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Online publication date: 06 August 2010

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Structure and photoconductive behaviour of a sanidic liquid crystal

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A series of [1]benzothieno[3,2-b][1]benzothiophene-2,7-dicarboxylate derivatives consisting of a flat, conjugated aromatic moiety containing sulphur hetero-atoms and substituted by terminal chains—ethyl, decyl, *Z*-4-decenyl or 2-(2-butoxyethoxy)ethyl—has been synthesized. These materials exhibit a smectic liquid crystalline phase, the stability of which was found to be strongly dependent on the length and the nature of the terminal chains. In the mesophase, the molecular arrangement within the smectic layer is characterized by a local stacking of the rigid parts similar to that found in discotic columnar systems. Finally, clear photoconductive behaviour was found in mechanically aligned samples of these liquid crystals.

1. Introduction

Photoconductive materials are characterized by an increase of their conductivity upon illumination. At the beginning of the 1980s, pioneering work aimed at obtaining photoconductive liquid crystals began. It was believed that molecular alignment in the mesophase should bring about an intermolecular overlap of π-orbitals of the charge carriers convenient for charge transport properties. The first investigations of photoconduction in liquid crystals were carried out on rod-shaped mesogens [1]. These studies however were essentially performed on the nematic phase and revealed that ionic conduction was predominant, due to the presence of ionic impurities or to photogenerated ions.

Since then little progress was made in this field until true electronic conduction was demonstrated in the discotic columnar phases of triphenylene derivatives, resulting in mobilities up to 10^{-1} cm^2 V^{-1} s^{-1} [2]. In these materials, the conduction (hole charge carriers) was found to follow mainly the direction of the stacks of disks, that is to say in the direction in which the π-orbital overlap is best.

Motivated by these results, a second set of studies started again quite recently to investigate the photoconduction in calamitic liquid crystals [3–10]. For some

of the reported materials, the authors presented evidence of free charge carrier conduction (electrons or holes) with high mobility. For instance, Funahashi and Hanna measured hole mobilities as high as 5×10^{-3} cm^2 V^{-1} s^{-1} in the SmA phase of a thiobenzothiazole derivative, and pointed out the importance of extremely pure compounds in order to avoid the parasite dark ionic current [5]. Tokuhisa *et al.* reported for an oxadiazole derivative an electron mobility which was found to increase on going from the disordered to the ordered smectic phase [10].

To our knowledge, photoconduction has not yet been explored in sanidic liquid crystals. Because of their lath-like core structure, sanidics can be considered as a class of liquid crystals intermediate between discotic columnar and calamitic liquid crystals. The lamello-columnar phases they usually exhibit might be of particular interest for charge transport properties due to the presence of columnar stacking.

This paper reports the synthesis and properties of a series of sanidic liquid crystal materials based on a flat conjugated aromatic core containing two sulphur hetero-atoms, namely the [1]benzothieno[3,2-b][1]-benzothiophene-2,7-dicarboxylate core, substituted at both extremities by flexible chains of varied nature, as drawn in figure 1.

We believe that this rigid aromatic core may provide the required charge-carrier generation property, and,

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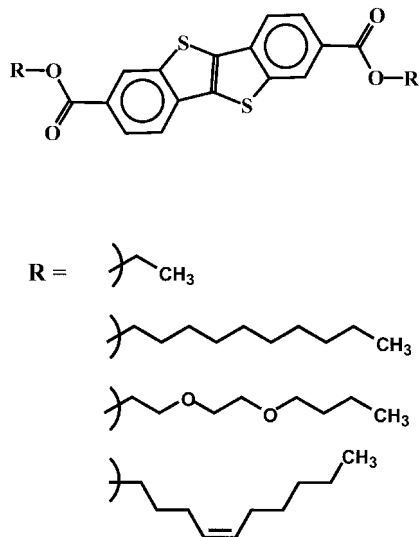e-mail: mery@michelangelo.u-strasbg.fr

Figure 1. Molecular structure of the disubstituted [1]benzo-thieno[3,2-b][1]benzothiophene-2,7-dicarboxylates

that its flatness and the presence of the sulphur hetero-atoms could favour good overlap of the π-orbitals and hence the presence of good free charge carrier photo-conduction. It is worth noting that polymeric compounds based on this molecular system have been used as photoconductors for electrophotographic applications [11].

