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# Bent-Core Liquid Crystals: Structures and Mesomorphic Properties

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## Abstract

Bent-core (BC) molecules became an attractive liquid crystal class due to their potential use in smart displays and photonic devices. In contrast to calamitic mesogens, bent-shaped mesogens are self-organized superstructures with remarkable properties, given the presence of polar order in mesophases, although the molecules themselves are not chiral. A particular interest represents the biaxial nematic liquid crystal materials that are used in display technology and allow a faster switching response, compared to calamitic liquid crystals, with considerably reduced costs. This chapter briefly reviews the bent-core liquid crystals with three different core units in the structure: (1) 2,5-disubstituted oxadiazole, (2) 1,3-disubstituted benzene, and (3) 2,7-disubstituted naphthalene. To the central bent units (BUs) containing reactive functional groups of phenolic or aminic type, various mesogenic groups are symmetrically or asymmetrically connected, via esterification or condensation reactions. The obtained compounds showed biaxial nematic and/or smectic mesophases with high transition temperatures in the case of oxadiazole derivatives or cholesteric and banana-type mesophases with lower transition temperatures in the case of benzene and naphthalene derivatives.

**Keywords:** liquid crystals, bent-core molecules, resorcinol, naphthalene, oxadiazole, azomesogens, biaxial, nematic, smectic, cholesteric

## 1. Introduction

Liquid crystal displays (LCDs) are omnipresent in modern world, representing probably the most prevalent, developed, and profitable technology of thermotropic liquid crystals [1, 2]. This application is based on their sensitivity to external electric and magnetic fields, when molecules align fast and at low voltages. This property was the basis for their use in other interesting applications, especially as sensors. Because of their fluid nature at a certain temperature, liquid crystals (LCs) are very easy to process in thin films, along with maintaining optical properties characteristic to crystalline materials, as the ability to rotate the polarized light plane (birefringence).

The discovery of portable devices and the introduction of easily used tactile displays resulted in a new change of direction in LCD technologies. Present researches focus on synthesis, characterization, and analysis of new mesogenic structures with high dielectric anisotropy ( $\Delta\epsilon$ ) (for inducing the decrease of voltage), low

rotational viscosity ( $\gamma_1$ ) (allowing fast switching), birefringence ( $\Delta n$ ) suitable to accurate display design, good solubility, and a broad nematic phase domain [2].

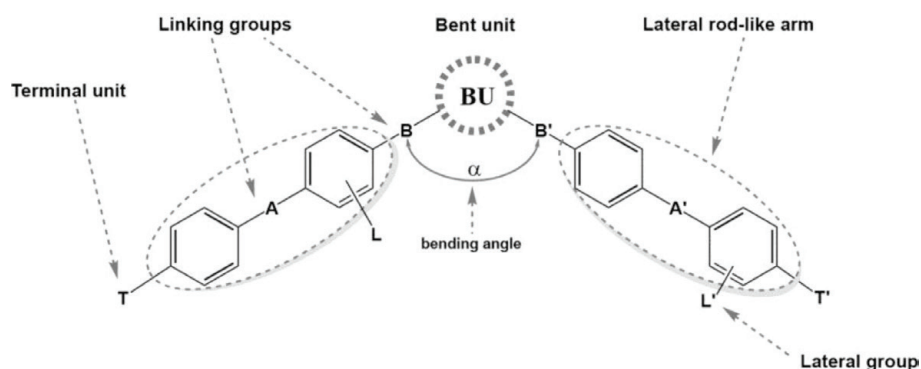
The increasing interest for bent-core (BC) liquid crystals in the past two decades is due to their ability to provide potential devices with fast switching response [3–7]. Therefore, the main purpose was to analyze the relation between biaxial molecular structures and electro-optical properties in this type of compound. From a technical point of view, the main objective is to look for the improvement of response time in order to reduce the motion effect in the case of large TVs and in displaying information in the case of tactile devices, respectively. The development of reliable functional materials that allow reduced chemical production cost was also considered [8].

Because of the bent shape that strongly deviates from linear symmetry axis, bent-core biaxial molecules are capable of special steric interactions, caused by the tendency to reduce the rotational disordering around the long axis. The bent-core molecules are preferentially packed into bent directions and parallelly aligned to each layer. Because of this imposed framing, each layer presents a spontaneous polarization (Ps), which is parallel or antiparallel to the molecular bent direction, while the molecules present the properties of switching without chirality, particularly useful for display screens. The existing bending angle between the arms permits the formation of unique self-organized systems with mesophases having no counterpart in conventional calamitic liquid crystals [4–7].

