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Liquid Crystals

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Armand Soldera^a; Jean-François Nicoud^a; Yves Galerne^a; Antoine Skoulios^a; Daniel Guillon^a

^a Institut de Physique et de Chimie des Matériaux de Strasbourg, Strasbourg Cedex, France

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PRELIMINARY COMMUNICATION

Synthesis and properties of new ferroelectric liquid-crystalline compounds having a tolane rigid core and an optically active alkyl sulphinate group

by ARMAND SOLDERA, JEAN-FRANÇOIS NICLOUD,
YVES GALERNE, ANTOINE SKOULIOS
and DANIEL GUILLON*

Institut de Physique et de Chimie des Matériaux de Strasbourg,
Groupe des Matériaux Organiques, ICS, 6, rue Boussingault,
67083 Strasbourg Cedex, France

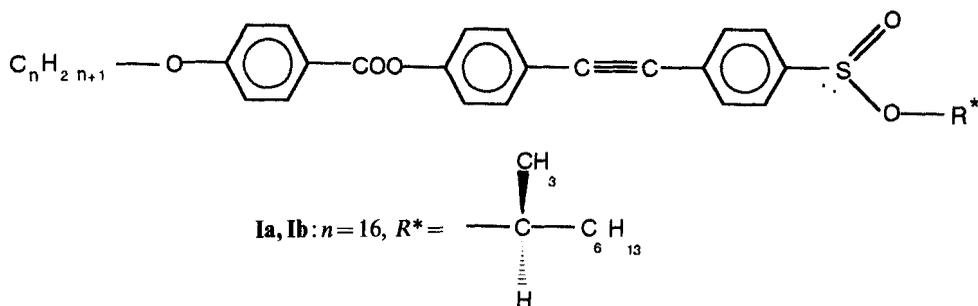
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The synthesis and the properties of new ferroelectric liquid-crystalline compounds with a tolane rigid core and an optically active alkyl sulphinate group are reported. These compounds contain two chiral centres: a sulphinate group and a branched aliphatic chain. The two pure diastereomers having opposite configurations on the sulphur have been isolated. The mesomorphic behaviour of these two compounds is different, only one exhibiting an enantiotropic chiral smectic C phase; this clearly demonstrates the role of the sulphur configuration in determining the thermotropic properties. The mesomorphic transition temperatures, the structural behaviour as a function of temperature and preliminary measurements of the spontaneous polarization are presented.

Since the electrooptical properties (fast switching and bistability) of ferroelectric chiral smectic C liquid crystals [1] were reported by Clark and Lagerwall [2], there has been considerable interest in the synthesis of new chiral smectic C materials exhibiting a large spontaneous polarization and a fast response to an applied electric field. The chiral centre of the molecule being placed close to the aromatic core, it is possible to increase the spontaneous polarization by enlarging the transverse dipole moment or by inhibiting the dipole rotation. The enlargement of the dipole moment can be achieved through a variety of dipoles, such as ether, ester, halogenated [3] or epoxy groups [4]. The inhibition of the dipole rotation can be obtained when positioning the dipole close to the chiral part of the molecule which also contains a relatively long terminal aliphatic chain on the external side of the chiral centre [5]. In order to satisfy these requirements and to introduce a new type of chiral centre in smectogenic molecules, we decided to synthesize 1,2-diphenylacetylene (or tolane) derivatives bearing a chiral sulphinate functionality directly attached to the rigid tolane core. A further advantage of introducing a sulphinate group in the molecule is the hope to lower the transition temperatures, since several sulphinate compounds are known to be oils at room

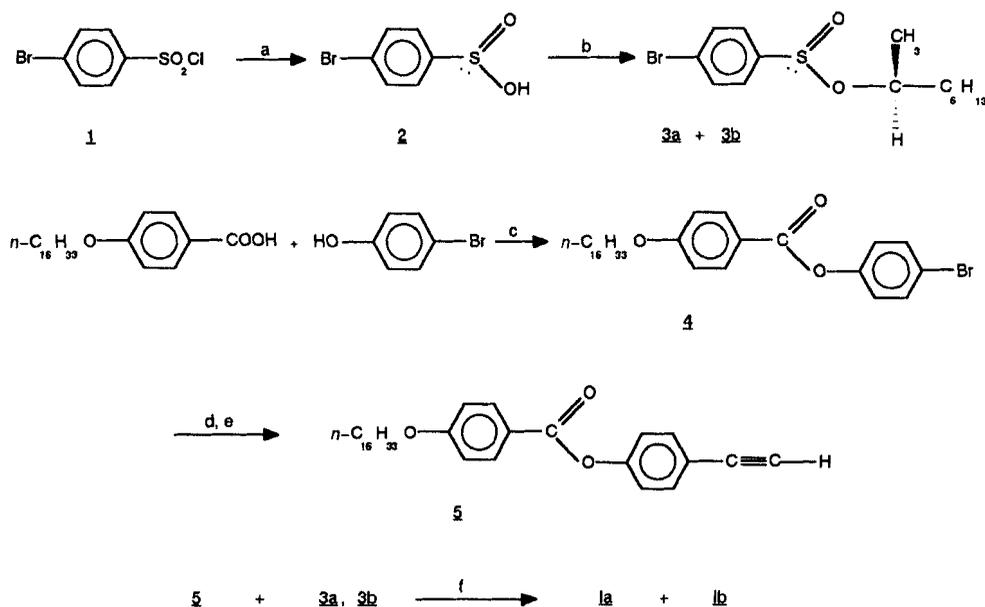
* Author for correspondence.