This core structure carrying short ethyl chains has already been synthesized by Kaszynski and Dougherty [12] in order to study its electrochemical properties. This material was found to exhibit a smectic phase (attributed to be SmA) ranging from 219 to 304°C. In order to obtain the mesophase at a much lower temperature, the terminal ethyl chains were replaced by longer chains of fixed length (ten atoms in chain length) of varied nature. The chains introduced were *n*-decyl, *Z*-4-decenyl and 2-(2-butoxyethoxy)ethyl. The effect of introduction of an unsaturated chain into a molecule has already been studied by Kelly [13] and Dyer and Walba [14] who showed the important variations of temperatures which can be attained by a modification of the *E* or *Z* type, as well as by the position of the unsaturation. Similarly, oligo-oxyethylene chains, are well known to provide a drastic decrease in transition temperatures [15, 16].

The [1]benzothieno[3,2-b][1]benzothiophene-2,7-dicarboxylate derivatives carrying different chains were synthesized by using, in large part, Kazsynski's pro-cedure. The mesomorphic properties of the compounds thus obtained were carefully investigated. Especially, the exact structure of the mesophase was analysed, and its thermal stability was studied as a function of the nature of the terminal chains. Finally, photoconduction was

investigated through photocurrent measurements under near UV illumination performed on aligned samples at different temperatures.

2. Synthesis

The synthetic route for the preparation of the materials is presented in the scheme. The synthesis of the [1]benzothieno[3,2-b][1]benzothiophene-2,7-dicarboxylates was carried out from the diethyl ester, which was prepared as already reported [12]. This pro-cedure consists of six steps. First, commercially available 4-(chlororomethyl)benzoic acid **1** is converted into the ethyl ester and nitrated to yield ethyl 4-(chloromethyl)-3-nitrobenzoate **2**. Two ester molecules are then condensed
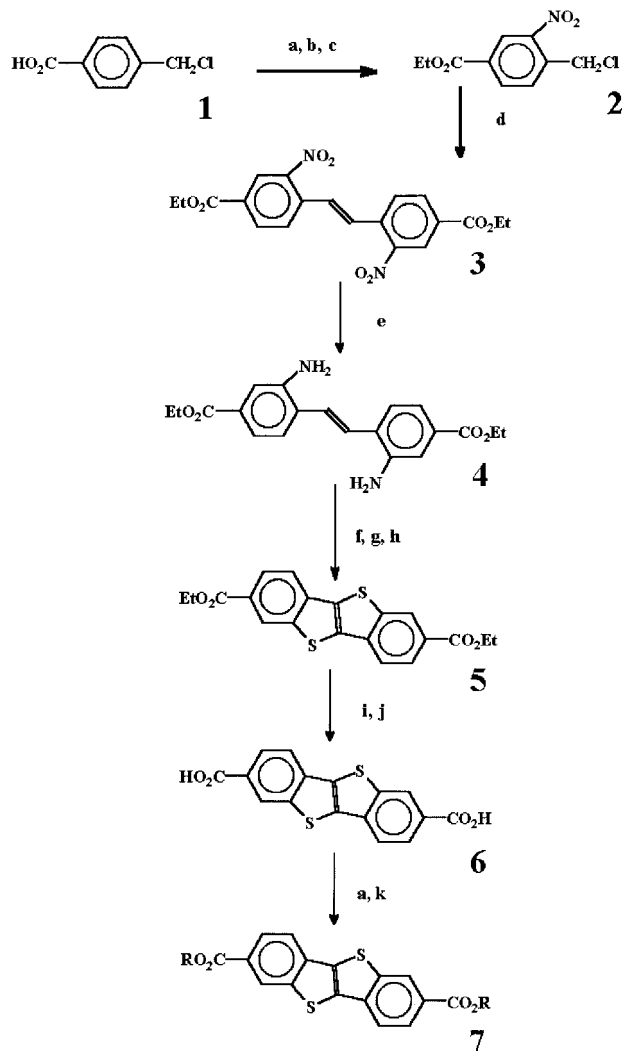
Scheme Synthesis of the disubstituted [1]benzothieno-[3,2-b][1]benzothiophene-2,7-dicarboxylates (a) $SOCl_2$, toluene; (b) EtOH; (c) HNO_3/H_2SO_4; (d) $EtO^- Na^+/$ EtOH; (e) Fe/HCl, EtOH; (f) $NaNO_2$, HCl; (g) KSCSOEt, $NiCl_2 \cdot 6H_2O$; (h) Br_2, AcOH; (i) KOH, EtOH; (j) H_2O/H^+; (k) ROH, toluene, pyridine.

to give diethyl 2,2′-dinitro-(*E*)-stilbene-4,4′-dicarboxylate **3** by treatment with sodium ethoxide. The nitro groups are reduced using iron powder in ethanol in the presence of hydrochloric acid to give compound **4**. The amino groups so formed are converted into xanthate groups via a bisdiazonium salt. Finally, treatment of the stilbene bisxanthate with bromine in acetic acid forms the fused thiophene rings. Using the diethyl [1]benzothieno[3,2-b]-[1]benzothiophene-2,7-dicarboxylate **5** thus obtained, replacement of the ethyl groups by longer chains was achieved by saponification followed by classical esterification with the corresponding alcohols leading to the target compounds **7a–c**. The characterization of the intermediates **1–5** gave good results, in perfect agreement with reported data [12]. A description of the syntheses of the diacid **6** and the diesters **7a–c** is given below.