The special properties of biaxial molecules stimulated the researches in the field, so that a large number of banana-type compounds with various fragment structural combinations have been synthesized [9–17].

In banana-type compounds, eight different complex mesophase morphologies have been identified until now ( $B_1, B_2, \dots, B_8$ ), the distinction between phases being made on the basis of optical textures and characteristic differences in X-ray diffraction diagrams [18–22]. Literature data showed that the appearance of B-type mesophases depends mainly on an adequate combination between central unit and lateral rigid units. The general structure of BC molecules includes two symmetrical/asymmetrical mesogenic units of rod-like type connected to central units by linking groups (**Figure 1**). Usually, the angle between the arms depends mainly on the type of the connecting groups (around  $120^\circ$  and  $140^\circ$ ) [23, 24].

Although remarkable progresses have been realized in thermal analysis, a precise correlation between BC chemical structures and their physical properties is still not possible, as for calamitic liquid crystal molecules. In many cases, molecules that present banana-type mesophases have a bent shape, but this does not always assure the mesophase appearance. Data show that for the appearance of B mesophases, two factors are necessary: (1) adequate distribution of charges along the arms [25] and (2) adequate bending angle [24].



**Figure 1.**  
General structure of banana-type liquid crystals.

The properties of biaxial liquid crystals can be influenced by the substituents of central nucleus, lateral arms, and terminal units. The central aromatic core generally consists of naphthalene, benzene, and heterocyclic units. A considerable influence may have the linking groups used for connecting the chemical structures. The most used connecting groups are of ester, azomethine, azo, stilbene, thiocarbonyl, or acryloyloxy type [26, 27]. The withdrawing or donating electronic groups may strongly affect the electronic density, the molecular flexibility, and the partial polarity of the molecule [25, 28]. The most interesting banana-type mesogenic compounds which presented switchable mesophase have been the ones containing azomethine groups. However, this linking group is thermally unstable in the presence of acidity and metallic surfaces, and some Schiff bases decomposing around 150°C, while others are stable up to 200°C.

Bent-core molecules containing azo linkages present remarkable properties because of the association of the photosensitive nature of azobenzene derivatives with ferroelectric liquid crystalline properties of BC compounds [13, 16, 29]. Although the first bent-core azo liquid crystalline compound was prepared by Vorländer in 1929, the pioneering work has been done by Prasad et al. who synthesized compounds containing aromatic rings and azo groups and presenting smectic phases [30]. Because of *trans-cis* photochemical isomerization of the azobenzene moiety, configurational modifications appear with significant changes on physical properties targeting dipole moment, refractive index, or viscosity [13].

The lateral substitution has a strong impact on liquid crystalline state or mesophase stability, respectively [31, 32]. The packing of molecules may be affected by size, polarity, and substitution position. The liquid crystalline properties may completely disappear after the introduction of bulky lateral substituents. Sometimes, interesting modifications have been observed in the switching behavior after the introduction of small polar substituents [9, 31, 33–35].

Hence, the study of biaxial LC based on bent-core units represents a very actual subject not only from a theoretical point of view but also for designing materials with special properties [36, 37]. The existence of a stable biaxial nematic mesophase can lead to a whole class of devices based on liquid crystals able to considerably improve the switching properties or behave as optical compensation films [38].

This chapter proposes to describe the relationship between the structure and supramolecular ordering properties of symmetrical and asymmetrical bent-core liquid crystals synthesized by our research group. In order to keep this chapter within a certain length, the detailed study on synthesis and complete characterization of compounds is not included here and may be found in the original papers [39–53]. In the following sections, the transition temperature (°C) and the type of mesophase for each compound are given below its chemical structure, while transitions in square brackets refer to monotropic phase. The phase behavior will be discussed in the text, where B stands for banana phase, Cr for crystal, LC for liquid crystal, Iso for isotropic phase, N for nematic phase, Sm for smectic phase, Ch for cholesteric phase, and d for decomposition process.

