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# Effect of heteroatom exchange (S/Se) in the mesomorphism and physical properties of benzochalcogenodiazole-based liquid crystals

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ABSTRACT

In order to investigate the effect on the structure-property relationship by the exchange of sulfur atom by selenium, a new series of fluorescent calamitic liquid crystals based on 4,7-disubstituted-2,1,3-benzoselenadiazole was successfully synthesized and characterized. The mesomorphic properties were studied by differential scanning calorimetry, polarized optical microscopy and X-ray diffraction. Thermal properties have evidenced the influence of changing sulfur by selenium atom in the formation of liquid crystalline phases and mesomorphism range. Photophysical studies were performed in chloroform solution, where these compounds displayed strong orange luminescent under UV light, with relevant quantum yields ($\Phi_F$ = 0.14–0.16) and greater solvatochromic dependence. Electrochemical studies showed oxidation and reduction patterns similar to 2,1,3-benzothiadiazoles analogues, however presenting lower band gap.

## 1. Introduction

Organic molecules able to exhibit liquid crystalline phases are of great interest for many areas of applied science, for instance, as organic light-emitting diodes (OLEDs), display technology (LCD), organic field effect transistors (OFETs), organic photovoltaic devices (OPVs), anisotropic ion transportation, and photo- and semiconducting materials [1–3]. Among these liquid crystalline behavior, molecules exhibiting smectic (Sm) and columnar phases are good candidates for applications as charge carrier mobility due to their arrangement in the mesophase [4]. In this way, the rational molecular design of new thermotropic liquid crystals for applications in advanced functional materials involves the selection of an appropriate central core, linking and peripheral group. Over several years, a large number of LC compounds containing heterocyclic central units have been synthesized. Heterocycles rings such as oxadiazoles [5–8], thiadiazoles [9,10], triazoles [11,12], pyrazoles [13,14] and isoxazoles [15] have been much investigated. Beyond these heterocycles, our group has experience in the synthesis and study of fluorescent thermotropic liquid crystals π-conjugated based on the 2,1,3-benzothiadiazole (BTD) [16–18].

In recent years, comparison of the effects caused by the presence of S or Se as heteroatom is becoming common for polymer and fluorophores [19–21], but extremely rare for LCs work. In terms of molecular design, selenium atom has larger size, less electronegativity, and is softer and more easily polarized than sulfur, what could have an important influence on the thermal, optical and electrochemical properties of selenium derivatives [4,22].

Mindful of the potential of benzochalcogendiazole, another interesting heterocycle is the 2,1,3-benzoselenadiazole (BSe). The BSe is similar to BTD with respect to strong and stable fluorescence, good thermal stability and good electron-withdrawing ability [23].

Herein, we describe the synthesis, characterization and study of thermotropic liquid crystals based on the heterocycle BSe with different alkoxy chains, rationalizing the impact of the exchange in the chemical and physical properties of these liquid crystals when compared to published data from BTD [24].

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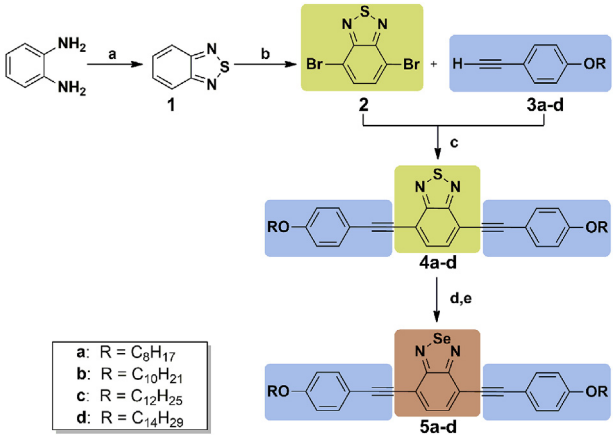


**Scheme 1.** Synthesis of the final compounds **5a-d**.

## 2. Results and discussion

### 2.1. Synthesis

The synthetic route followed for the preparation of the final compounds based on 2,1,3-benzoselenadiazole **5a–d** is presented in Scheme 1. The synthesis follows the same procedure already adopted in ours previous works [16,24]. It starts from the condensation of *o*-phenylenediamine with thionyl chloride and bromination of the heterocycle to obtain the 4,7-dibromo-2,1,3-benzothiadiazole (**2**). The Sonogashira coupling reaction between the aryl dibromide **2** and two equivalents of terminal aryl acetylenes **3a–d** allowed to obtain the intermediates molecules **4a–d**. The 2,1,3-benzothiadiazole molecules underwent procedures for sulfur extrusion with sodium borohydride and catalytic cobalt chloride in mixture of ethanol/tetrahydrofuran (1:1) to obtain the respective diamines in 62–88% yield [25]. In the literature, some works report about the instability of similar diamines [26,27], for this reason after isolation and purification the last reaction was performed immediately without characterization. The target compounds **5a-d** were obtained by cyclization of the diamines intermediates with selenium oxide in a mixture of ethanol/THF as solvent under heating. After purification by chromatograph column, the desired final compounds were obtained in good yields (52–88%). All final compounds **5a–d** synthesized were characterized by $^{1}H$ and $^{13}C$ NMR, mass spectrometry and IR spectroscopy.