In order to minimize the presence of ionic impurities and thus the presence of a dark ionic current during photocurrent measurements, particular care was taken over the purification of the compounds. The liquid crystalline materials were systematically purified by chromatography on silica gel, followed by one recrystallization from ethanol and five from hexane before studying them (the hexane was of high quality grade and previously filtered through a 0.5 μm pore size filter).

2.1. *Benzothieno[3,2-b]benzothiophene-2,7-dicarboxylic acid 6*

Diethyl benzothieno[3,2-b]benzothiophene-2,7-dicarboxylate (640 mg, 1.8 mmol) was saponified using potassium hydroxide (430 mg, 7.8 mmol) in a mixture of 50 ml of ethanol and 20 ml of water. The mixture was heated at reflux for 24 h, when the condenser was removed and the temperature was maintained for 2 h to evaporate the ethanol. The resulting suspension was cooled to 0°C, diluted with 10 ml of iced water and acidified with 5 ml of dilute HCl (10%). The precipitate was filtered off, washed with water (2 × 50 ml), hexane (2 × 20 ml) and then dried under reduced pressure for 24 h at 80°C to give 330 mg (99%) of yellow powder. This compound decomposes ($T_{dec} = 283°C$) before melting. IR (KBr, cm^{-1}): 3100–2500 (broad), 1684, 1592, 1415, 1289, 1242, 830, 766, 721. NMR analysis could not be carried out because of the poor solubility of the compound. Anal: calc. for $C_{16}H_8O_4S_2$, C 58.52, H 2.46, O 19.49, S 19.53; found, C 56.92, H 2.79, O 21.24, S 19.00%. This analysis seems to indicate the presence of one molecule of water for two molecules of diacid: calc. for $C_{32}H_{16}O_8S_4.H_2O$, C 56.97, H 2.67, O 21.36, S 18.99%.

2.2. *Esterification of benzothieno[3,2-b]benzothiophene-2,7-dicarboxylic acid*

All the diesters were synthesized using the following procedure. To a solution of the diacid (315 mg, 1 mmol)

in 10 ml of toluene were introduced 10 ml of thionyl chloride. The mixture was heated at reflux for 5 h and then cooled to room temperature. Evaporation to dryness under reduced pressure gave a residue which was immediately dissolved in a mixture of 10 ml of pyridine, 10 ml of toluene and the corresponding alcohol (32 mmol). The mixture was heated at reflux for 6 h, and then allowed to cool to room temperature. Diethyl ether was introduced and the organic phase was washed with acidic water, water, saturated aqueous NaHCO$_3$, and finally with water. The ethereal phase was dried over MgSO$_4$, filtered and the solvent eliminated under reduced pressure. The crude product was purified by chromatography on silica gel (ethyl acetate:hexane, 1:5 as eluent) and recrystallized from ethanol to give the diester derivatives as white crystals (55–65%). Further purification was made by recrystallizing the products five times from hexane.

2.2.1. *Didecyl benzothieno[3,2-b]benzothiophene-2,7-dicarboxylate 7a*

^{1}H NMR: δ (CDCl$_3$) 0.9 (t, 6H); 1.3 (m, 28H); 1.8 (q, 4H); 4.4 (t, 4H); 7.9 (d, $J = 8.4$, 2H); 8.18 (dd, $J_1 = 8.4$, $J_2 = 1.3$, 2H); 8.66 (d, $J = 1.3$, 2H). Anal: calc. for $C_{36}H_{48}O_4S_2$, C 71.01, H 7.95, O 10.50, S 10.53; found, C 70.47, H 7.92, O 10.77, S 10.40%. MS, *m/z* 608 (M, 100), 451 (43), 292 (34), 169 (30).