## **2. Relationship between structure and liquid crystalline properties**

The mesomorphic behavior of bent-core compounds synthesized in our group was described through a systematic study that reviewed the nature of central bent core; the position, size, and the role of lateral substitution in the central unit; the symmetry or non-symmetry of rigid calamitic wings; the length, polarity, and micro-segregation of the terminal flexible chains; and the presence of the cholesteric moiety. The influence of the structure of calamitic wings was also considered,

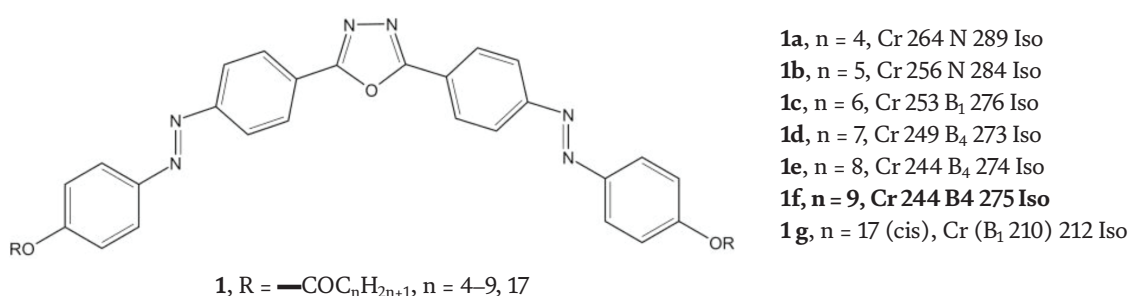
regarding the number of aromatic rings and the nature of linking groups that contribute through polarity, orientation, and flexibility.

According to their core, banana-shaped compounds were divided into three categories: (1) 2,5-disubstituted oxadiazole; (2) 1,3-disubstituted benzene; and (3) 2,7-disubstituted naphthalene.

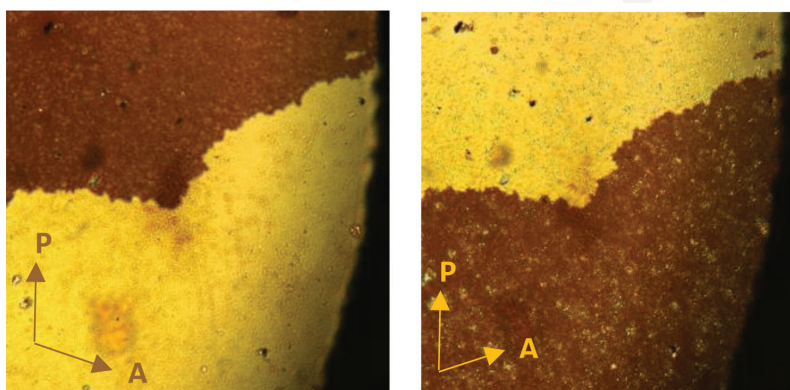
## 2.1 Bent-core compounds based on oxadiazole core

Among heterocyclic liquid crystals, the central unit in 2,5-disubstituted-[1,3,4] oxadiazoles assures the optimum geometry for bent-shaped molecules. Generally, the bending angle determined by the presence of 2,5-disubstituted oxadiazole central unit is between  $134$  and  $140^\circ$ , larger than the typical value of  $120^\circ$  in 1,3-disubstituted benzene unit. Moreover, the presence of three polarizable heteroatoms causes a high dipole moment that affects phase transition temperatures and mesophase types. Therefore, the presence of bent-shape and dipolar nature of the oxadiazole core together makes these compounds very attractive for applications.

When the central unit is symmetrically substituted with two azobenzene units with alkanoyloxy flexible chain ends (compound **1**), the mesomorphic properties vary with the number of carbon atoms.



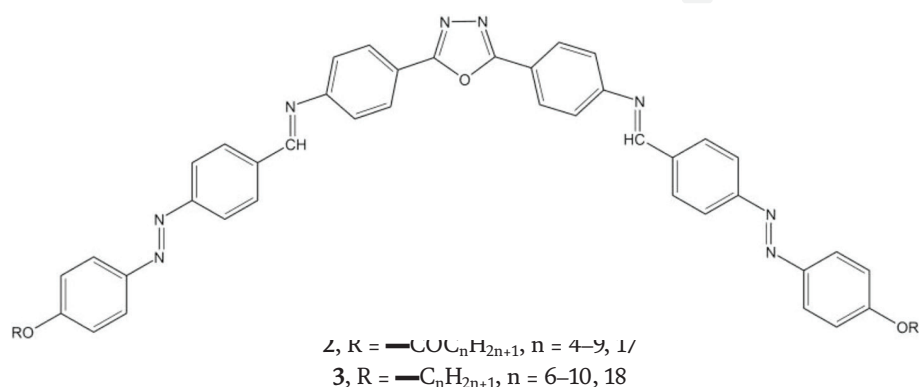
Thus, for compounds of type **1** containing a smaller number of carbon atoms ( $n = 4, 5$ ), the mesophase is of nematic type with characteristic Schlieren texture. The change occurs for  $n = 6$ , when the compound shows the lowest liquid crystalline domain on heating, but dendritic-like texture on cooling, characteristic of B<sub>1</sub> phase [39]. Further increase of carbon atoms results in progressive growth of the mesomorphic intervals, with B<sub>4</sub> chirally separated domains, evidenced on cooling by dark and bright domains after rotation of one of the polarizers clockwise or anticlockwise from the crossed ( $90^\circ$ ) position (**Figure 2**). On the other hand, the



