the molecules in the S_C^* phase for the members of the ***m*-BTS-O12** series.

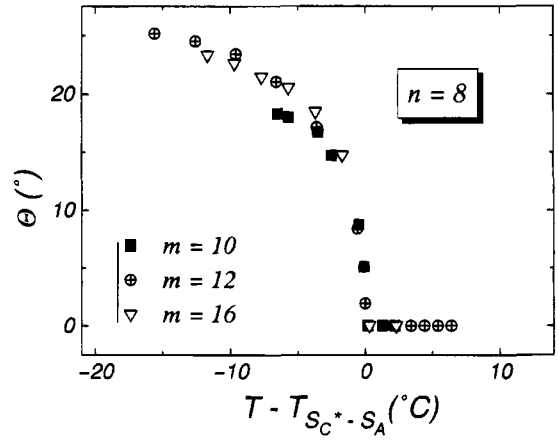


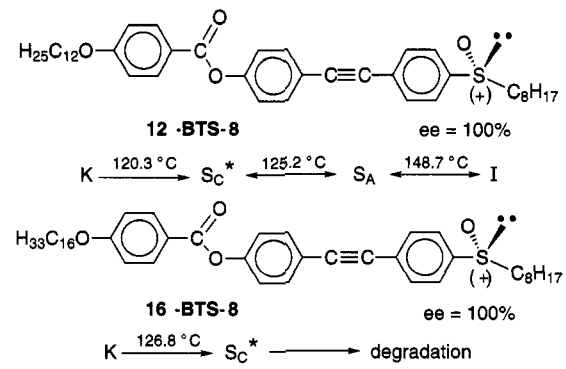
Figure 13. Temperature dependence of the tilt angle of the molecules in the S_C^* phase for the members of the ***m*-BTS-O8** series.

sulfoxide to the sulfinamide mesogens can be understood, since sulfinamides have generally lower melting points than sulfoxides, the occurrence of the S_B phase inside the sulfinamide series remains still unexpected. Indeed, due to the lateral steric effects, a lateral group (as the methyl group connected to the sulfinyl's nitrogen atom) should generally stabilize the tilted phases preferentially to the orthogonal ones. Further studies are required to clarify this phenomenon.

Conclusion

In this paper, we have demonstrated the possibility of obtaining ferroelectric smectic C* phases with molecules containing a sulfinyl group as unique chiral center. No degradation or racemization was detected with the chiral ***m*-BTS-On** sulfinate mesogens, even when these compounds were heated for a few hours in the isotropic phase. Thanks to such a good stability, the sulfinate compounds have been then investigated for their electrooptical properties. Large spontaneous polarization (up to 300 nC/cm^2) and short response times (down to a few microseconds) were measured; the results of these electrooptical studies will be published in a forthcoming paper.

Scheme 8



Scheme 9

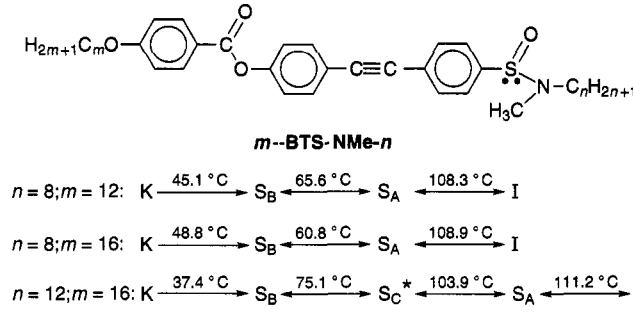


Table 14. Transition Enthalpies (kJ mol^{-1}) of the 12-BTS-8 Sulfoxide and of the *m*-BTS-N(Me)*n* Sulfinamide Compounds

	ΔH (kJ mol^{-1})			
compound	K–S_C^* (K–S_B)	S_B–S_A (S_B–S_C^*)	S_C^*–S_A	S_A–I
12-BTS-8	35.03		0.058	6.40
12-BTS-N(Me)-8	(14.36)	1.54		1.52
16-BTS-N(Me)-8	(19.27)	4.22		4.57
16-BTS-N(Me)-12	(6.21)	(6.74)		6.04

Acknowledgment. We would like to thank Dr. A. Skoulios for many fruitful discussions and Miss L. Oswald for very helpful technical assistance.