2.2.2. *Di[2-(2 butoxyethoxy)ethyl] benzothieno[3,2-b]-benzothiophene-2,7-dicarboxylate 7b*

^{1}H NMR: δ (CDCl$_3$) 0.9 (t, 6H), 1.25 (m, 4H), 1.35 (m, 4H), 3.5 (t, 4H), 3.6 (m, 4H), 3.7 (m, 4H) 3.9 (m, 4H), 4.6 (m, 4H), 7.9 (d, $J = 8.4$, 2H), 8.2 (dd, $J = 1.4$ and 8.4, 2H), 8.7 (d, $J = 1.4$, 2H) Anal: calc. for $C_{32}H_{40}O_8S_2$, C 62.32, H 6.54, O 20.75, S 10.40; found, C 62.43, H 6.52, O 20.81, S 10.30%. MS, *m/z* 617 (M + 1, 50), 455 (100).

#### 2.2.3. *Di(Z-4-decenyl) benzothieno[3,2-b]-benzothiophene-2,7-dicarboxylate 7c*
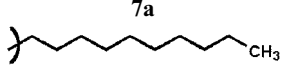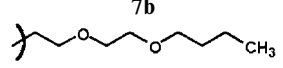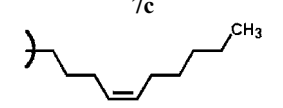
^{1}H NMR: δ (CDCl$_3$) 0.86 (t, 6H), 1.27 (m, 12H), 1.89 (m, 4H), 2.06 (q, 4H), 2.27 (q, 4H), 4.4 (t, 4H), 5.44 (m, 2 × 2H), 7.96 (d, $J = 8.4$, 2H), 8.17 (dd, $J = 1.4$ and 8.4, 2H), 8.66 (d, $J = 1.4$, 2H). Anal: calc. for $C_{36}H_{44}O_4S_2$, C 71.52, H 7.40, O 10.63, S 10.66; found, C 71.49, H 7.33, O 10.58, S 10.60%. MS, *m/z* 604 (M, 35), 449 (100).

3. Results and discussion

3.1. *Mesomorphic properties*

The transition temperatures of the compounds are presented in table 1. The clearing temperatures were determined by polarizing optical microscopy and the melting points by DSC. The biphasic domain observed

Table 1. Transition temperatures of the [1]benzothieno[3,2-b][1]benzothiophene-2,7-dicarboxylate diesters. Effect of the nature of the terminal chains on the melting (T_m) and clearing (T_{cl}) temperatures as compared with the didecyl derivative **7a**.

Compound	Temperatures/°C	Change of temperature as compared with **7a**	
		T_m/°C	T_{cl}/°C
5 (—CH₃)	Cr 220 S$_{(A)}$ 298 I	+92	+174
7a (—CH₃)	Cr 127.5 (S$_{(A)}$ 123.9) I ↑— 116 ↲	—	—
7b (—O—O—CH₃)	Cr 85.5 I ↑— 74.8 ↲	−42	< −49
7c (—CH₃)	Cr 83.5 S$_{(A)}$ 95.6 I ↑— 62 ↲	−44	−28

at the isotropic–mesomorphic transition never exceeded 0.1°C and therefore was a good indication of the high purity of the compounds.

As a first observation, the mesomorphic temperature range for the diethyl ester **5** (220°–298°C) is similar to that reported by Kaszynski and Dougherty (219°–304°C) [12]; the slight difference in the clearing point is probably due to decomposition which commences above 230°C, as checked by TGA measurements.

All the liquid crystal materials exhibit a unique and similar mesophase and on the basis of texture observation, this behaves as a SmA phase. However, this result was not in full agreement with the data obtained by X-ray diffraction: the mesophase present in our compounds appeared to be more complex. This is why this mesophase is called for now S$_{(A)}$ and the investigation of its structure is discussed separately in the next section.

The transition temperature of this mesophase is found to be strongly dependent both on the length and the nature of the terminal chains (table 1). First, lengthening the terminal chains from ethyl (compound **5**) to decyl (compound **7a**) produces a drastic destabilization of the smectogenic character. The drop in the clearing temperature (174°C) is much more pronounced than that for the melting point (92°C), resulting in a monotropic S$_{(A)}$ phase for the didecyl derivative **7a**.

Secondly, the nature of the terminal chains is also found to affect significantly the thermal stability of the S$_{(A)}$ phase in our compounds. By keeping the same chain length (ten atoms in chain length), three kinds of terminal chain have been investigated, namely (i) a saturated chain, *n*-decyl (**7a**); (ii) an etherated chain containing two oxygen atoms, 2-(2-butoxyethoxy)ethyl (**7b**); and (iii) a chain containing a central *cis*-unsaturation, *Z*-4-decenyl (**7c**).