**Figure 2.** Textures of B<sub>4</sub> chiral domains' phase of compound **1f** at  $T = 175^\circ\text{C}$  between slightly de-crossed polarizers from  $90^\circ$  by about  $\pm 5^\circ$ .

introduction of elaidic or oleic units ( $n = 17$ , *cis*, *trans*) on the terminal chain destabilizes (**1 g**, monotropic) or suppress the mesophase.

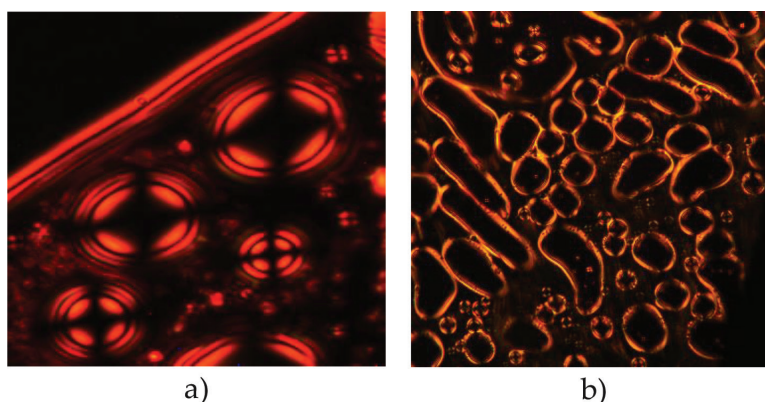
Compounds of type **2**, containing one more benzene ring in each side arm and azomethine linking groups, exhibited a rich polymorphism, induced by repulsion effects between the hydrogen atom of the azomethine group and the aromatic system. The compounds presented smectic phase and/or characteristic nematic droplets or Schlieren textures on broad domains (between 89 and 169°C), which go up to high transition temperatures (higher than 330°C), with decomposition before isotropization [40]. Thermal degradation studies revealed that the compounds with even methylene groups show a lower stability compared to those with odd ones [41].



**2a**,  $n = 4$ , Cr<sub>1</sub> 228 Cr<sub>2</sub> 244 Sm 264 N 333 Iso (d)  
**2b**,  $n = 5$ , Cr<sub>1</sub> 214 Cr<sub>2</sub> 232 N 342 Iso (d)  
**2c**,  $n = 6$ , Cr<sub>1</sub> 80 Cr<sub>2</sub> 134 N 253 Iso (d)  
**2d**,  $n = 7$ , **Cr<sub>1</sub> 64 Cr<sub>2</sub> 174 Sm 219 N 343 Iso (d)**  
**2e**,  $n = 8$ , Cr<sub>1</sub> 193 Cr<sub>2</sub> 204 Sm 249 N 321 Iso (d)  
**2f**,  $n = 9$ , Cr<sub>1</sub> 192 Cr<sub>2</sub> 204 Sm 234 N 332 Iso (d)  
**2g**,  $n = 17$ , Cr<sub>1</sub> 96 Cr<sub>2</sub> 194 N 335 Iso (d)

