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Towards a new class of ferroelectric liquid crystal molecules for nonlinear optical applications

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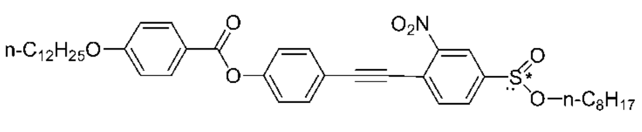
The synthesis of a new molecule specifically designed to exhibit both ferroelectric and nonlinear optical properties is presented. This molecule possesses an optically active phenyl sulphinic group, which introduces a dipole moment directly linked to the chromophore group, with a nitro group in the *meta*-position. The rest of the molecule comprises a tolane and a benzoate group. Such a structure results in an enantiotropic smectic C*–smectic A phase sequence in its polymorphism. A first measurement of the spontaneous polarization shows a high value. The polymorphism of the racemic homologous molecule possessing the nitro group in the *ortho*-position is also presented, and also shows the smectic C–smectic A phase sequence.

1. Introduction

The designing of new mesogenic molecules exhibiting both ferroelectric and nonlinear optical (NLO) properties is of considerable interest since non-centrosymmetry is achieved and the alignment of molecules is greatly enhanced. However the first NLO property measurements revealed low values of the second order susceptibility, $\chi^{(2)}$ [1]. The reason for this is because the principal component of the microscopic first hyperpolarizability, β, which is roughly directed along the director, is perpendicular to the non-vanishing dipole, the polar direction. To counteract this difference, the smectogen C molecules have to be processed into an appropriate 'push–pull' structure, i.e. donor–spacer–acceptor array, in order to be aligned and fixed along the polar direction. Walba *et al.* first synthesized a molecule which meets such a design, W314 [2]. This molecule possesses a functionalized aromatic ring with the NLO chromophore group constituted by a nitro group in the *ortho*-position of the chiral chain. The nitro group is thus oriented along the polar axis by steric coupling of the aryl substituent with the stereo centre. Such a design subsequently increased the macroscopic NLO coefficient. Since then various attempts have been made to increase β along the polar axis [3, 4].

In this paper, a new approach to increasing the coupling between the chromophore group and the chiral centre is proposed. As argued by Walba *et al.*, the coupling of the nitro group and the chiral centre on W314 is of great importance for obtaining enhanced NLO properties. Consequently, linking the chiral centre to such a chromophore group would increase this coupling and therefore the macroscopic NLO properties.

In fact, the positioning of the sulphinate group, a chiral centre, directly linked to a rigid core, can lead to smectogen C molecules [5]. The measurement of spontaneous polarization [6] revealed the importance in damping the chiral rotation, as hinted by the Boulder model [7]. Molecule **I** matches such a design. It presents a chiral sulphinate group attached to a rigid core carrying the NLO chromophore group. The acceptor group, a nitro group, is in the *meta*-position to the chiral centre. It should be noted that the rigid core consists of a tolane and a benzoate group to offset the significant elbow introduced by the sulphinate group. Additional molecules are presently being investigated to



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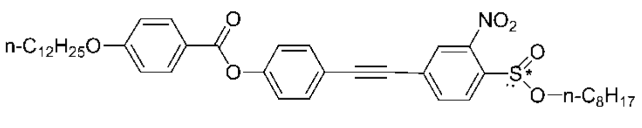