Substitution with 2-(2-butoxyethoxy)ethyl chains gives the highest thermal destabilization of the mesomorphic properties. When compared with **7a** substituted with saturated decyl chains, **7b** with etherated chains has a melting point depressed by 42°C, with total suppression of the mesophase. Surprisingly, substitution of the decyl chains by the *cis* (or *Z*) unsaturated chains gives a similar and strong decrease of the melting point (44°C), but in this case, the clearing temperature is shifted down by only 28°C. As a result, compound **7c** exhibits an enantiotropic S$_{(A)}$ phase stable over a 12°C temperature range when it is only monotropic in **7a**.

These results clearly show that it has been possible, by only changing the nature of the terminal chains, to stabilize or totally suppress the mesophase in these liquid crystal materials. In an attempt to understand how the nature of the chains can stabilize the mesomorphic properties, it is necessary to discuss separately their effects on the melting and on the clearing temperatures.

The melting temperature (T_m) depends upon crystal stability. Therefore, any geometric perturbations in the packing of the molecules will depress the melting point. As regards terminal chains, this constraint can be brought about by introduction in the aliphatic chains of a moiety of different molecular area, such as a dimethylsiloxane segment [17–19]. Another kind of perturbation can be obtained by insertion of an elbow, as in the case of a C=C link of the *cis*-type, leading to an angular perturbation in the side chain packing. This 'elbow'

effect has been used in the present work to decrease the melting temperature in compound **7c**. The effect of the presence of *cis*- or *trans*-unsaturation(s) on melting temperature is demonstrated by the data in table 2 for stearic acid and its unsaturated derivatives [20]. These T_m values show that *cis*-unsaturation produces a much higher depression of the melting temperature than *trans*-unsaturation, and that this effect is enhanced with increasing number of *cis*-unsaturated links. The influence of the introduction of C=C unsaturated links on mesogens has also been reported by Kelly [13] and by Dyer and Walba [14]. In particular, Walba showed in a study of mesogens bearing aliphatic C_{18} chains that insertion of a *cis*-unsaturated link strongly decreased the melting temperature. He also reported that two *cis*-unsaturations further depressed T_m, while little variation was obtained in the case of *trans*- (or *E*) unsaturation. Both authors showed that these effects were maximized when the *cis*-unsaturation(s) is (are) rather localized in the middle of the chains.

The explanation of the strong decrease in T_m obtained for compound **7b** substituted with etherated chains is more delicate. The main differences between oligo-(oxyethylene) chains and aliphatic chains of the same length are polarity, the helicoidal conformation of the former chains and probably to a less extent the flexibility [16]. The etherated chains being very short in our case, the helicoidal conformation of the chains cannot be held responsible for the decrease in the melting point. Therefore, it remains unclear whether the crystal destabilization observed for compound **7b** is due only to a change in chain flexibility.
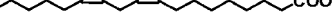
The clearing temperature (T_{cl}) depends upon the tendency for microsegregation. As a matter of fact, for a classical rod-shaped liquid crystal material, a strong amphiphilic character arising between the core and the chains will stabilize smectic phases and increase the clearing point. One major requirement for a strong amphiphilic character consists in having a large difference in polarizability between the core and the peripheral tails. Thus, in the present case, the core possesses a rather high polarizability and the chains have different polarities increasing in the order decyl to *Z*-4-decenyl to 2-(2-butoxyethoxy)ethyl. Consistent with the expected decrease of amphiphilic character in this sequence, compound **7a** with the least polar decyl chains exhibits the highest clearing point ($T_{cl} = 123.9°C$). Inversely, the most polar etherated chains depress T_{cl} so much that the mesophase is totally suppressed in **7b**, leading to a T_{cl} value virtually below the crystallization temperature (i.e. $T_{cl} < 74.8°C$). For the decenyl chains, the presence of the *cis*-unsaturation increases only slightly the polarizability of the paraffinic chain and therefore the clearing temperature of **7c** ($T_{cl} = 95.6°C$) is weakly depressed as compared to compound **7a** with saturated decyl chains. The influence of oligo(oxyethylene) and unsaturated paraffinic chains in the stabilization of mesogenicity has already been reported in the literature [13–16]. More generally, the present results are in agreement with the concept of amphiphilicity in liquid crystallinity which has been widely discussed by Skoulios and Guillon [21], and more recently by Tschierske [22].