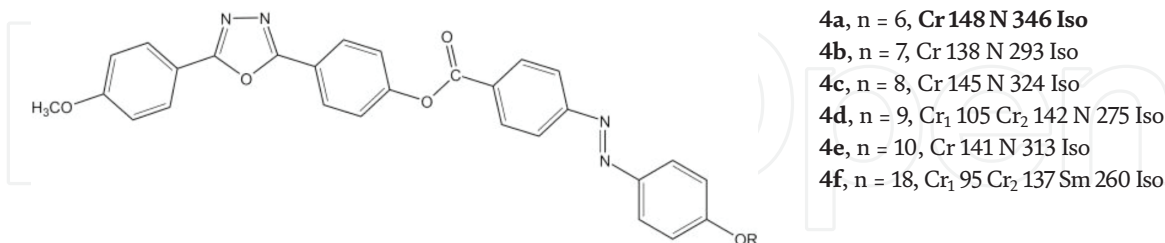
**3a**,  $n = 6$ , Cr<sub>1</sub> 113 Cr<sub>2</sub> 254 N 326 Iso  
**3b**,  $n = 7$ , Cr 239 N 327 Iso  
**3c**,  $n = 8$ , Cr 229 N 330 Iso  
**3d**,  $n = 9$ , Cr 219 N 322 Iso  
**3e**,  $n = 10$ , **Cr 184 N 321 Iso**  
**3f**,  $n = 18$ , Cr 172 N 280 Iso

Replacing the acyloxy terminal chain with an alkoxy one in compounds of type **3** results in decreasing the isotropization temperatures alongside with mesomorphic domains. For this class, the compound with 10 carbon atoms in the aliphatic chain showed the highest stability of mesophase. All compounds presented similar polymorphism to that of **2**, analogous with nematic droplet phases or Schlieren textures, characteristic of bent-core compounds (**Figure 3**).



**Figure 3.**  
Optical micrographs of mesophases: (a) **3a**, 285°C, heating; (b) **3e**, 205°C, cooling.

The asymmetric hockey-stick derivatives of type **4** showed the widest mesophase domains (between 123 and 198°C), compared to compounds **1–3** [42]. The mesophase behavior was explained by the strong dipolar interactions between molecules, determined by the asymmetric substitution of the oxadiazole core with a shorter side arm, where the molecules bend is not emphasized as for classical bent-core compounds.



**4a**, n = 6, Cr 148 N 346 Iso  
**4b**, n = 7, Cr 138 N 293 Iso  
**4c**, n = 8, Cr 145 N 324 Iso  
**4d**, n = 9, Cr<sub>1</sub> 105 Cr<sub>2</sub> 142 N 275 Iso  
**4e**, n = 10, Cr 141 N 313 Iso  
**4f**, n = 18, Cr<sub>1</sub> 95 Cr<sub>2</sub> 137 Sm 260 Iso

**4**, R = —C<sub>n</sub>H<sub>2n+1</sub>, n = 6–10, 18

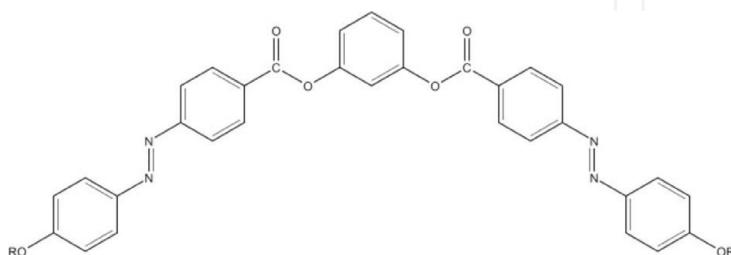
As for previous compounds, the stability of mesophases follows the odd-even effect, because of changing the ability to order into mesophase. Thus, the increase of aliphatic chain to 18 carbon atoms induces changes in supramolecular ordering, which leads to the narrowest mesophase range. All the compounds showed mesophases ordered into nematic phases of ribbon type or with characteristic Schlieren textures. The last compound of the series (n = 18) presented smectic textures.

## 2.2 Bent-core compounds based on benzene core

1,3-Disubstituted benzene derivatives represent the first class of synthesized bent-core liquid crystals, with the largest number of reported compounds [22]. Our studies are based on two types of benzene core: resorcinol and 1,3-diaminobenzene.

### 2.2.1 Resorcinol central unit

The symmetric disubstitution of resorcinol with dimeric azomesogens or imino-azo mesogens with terminal flexible chains results in mesomorphic compounds evidencing Sm or B phases with relatively stable mesophase domains. In the case of compound **5a**, SmB dendritic textures were identified from isotropic melt that changed into a B<sub>1</sub> mosaic one at lower temperature [43].