temperature [6]. The general structure of the mesogens considered in the present work is



When R^* is a chiral alkyl group, two diastereomeric sulphinates of type **I** are possible, having opposite configurations at the chiral sulphur centre. In a first attempt to study the effects of such unusual chirality on the mesomorphic properties of S_C^* liquid-crystalline compounds, we have prepared the two compounds **Ia** and **Ib** where $n=16$ and R^* is the optically active (*S*)-1-methyl-heptyl group. **Ia** and **Ib** have been isolated as chemically pure materials from the diastereomeric mixture obtained by esterification of the corresponding racemic sulphinic acid and the optically pure (*S*)-(+)-2-octanol.

The synthetic route to compounds **Ia** and **Ib** is shown in the scheme:



- (a) $Na_2SO_3, HCl, 80^\circ C$; (b) (*S*)-(+)-2-octanol, 2-chloro-*N*-methylpyridinium, Et_3N, CH_2Cl_2 ; (c) DCC/DMAP, CH_2Cl_2 ; (d) $H-C\equiv C-TMS, PdCl_2-Cu(OAc)_2, H_2O-PPh_3, (i.Pr)_2NH$; (e) $(n-Bu)_4N^+F^-$; THF; (f) $PdCl_2-Cu(OAc)_2, H_2O-PPh_3, (i.Pr)_2NH$.

Scheme.

4-Bromobenzenesulphonylchloride (**1**) was reduced to the corresponding sulphinic acid (**2**) [7], then esterified to the mixture of diastereomeric sulphinates **3a**, **3b** with

(*S*)-(+)-2-octanol according to Furukawa's procedure [8,9]. Attempts to isolate the pure diastereomers **3a** and **3b** from the viscous oily mixture led to substantial isomerization to the isomeric sulphone; the mixture was used for the next step without separation. The terminal acetylene (**5**) was prepared by the coupling reaction of the arylbromide (**4**) with trimethylsilylacetylene using a palladium catalyst, followed by deprotection of the acetylenic moiety according to Hagihara's procedure [10]. Desilylation to the ethynyl compounds was proved to be more efficient by using tetra-*n*-butylammonium fluoride in THF, rather than by the classical method using aqueous methanolic potassium hydroxide.

Compounds **Ia** and **Ib** were finally obtained in good yields by coupling the aromatic acetylene **5** with the mixture **3a**, **3b** using a palladium catalyst in a dialkylamine solvent. An initial separation by column chromatography over silica gel affords a pure diastereomer called **Ia**. The other diastereomer **Ib** was obtained as a pure material from the residue by preparative TLC. Both **Ia** and **Ib** so obtained are considered to be free of contamination by the other diastereomer, as shown by their ^1H and ^{13}C NMR spectra (several NMR signals of **Ia** and **Ib** are highly differentiated). Each of them showed satisfactory microanalysis and were found to be thermally stable. 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. Work is in progress to establish the absolute configuration of sulphur in **Ia** and **Ib**.

Investigation of the liquid-crystalline polymorphism has been carried out using polarized optical microscopy, differential scanning calorimetry and X-ray diffraction. The optical microscope was equipped with a Mettler FP 82 hot stage; the DSC measurements were performed with a Perkin-Elmer DSC 7 calorimeter; X-ray diffraction patterns were recorded photographically using a Guinier focusing camera equipped with a bent quartz monochromator ($\text{Cu-K}_{\alpha 1}$ radiation from a Philips PW-1009 generator) and an electric oven. The measurements of the spontaneous polarization were performed by applying a triangular voltage to the cell, the ITO coated glass plates of which were treated with polyimide.