3.2. *Structural properties*

The determination of the exact structure of the $S_{(A)}$ phase is of great importance since it will be responsible in large part for the photoconductive behaviour of the liquid crystals system. As already mentioned, on the basis of texture observations Kaszynski reported that the mesophase exhibited by diethyl [1]benzothieno[3,2-b]-[1]benzothiophene-2,7-dicarboxylate **5** was SmA [12]. In fact, observation of this mesophase in our materials by polarizing microscopy did give a typical SmA fan-like texture using planar alignment conditions and gave no birefringence with homeotropic alignment by using glass slides treated with octadecyltrichlorosilane. However

Table 2. Influence of the type and position of chain unsaturation on the melting temperatures (T_m) of stearic acid derivatives.

Compound	Name	$T_m/°C$
	octadecanoic acid	+70
	Z-9-octadecenoic acid	+16
	E-9-octadecenoic acid	+45
	Z,Z-9,12-octadecadienoic acid	−5
	E,E-9,12-octadecadienoic acid	+57
	Z,Z,Z-9,12,15-octadecatrienoic acid	−11

the assignment as a SmA phase was not completetely consistent with the results obtained by X-ray diffraction, as can be seen in a typical diffraction pattern given in figure 2.

First, the layer spacing was smaller than the molecular length determined by molecular modelling. As an example, the didecenyl derivative **7c** gave an interlamellar spacing of 31.5 Å (figure 2), while its molecular length is 37.3 Å. This result suggested the presence of a tilted phase (SmC) which was incompatible with both the optical observations using homeotropic alignment and the observed decreasing layer spacing with increasing temperature.

Second, two diffuse bands can be noticed in the wide angle region of the X-ray diffraction pattern (figure 2). The first one corresponds to a distance of 4.7 Å, which is characteristic of the intermolecular separation of the melted chains. The second diffuse band corresponds to a distance of 3.5 Å and is observable only in the mesophase, but not in the isotropic state. This value of 3.5 Å is unusual in mesophases of calamitics, but is frequently encountered in mesophases of discotics where it represents the intermolecular separation of the π-stacking of the aromatic cores in columnar systems.

In order to interpret these results and determine the structure of the mesophase, we made the assumption of a lamellar structure of locally crossed molecules. Thus, when the paired molecules are oriented on average along the layer normal, this structure allows for the possibility of a layer spacing smaller than the molecular length. By molecular simulation, we found that the tilt angle (between molecular axis and layer normal) necessary to match the molecular length with the layer spacing is about 35°. Representations of these crossed molecules in the case of the decenyl derivative **7c** are drawn in figure 3. From this model, one can easily see that the pairing of the molecules is possible because of the flatness
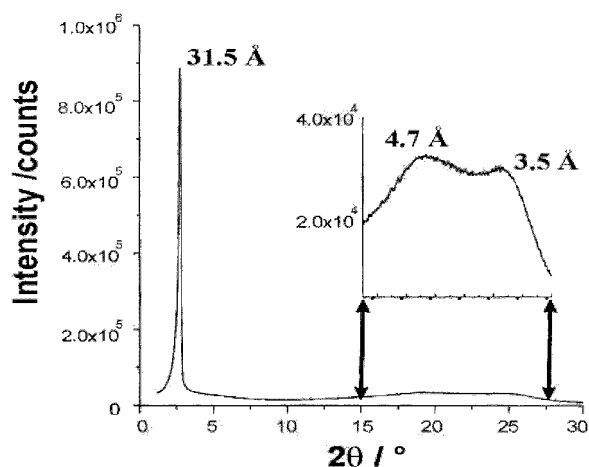
of the aromatic cores. The sanidic shape of these mesogens then favours intermolecular core–core interactions, similar to those found in columnar phases of discotics. The presence of the second diffuse band (3.5 Å) obtained by X-ray diffraction supports this assumption (see figure 2). Another important point needs to be made from the model presented in figure 3. The rotation of two molecules through the correct angle to fit the molecular length to the layer spacing leads to the sulphur atoms of adjacent molecules facing each other. This observation strongly suggests the presence of specific sulphur–sulphur intermolecular interactions which stabilize the local columnar order. In fact, sulphur–sulphur non-bonded interactions are well known to stabilize the packing of a large number of sulphur-containing molecules (through the p_z orbitals of the sulphur atoms) at a distance of about 3.5–3.7 Å, as is the case in TTF derivatives [23].