**5**, R = —C<sub>n</sub>H<sub>2n+1</sub>, n = 6–10

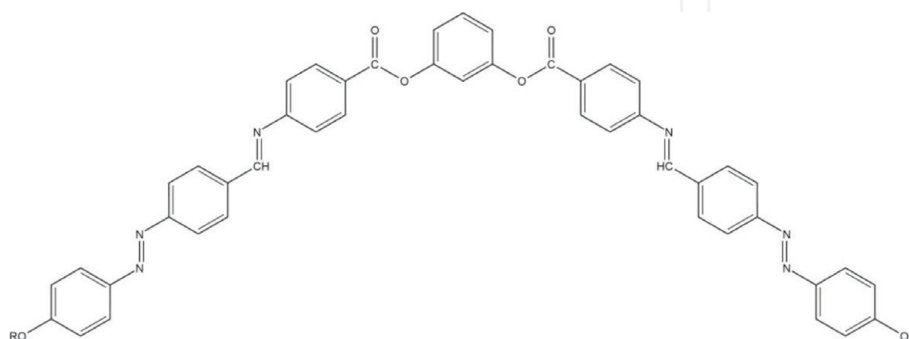
**5a**, n = 6: Cr<sub>1</sub> 116 Cr<sub>2</sub> (SmB 163) 168 Iso  
**5b**, n = 7: Cr<sub>1</sub> 111 Cr<sub>2</sub> 142 SmB 163 Iso  
**5c**, n = 8: Cr<sub>1</sub> 94 Cr<sub>2</sub> 143 SmB 159 Iso

**5d**, n = 9: Cr<sub>1</sub> 100 Cr<sub>2</sub> 147 Iso  
**5e**, n = 10: Cr<sub>1</sub> 100 Cr<sub>2</sub> 148 Iso

Increasing the alkyl chain to 7 (compound **5b**) and 8 (compound **5c**) carbon atoms stabilized the mesophase but only on a relatively narrow interval of

temperature. Further increase in the length of the chain completely destabilized the liquid crystalline behavior due to the disorder induced by the flexible unit in relation to the rigid one, so compounds **5d** and **5e** are non mesomorphic [43].

Compounds **6a–e** show predominantly smectic phases with characteristic fan-shaped textures [44]. Oily streak texture was identified in the case of compound **6e** on first heating, that poorly developed into fan-like textures with striations across individual fans from the isotropic melt (**Figure 4a, b**). The mesophase domains are better stabilized for the first (**6a**) and the last compounds (**6e**) of this series. The insertion of polar acyloxy linkage between terminal chain and aromatic ring increases the physical interactions between molecules, with consequences on the isotropization temperatures together with increases of the mesophase domains at around 30°C (compound **7a**) [44].

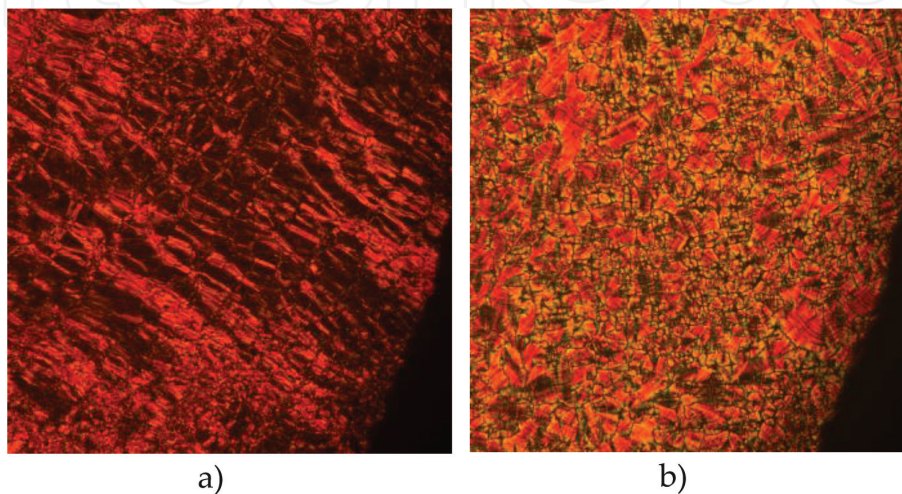


**6**, R =  $\text{—C}_n\text{H}_{2n+1}$ , n = 6–10  
**7**, R =  $\text{—COC}_n\text{H}_{2n+1}$ , n = 5–9

**6a**, n = 6: Cr<sub>1</sub> 159 Cr<sub>2</sub> 181 Cr<sub>3</sub> 215 Sm 294 Iso  
**6b**, n = 7: Cr<sub>1</sub> 151 Cr<sub>2</sub> 181 Cr<sub>3</sub> 213 Sm 276 Iso  
**6c**, n = 8: Cr<sub>1</sub> 136 Cr<sub>2</sub> 202 B<sub>1</sub> 267 Iso  
**6d**, n = 9: Cr 195 B<sub>3</sub> 260 Iso  
**6e**, n = 10: Cr<sub>1</sub> 152 Cr<sub>2</sub> 177 B<sub>3</sub> 259 Iso