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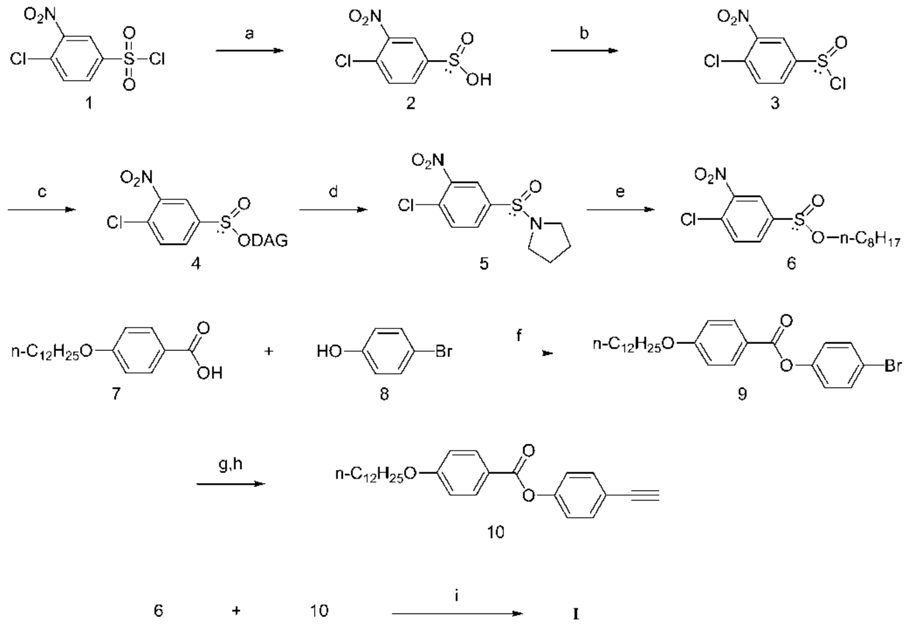
modify this core, such as molecule **II**, which will be optically active. In this first paper on such compounds, only the synthesis of molecule **I** is presented. Subsequent papers will describe the general synthesis of these molecules, a comparative study, and their NLO measurements.

2. Experimental

The synthesis of molecule **I** is outlined in the scheme. Optically active molecule **I** is obtained by combining the optically active chloro-benzene sulphinyl group **6** with the ethynyl compound **10**. To obtain the chiral sulphinyl group, 4-chloro-3-nitrobenzenesulphonyl chloride **1** is first reduced [8] to the corresponding sulphinic acid **2** which is then directly chlorinated with thionyl chloride. The racemic sulphinyl chloride **3** is then esterified with diacetone-D-glucose (DAG), according to the highly diastereoselective DAG methodology developed by Fernández *et al.* [9]. It should be noted that esterification with DAG yields a better enantioselectivity than with (-) menthol [10]. The nucleophilic substitution of pyrrolidine Grignard reagent on the diastereomeric mixture of DAG sulphinates (**4**), containing a diastereomeric excess (88%) of the (*S*)-sulphinate, occurs with an inversion of configuration at the sulfur atom [11]. Studies are presently in progress to increase this excess. The configuration at the sulphur atom is assumed to be (*S*), according to the base stereodirecting effect reported by Fernández *et al.* [12]. Further studies must be carried out to confirm such a configuration.

The resulting sulphinamide **5** is alcoholysed with 1-octanol to obtain octyl (*S*)-4-chloro-3-nitrobenzenesulphinate (**6**), in the presence of trifluoroacetic acid as catalyst. This reaction is known to proceed with inversion of configuration at the sulphur and conservation of high enantiomeric excess with a primary alcohol [13]. The tolane part **10** is obtained by the coupling reaction of trimethylsilylacetylene with the bromobenzoate **9** using tetrakis(triphenylphosphine)-palladium as catalyst [14], followed by a deprotection of the ethynyl group with tetrabutylammonium fluoride [15]. The same palladium-catalysed coupling reaction is used to link the optically active sulfinate (6) with the tolane part, and thus to obtain molecule **I**.

Investigation of the phase transition temperatures was carried out using differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD). The DSC measurements were performed using a DSC-7 Perkin-Elmer apparatus. The optical microscope was equipped with a hot stage. XRD patterns were obtained from a Siemens/Bruker instrument with a Kristalloflex 760 generator (Cu-K$_{\alpha1}$). Spontaneous polarization was measured by applying a triangular wave voltage through a cell containing the FLC compound [16].



Scheme. Synthesis of molecule I. (a) CH3(C6H4)SH, Et3N, AcOEt, −78°C (b) SOCl2, reflux (c) DAG, (i-Pr)2NEt, toluene, −78°C (d) (C4H8)NMgBr, THF, −78°C (e) n-C8H17OH, CF3COOH, toluene,−78°C (f) DCC, DMAP, CH2Cl2 (g) TMS-≡, Pd(PPh3)4,CuI, Et3N (h) (n-Bu)4NF, THF (i) Pd(PPh3)4,CuI, Et3N.