In summary, the most probable model of the molecular organization within the $S_{(A)}$ phase would consist of an untilted lamello-columnar arrangement of the stacked rigid cores, two neighbouring cores being tilted in opposite directions with respect to the layer normal. The flatness of the mesogenic core and the specific sulphur–sulphur interactions are thought to be responsible for the alternate tilting of the cores. In figure 4 is given a sketch of the structure of the mesophase for the decenyl derivative **7c**. It is worth noting that the presence of columnar order inside the smectic layers has already been reported by Levelut *et al.* [24] in a charge-transfer complex of tetrathiofulvalene and TCNQ by Malthête *et al.* [25] in hydrogen-bonded diamide systems; and more recently by El-ghayoury *et al.* [26] in o-palladated bipyridine complexes, and by Shimizu *et al.* [27] in long-chain tetraphenylporphyrins.

3.3. *Photoconductive measurements*

The photoconductive behaviour of liquid crystal **7c** was investigated by measuring the photocurrent as a function of temperature and so, as a function of the type of phase encountered. The cells used consisted of two ITO-coated glass plates whose surfaces were mechanically rubbed with teflon [28, 29] in order to realize homogeneous alignment with a bookshelf geometry in the $S_{(A)}$ phase. The cell thickness was achieved by the use of 27 μm Mylar foils, and the active cell area was of the order 1 cm². The cell was filled by capillarity using the isotropic state. This filling was performed under vacuum to eliminate any traces of oxygen that could increase the possibility of degradation of the compound in UV light and promote the presence of ionic impurities via the formation of O_2^- anions [1]. Before any measurements were made, the homogeneous molecular alignment in the $S_{(A)}$ phase was checked all over the surface of the cell by polarizing optical microscopy. A d.c. voltage of 10 V

Figure 2. X-ray diffraction diagram for compound **7c** in the $S_{(A)}$ phase (90°C).
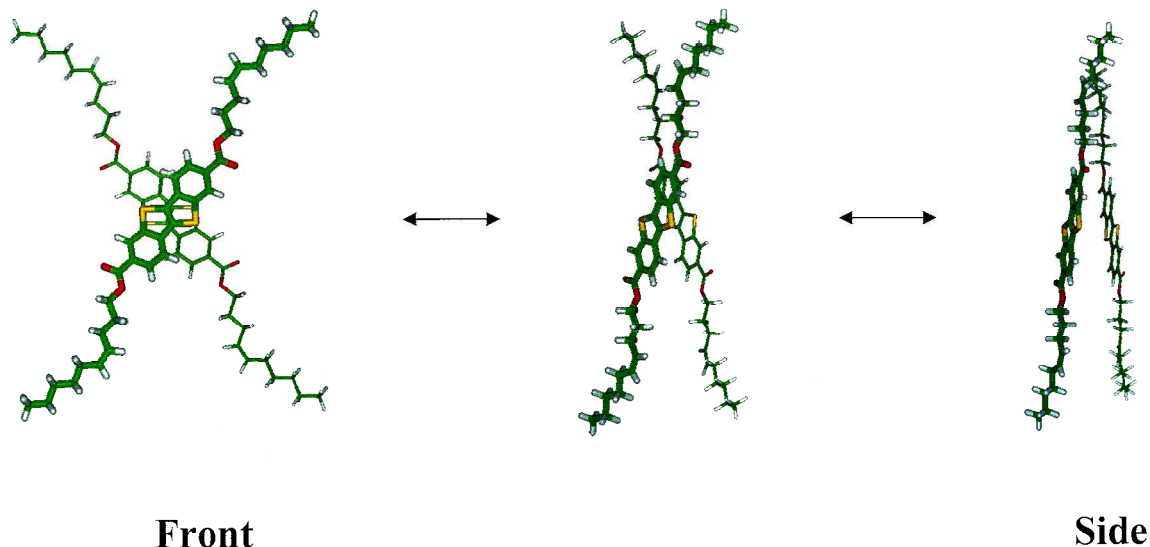
Front　　　　　　　　　　　　　　　　　　　　**Side**

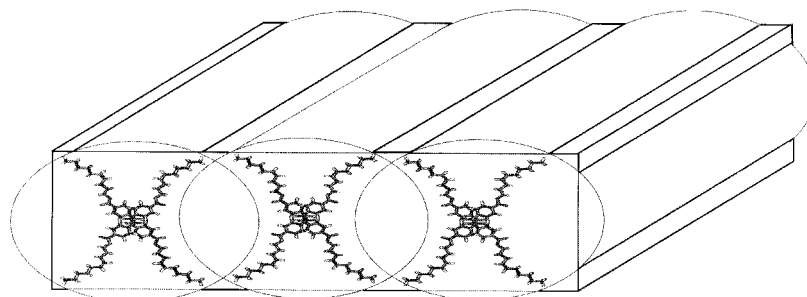Figure 3.　Proposed local organization of crossed molecules of **7c** in the $S_{(A)}$ phase.