On heating compound **Ia**, DSC and optical microscopy show two main transitions, one at 67.5°C corresponding to the transition from the crystalline phase to a mesomorphic phase, and the other at 92.7°C corresponding to the transition from the mesophase to the isotropic liquid. On cooling, the last transition is reversible at 92.1°C , whereas the crystalline phase reappears only at 55.6°C . Under the microscope, the mesomorphic domain is characterized by another transition observable, on cooling, at 80°C between a fan shaped (or focal conic) texture to a regularly striated texture. Moreover, at 70°C for example, the observation of interference colours indicates clearly the presence of horizontal cholesteric planes (see figure 1). This seems all the more indicative of the presence of smectic A and chiral smectic C phases.

The X-ray diffraction patterns, measured as a function of temperature within the mesomorphic domain of compound **Ia**, 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 2. It shows clearly the existence of two distinct regions within the temperature range of the mesomorphic domain: a low temperature regime where the spacing decreases regularly with temperature up to about 80°C , and a high temperature regime where the spacing is almost constant (44.5 \AA) and is of the same order of magnitude as the molecular length found by molecular modelling (46 \AA). Although no

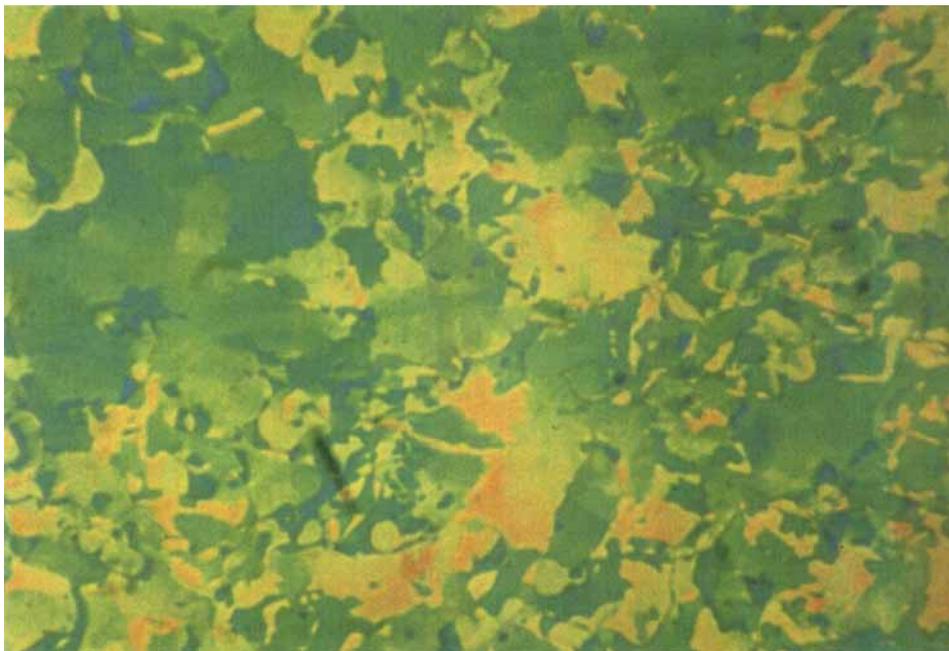


Figure 1. Optical texture of **1a** at 70°C showing the cholesteric planes parallel to the glass plates.