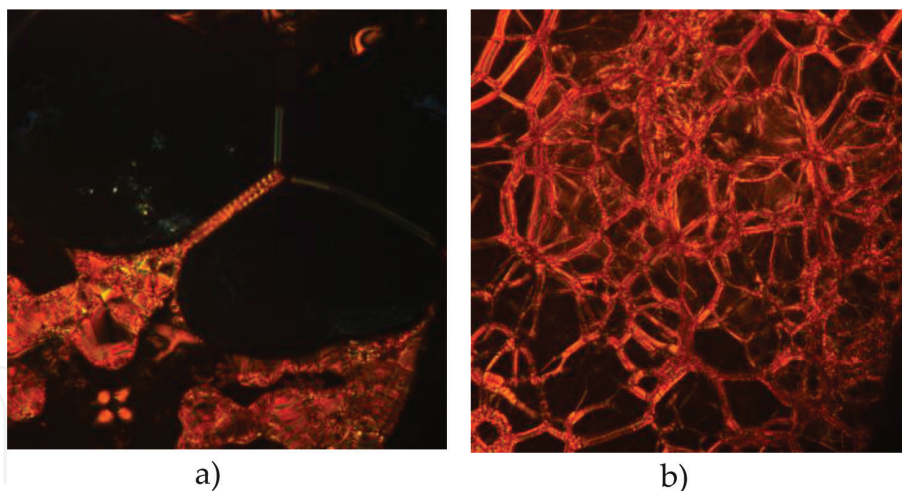
**7a**, n = 5: Cr<sub>1</sub> 169 Cr<sub>2</sub> 202 Sm 315 Iso  
**7b**, n = 6: Cr<sub>1</sub> 164 Cr<sub>2</sub> 209 Sm 304 Iso  
**7c**, n = 7: Cr<sub>1</sub> 146 Cr<sub>2</sub> 207 Sm 285 Iso  
**7d**, n = 8: Cr<sub>1</sub> 148 Cr<sub>2</sub> 202 Sm 288 Iso  
**7e**, n = 9: Cr<sub>1</sub> 148 Cr<sub>2</sub> 195 B<sub>2</sub> 287 Iso

As for previous compounds of type **6**, predominately smectic phases were identified on heating and nematic and smectic phases on cooling, respectively. However, banana B<sub>7</sub> phase has been identified in the case of compound **7b** on cooling from the isotropic melt, with characteristic spiral and circular domains and equidistant line pattern (**Figure 5a**). Thin filament texture in a spiral fashion network, which preceded smectic phase, was visible on heating for compounds **7d** and **7e** (**Figure 5b**).



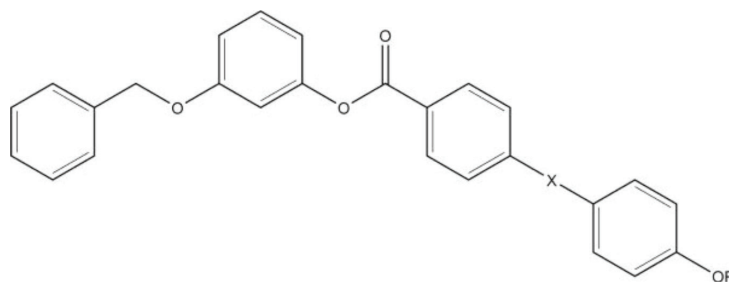
**Figure 4.**  
Optical micrographs of mesophases of compound **6e**, (a) 195°C, heating; (b) 170°C, cooling.





**Figure 5.**  
Optical micrographs of mesophases: (a) **7b**, 280°C, cooling and (b) **7e**, 280°C, heating.

The asymmetric disubstitution of resorcinol resulted in bent-core compounds containing only one typical mesogenic arm, formed by two aromatic rings connected via ester or azo linking groups and containing alkyloxy terminal flexible chains, while the other arm contained only a benzyl unit [45]. In this case, the liquid crystalline behavior depends on the type of the linkage between the aromatic rings in the long arm. Hence, the presence of azo linkage allows the formation only of monotropic phases (compounds **8a–e**).