Figure 4.　Proposed model for the molecular organization of mesogen **7c** in a smectic layer of the $S_{(A)}$ phase.

was applied to the cell and the sample was illuminated by a Xenon lamp (XBO/75 W); a shutter was used to mask and unmask the light. The photocurrent was obtained by measurement with an electrometer (150 A Microvolt Ammeter, Keithley Instrument) of the difference in current between the illuminated and dark states. The temperature of the sample was controlled by a heating stage (Mettler FP82). In order to prevent as much as possible current variations due to thermal effects, the infrared components of the light source were filtered out by a water cell. The optical absorption of compound **7c** in solution in dichloromethane presents two maxima at 331 nm (log ε = 4.59) and 322 nm (log ε = 4.67). Because of the cut-off by the glass cell at 320 nm, the effective wavelength for the charge carrier generation was therefore operating in the absorption tail of compound **7c**.

The results for the temperature dependence of the photocurrent for compound **7c** are presented in figure 5. During the first heating process, a very weak photocurrent was detected in the polycrystalline state. At the Cr–$S_{(A)}$ transition, the photocurrent increased stepwise to reach a plateau and then increased steeply beyond the clarification point. Upon cooling from the isotropic
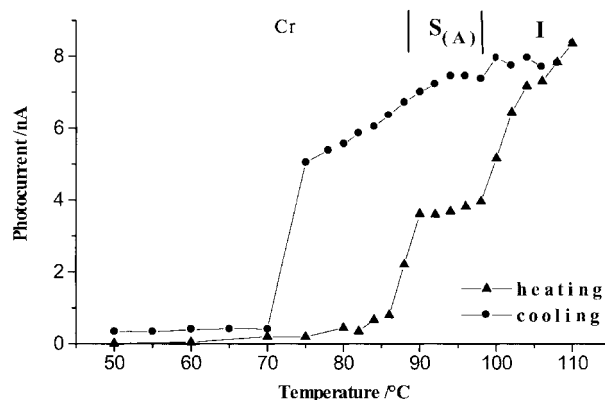
Figure 5.　Temperature dependence of the photocurrent for compound **7c.**

state, the photocurrent monotonously decreased through the $S_{(A)}$ phase and drastically fell at the crystallization point. Indeed, a higher photocurrent is detected on cooling due to better molecular alignment. The decrease of the photocurrent observable on cooling in the mesophase might possibly be due to partial degradation of the compound, which could be detected after several

hours of heating/illumination treatment. However, what-ever happens in the heating or cooling process, the values of the photocurrent are much higher in the $S_{(A)}$ phase than in the polycrystalline state. The main explanation of this effect must most probably rely on the increased lifetime of the carriers due to the disappearance of deep traps at grain boundaries in the aligned mesophase [4]. The most striking result however remains the higher photocurrent measured for the isotropic state than the $S_{(A)}$ phase. This behaviour has already been observed for a calamitic mesogenic system for which the inter-pretation was based on better charge carrier generation in the isotropic state [4]. The authors argued that the effective light absorption should be better in a homo-geneous liquid free from light scattering rather than in a liquid-like mesophase.

By checking the photocurrent dependence with the polarity of the applied voltage, the majority of the charge carriers have been identified as holes. However, whatever the type of phase encountered, the dark current pre-ponderates over the photocurrent, this propensity being more marked in the isotropic state.

4. Conclusions

A series of sanidic mesogens based on the core [1]benzothieno[3,2-b][1]benzothiophene-2,7-dicarb-oxylate has been synthesized and characterized. This core has been substituted at both extremities by flexible chains of various length and nature. The rigid central part of these molecules is special in being flat and fully conjugated and in containing two sulphur hetero-atoms. The materials were found to exhibit an unusual smectic A phase presenting a local columnar order inside the smectic layers. This distinctive feature is believed to arise from specific sulphur–sulphur intermolecular inter-actions leading to a local organization of alternately tilted crossed molecules inside the smectic layers. The stability of this mesophase was found to be strongly dependent upon the length and the nature of the terminal chains. In fact, the incorporation of the unsaturated Z-4-decenyl chains produces the highest stabilization of the mesophase at lower temperatures when compared with saturated decyl chains. Finally, the photoconduction has been investigated for one of these materials. Even though the presence of dark current was found to be preponderant, the compound clearly exhibited a photo-current whose amplitude was higher in the $S_{(A)}$ phase than in the crystalline phase. However, the presence of the high photocurrent observed in the isotropic state remains open to interpretation. Studies are currently in progress to characterize further the photoconduction in these sanidic liquid crystalline materials.

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