### 2.2. Liquid crystalline behavior

The mesomorphic behavior of compounds **5a-d** was characterized and studied by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The transition temperatures and enthalpy values for the final compounds are summarized in Table 1. The liquid crystalline properties of final compounds were confirmed by X-ray diffraction (XRD). The investigation of the thermal stability of the target molecules was performed by thermogravimetric analysis (TGA), which indicated high thermal stability, with decomposition temperatures above 401 °C, under nitrogen atmosphere. The thermal stability of the benzoselenadiazole compounds **5a-d** is clearly lower than the corresponding benzothiadiazole **4a-d.**

All final compounds **5a-d** exhibited liquid crystalline behavior presenting exclusively smectic mesophases. The textures observed by POM on cooling from the isotropic liquid were identified as smectic phase, what is consistent with the molecular anisometry of these compounds. On the cooling cycle it is possible to observe the growth from the isotropic melt of elongated gems or smectic *bâtonnets,* revealing the transition Isotropic-smectic [28]. It is important to emphasize that all the intermediate molecules **4a-d** also present mesomorphic behavior however displaying nematic and smetic phases [24].

**Table 1**
Phase transition temperatures (°C) and enthalpies (kJ mol$^{-1}$) for compounds **4a-d** and **5a-d.**

| Compound | Transition[d] | T/°C, heating (ΔH/kJ mol$^{-1}$)[a] | T/°C, cooling (ΔH/kJ mol$^{-1}$)[a] | $T_{dec.}$/°C[b] |
|---|---|---|---|---|
| **4a** | Cr-N | 141 (91.8) | 133 (- 90.7) | 448 |
| | N-I | 176 (3.5) | 175 (- 3.6) | |
| **5a** | CrI-CrII | 28 (5.3) | 11 (−6.2) | 409 |
| | CrII-SmC | 155 (12.5) | 146 (−14.4) | |
| | SmC-I | 189 (1.8) | 186 (−0.7) | |
| **4b** | Cr-N (Cr-SmC)[c] | 128 (63.2) | 114 (−65.9) | 468 |
| | (N-SmC)[c] | – | 130 (−5.0) | |
| | N-I | 157 (2.6) | 157 (−3.1) | |
| **5b** | CrI-CrII | 57 (25.3) | 39 (−20.3) | 415 |
| | CrII-SmC | 147 (17.1) | 134 (−19.9) | |
| | SmC-I | 200 (10.2) | 196 (−8.4) | |
| **4c** | CrI-CrII | – | 105 (−9.8) | 481 |
| | CrII-SmC | 119 (65.6) | 113 (−50.4) | |
| | SmC-N | 143 (4.7) | 142 (−4.4) | |
| | N-I | 152 (3.5) | 151 (−4.7) | |
| **5c** | CrI-CrII | 77 (22.8) | 60 (−18.3) | 401 |
| | CrII-SmC | 134 (18.4) | 119 (−15.1) | |
| | SmC-I | 191 (3.5) | 187 (−3.6) | |
| **4d** | Cr-SmC | 96 (81.6) | 77 (−58.3) | 445 |
| | SmC-N | 115 (39.6) | 108 (−30.6) | |
| | N-I | 146 (11.8) | 142 (−11.7) | |
| **5d** | CrI-CrII | 88 (37.5) | 63 (−28.9) | 405 |
| | CrII-SmC | 133 (31.2) | 108 (−33.8) | |
| | SmC-I | 190 (15.5) | 188 (−12.7) | |

[a] Determined by POM and DSC measurements (10 °C/min) on second heating cycle.
[b] Determined by TGA, onset of decomposition in nitrogen (20 °C/min).
[c] Observed on cooling cycle.
[d] Cr = Crystal, N = Nematic, SmC = Smectic C, I = Isotropic liquid.

The presence of the smectic C (SmC) phase was confirmed from the microscopic observation of the characteristic *striated* texture, followed by the appearance of a *broken fan-shaped* texture. Two representative photomicrographs of the natural texture for the compounds **5c** and **5d** are presented in Fig. 1. A characteristic *schlieren* texture typical of SmC phase it is observed at 186 °C for **5c** (Fig. 1a) and a broken fan-shaped texture for **5d** at 158 °C (Fig. 1b). Interestingly different from benzothiadiazoles **4a-d**, the formation of nematic mesophases for benzoselenadiazole-based molecules has not been observed, demonstrating the impact of the selenium atom on such systems. The exchange of

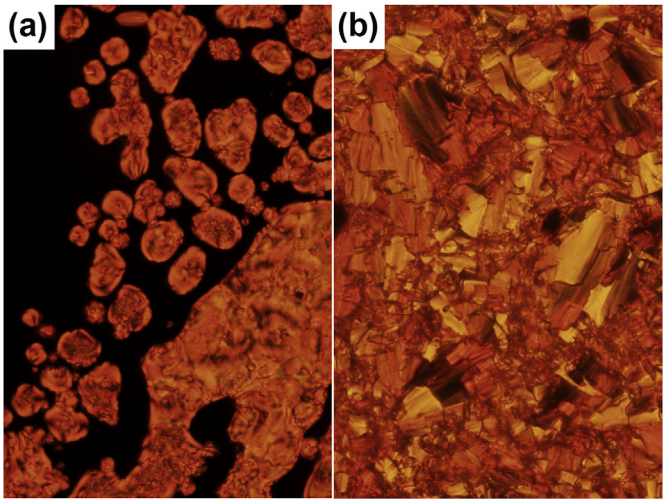


**Fig. 1.** Polarized optical photomicrographs of compounds **5c** at 186 °C (left) and **5d** at 158 °C (right) on cooling cycle.