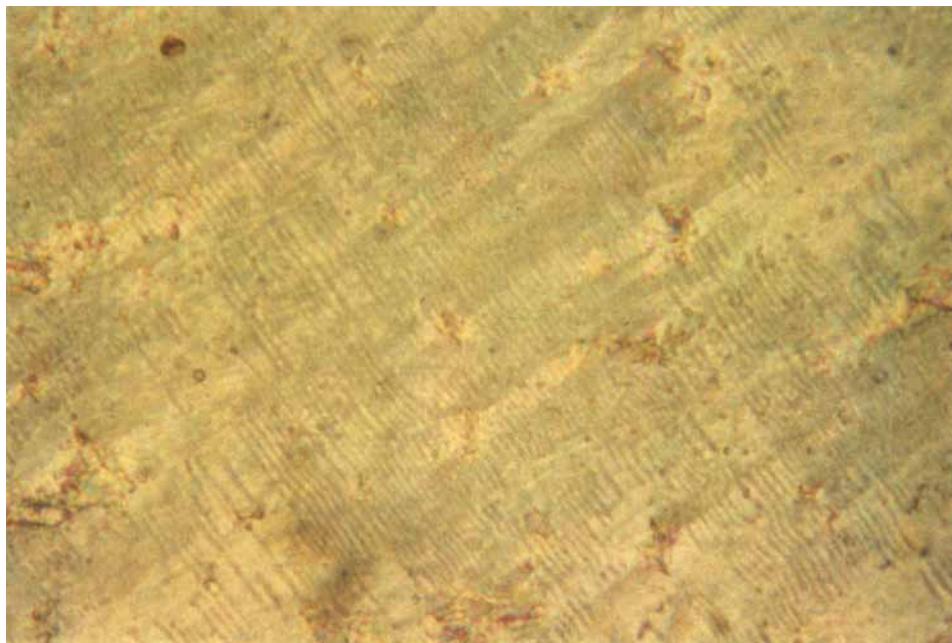


Figure 4. Typical optical texture of an equimolar mixture of **1a** and **1b** in the chiral smectic C phase.

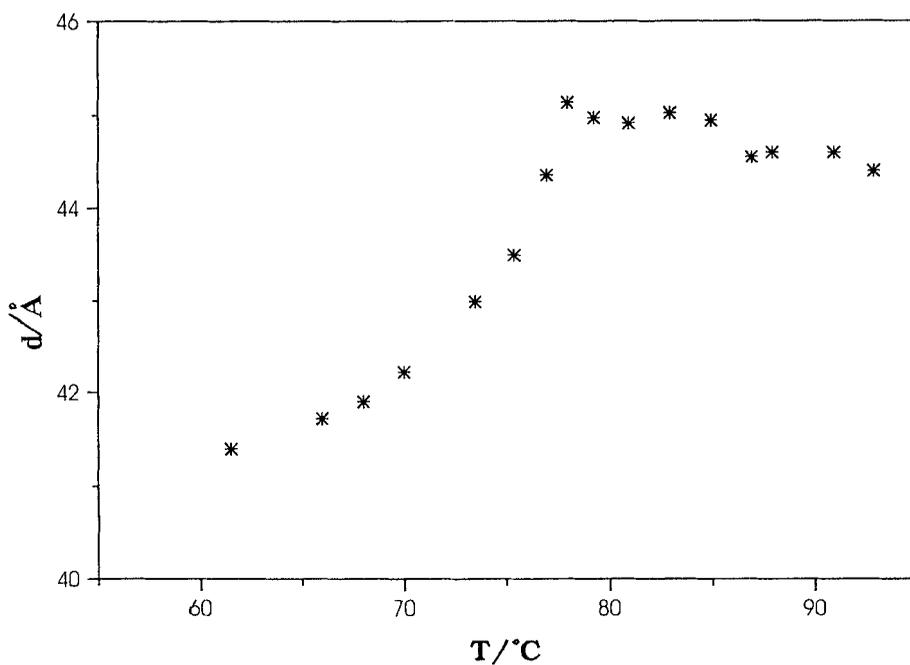


Figure 2. Layer spacing of the smectic A and chiral smectic C phases of Ia as a function of temperature.

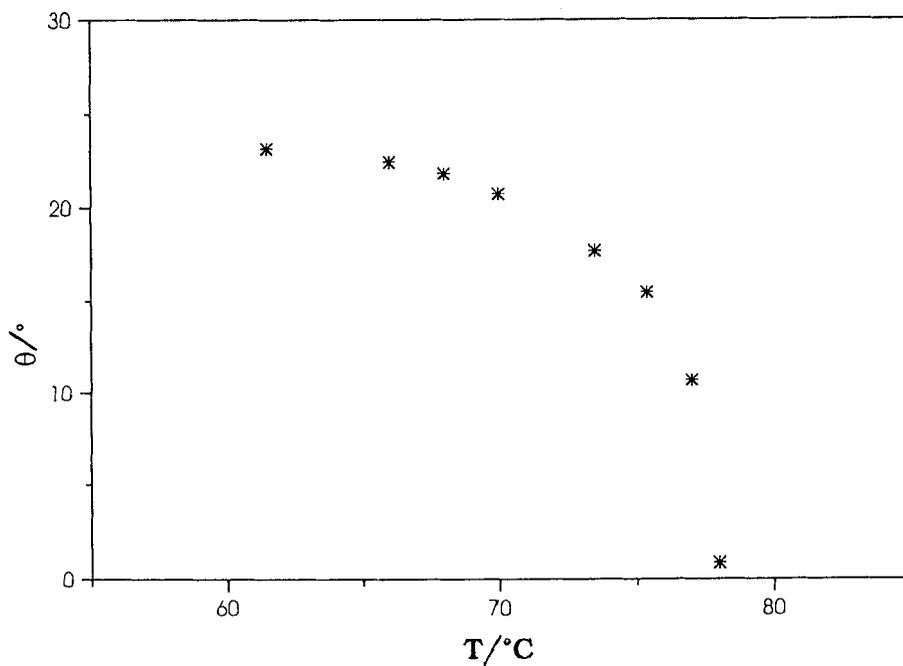
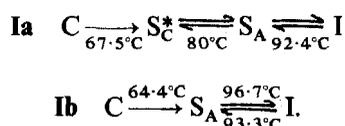