3. Results and discussion

Molecules **I** and **II** both exhibit enantiotropic smectic A and smectic C phases. Their transition temperature diagrams are:

$$\mathbf{I}\quad \mathrm{Cr} \xrightleftharpoons[38.4^\circ\mathrm{C}]{57.1^\circ\mathrm{C}} \mathrm{SmC}^* \xrightleftharpoons[72.6^\circ\mathrm{C}]{73.5^\circ\mathrm{C}} \mathrm{SmA} \xrightleftharpoons[77.2^\circ\mathrm{C}]{78.9^\circ\mathrm{C}} I$$

$$\mathbf{II}\quad \mathrm{Cr} \xrightleftharpoons[2.9^\circ\mathrm{C}]{46.7^\circ\mathrm{C}} \mathrm{SmC}^* \xrightleftharpoons[78.2^\circ\mathrm{C}]{77.8^\circ\mathrm{C}} \mathrm{SmA} \xrightleftharpoons[86.6^\circ\mathrm{C}]{87.8^\circ\mathrm{C}} I$$

For compound **I**, the X-ray interlamellar distance found in the smectic A phase is 39.5 Å. The Guillon–Skoulios relation [17] is then applied to determine the tilt angle in the smectic C phase. The tilt angle behaviour versus temperature is shown in the figure.

The polymorphism of both molecules is analogous to that of the homologous molecule which does not contain the nitro group [10]. Nevertheless, the transition temperatures for molecules **I** and **II** are lowered. This variation is actually in agreement with Gray's results [18]: the nitro group broadens the molecules, and therefore tends to decrease the thermal stabilities of the mesophases.

A value of $120\,\mathrm{nC\,cm^{-2}}$ at 65°C was found for the spontaneous polarization of molecule **I**. However, as pointed out by Guillon [19], the presence of a small enantiomeric excess (e.e.) obviously decreases the value of $\mathbf{P}_\mathrm{S}$. Since this e.e. for molecule **I** is lower than 88% due to the diastereomeric excess (88%) of molecule **4**, higher values of $\mathbf{P}_\mathrm{s}$ are expected.

Molecule **I** possesses a chiral centre directly linked to the NLO chromophore group, and exhibits the smectic C phase in its polymorphism. Nevertheless, a direct steric coupling is obtained when the nitro group is in the *ortho*-position to the chiral centre. Such a molecule, molecule **II**, exhibits the smectic C phase in its polymorphism, but investigations are presently in progress to make it optically active. Comparison between molecules **I** and **II** will be the subject of a forthcoming publication.

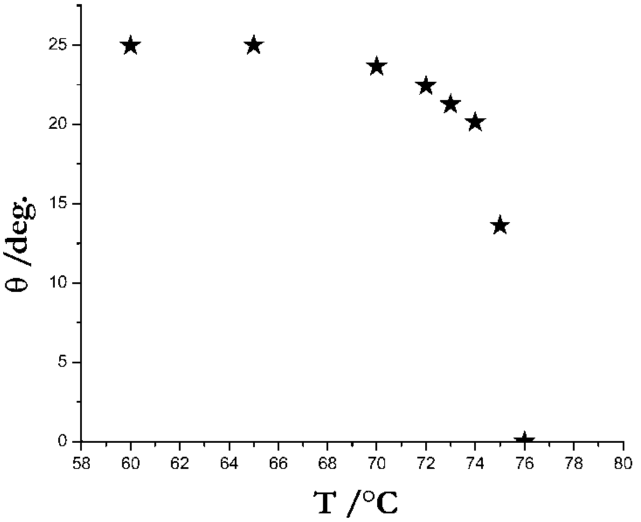


Figure. Tilt angle of the director in the chiral smectic C phase of molecule **I** with respect to the temperature.

4. Conclusion

In conclusion, we report the synthesis, polymorphism determination and the first measurement of $\mathbf{P}_\mathrm{s}$ of a molecule which possesses a chiral centre directly linked to the chromophore group. To observe the influence of such a design on the macroscopic NLO properties, hyperpolarizability measurements must be performed. Nevertheless, molecules **I** and **II** open the way to a new family of smectogen C molecules specifically designed to exhibit enhanced NLO properties.

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