Figure 3. Tilt angle of the director in the chiral smectic C phase of Ia as a function of temperature.

harmonics of the Bragg reflection can be observed to confirm the lamellar nature of the mesophases, the first regime is typical of a chiral smectic C phase, in agreement with the cholesteric planes observed under the microscope, and the second is typical of a smectic A phase. By taking the spacing in the smectic A phase as corresponding to the length of one molecule, the tilt angle, θ , of the director in the chiral smectic C phase is calculated through the relation: $\cos(\theta) = d_C/d_A$ [11] and its variation as a function of temperature is represented in figure 3; the ideal value for θ , 22.5° , is obtained at about 60°C .

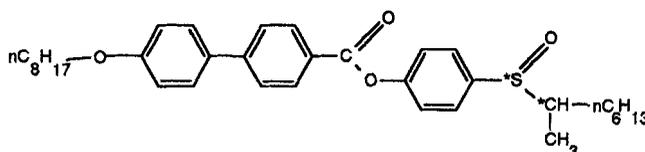
As for compound **Ib**, DSC measurements and optical microscopy observations show the existence of a mesomorphic domain between 64.4 and 96.7°C on heating, and between 93.3 and 47.8°C on cooling. This mesomorphic range is characterized by the same optical textures as those already observed for compound **Ia**, with the exception that neither regularly striated textures nor cholesteric planes could be observed. The X-ray diffraction patterns of compound **Ib** measured 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 is stable around 46.5 \AA . This value, very close to the molecular length (46 \AA), shows clearly that the mesomorphic domain corresponds in fact to a single smectic A mesophase.

Thus, the transition temperature diagrams of **Ia** and **Ib** are



Attempts to measure a spontaneous polarization in the chiral smectic C phase of compound **Ia** were unsuccessful, presumably due to orientation difficulties. However, a value of 5 nC cm^{-2} was found for an equimolar mixture of compounds **Ia** and **Ib**, which exhibits a chiral smectic C phase between 48 and 66°C , a typical optical texture of the ferroelectric phase of this mixture is presented in figure 4.

Since the commencement of our work, the introduction of a chiral centre directly connected to the core aromatic ring for the synthesis of ferroelectric liquid-crystalline compounds, has been reported. Kusumoto *et al.* [12] have described a series of chiral esters bearing one or two asymmetric carbon atoms surrounding a carboxyl group. The two diastereomeric esters obtained from (*S*)-(+)- or (*R*)-(-)-2-octanol show slight differences in their mesomorphic properties (no S_C^* phase is observed), and moderate P_s when used as chiral dopants. They prepared several O-acyl cyanohydrin derivatives bearing the polar cyano group on a chiral carbon centre directly connected to the aromatic core ring. No stable S_C^* phases were found with this series, but the compounds were shown to be excellent chiral dopants for ferroelectric liquid crystals [13]. The introduction of a chiral sulphur centre was recently described by the same Japanese group. For example 4'-octyloxybiphenyl-4-carboxylate esters of the diastereomeric chiral 4-(2-octylsulphinyl)phenol,



which contains nearly the same chiral centres as **1a** and **1b**, do not exhibit S_C^* phases. However, when used as chiral dopants they can induce fairly large spontaneous polarizations. This can be tentatively explained by the restricted free rotation of the alkyl chain due to the methyl side group close to the chiral sulphur centre, reducing the probability of unfavourable conformers, thus fixing the dipole of the sulphoxide moiety [14].

As a conclusion, we have described for the first time the synthesis and the liquid-crystalline properties of compounds having both a tolane rigid core and an optically active alkyl sulphinate group. Two pure diastereomers having opposite configurations on the sulphur have been isolated and exhibit different mesomorphic behaviour. One forms chiral smectic C and smectic A phases, whereas the other exhibits only a smectic A mesophase. This clearly indicates the role of the sulphur configuration in the thermotropic properties of such compounds. Although no spontaneous polarization was measured for the pure chiral smectic C sample, preliminary measurements with mixtures of the two compounds **1a** and **1b** indicate that the chiral smectic C derivative can be used as a chiral dopant. Work is in progress to investigate sulphinate mesomorphic derivatives bearing a chiral sulphur atom as the unique chirality centre.

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