**8**, X = —N=N—, R = —C<sub>n</sub>H<sub>2n+1</sub>, n = 6–10

**9**, X = —OCO—, R = —C<sub>n</sub>H<sub>2n+1</sub>, n = 6–10

**8a**, n = 6: Cr (B<sub>1</sub> 95) 113 Iso

**8b**, n = 7: Cr (B<sub>1</sub> 65) 121 Iso

**8c**, n = 8: Cr (B<sub>1</sub> 95) 117 Iso

**8d**, n = 9: Cr (B<sub>1</sub> 86) 100 Iso

**8e**, n = 10: Cr (N 87) 97 Iso

**9a**, n = 6: Cr 46 B<sub>1</sub> 105 Iso

**9b**, n = 7: Cr (B<sub>1</sub> 65) 106 Iso

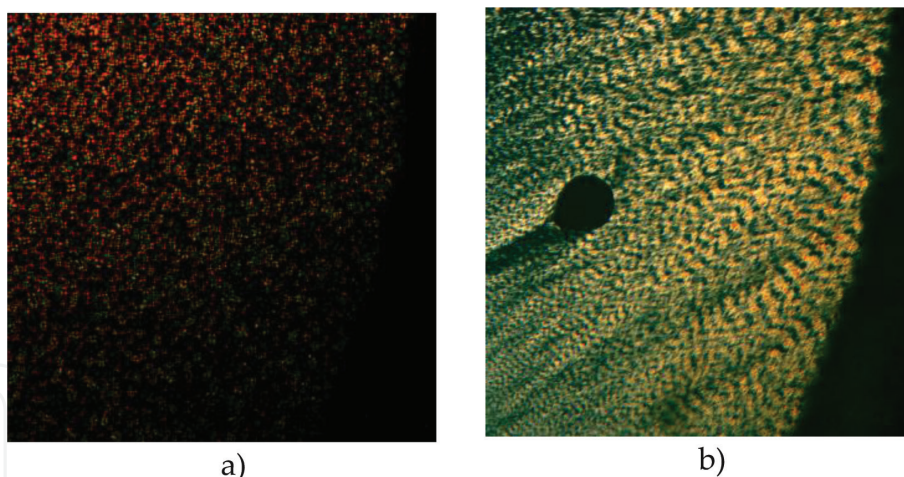
**9c**, n = 8: Cr 75 B<sub>1</sub> 94 Iso

**9d**, n = 9: Cr (B<sub>1</sub> 45) 90 Iso

**9e**, n = 10: Cr 71 B<sub>x</sub> 90 Iso

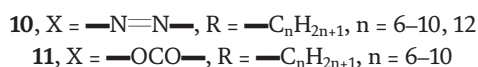
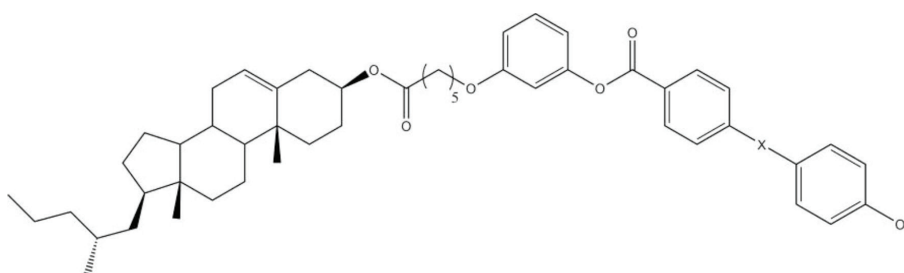
The mesophase appearance was identified mainly as mosaic textures of the banana B<sub>1</sub> phase that precedes the focal conic domains from isotropic melt on cooling (**Figure 6a**) for compounds **8a–8d**, while the increase of the terminal chain to 10 carbon atoms favors the formation of the nematic phase.

In contrast to compounds **8a–8e**, the presence of the carbonyloxy linkage in compounds **9a–9e** stabilizes the mesophase mostly into enantiotropic behavior, with typical cylindrical focal conic domains that succeed the nematic phase on cooling. In the case of compound **9d**, the coexistence of a fingerprint-like texture and a focal pseudo-isotropic region (black) was observed on cooling (**Figure 6b**). It was noted that the liquid crystalline behavior and transition temperatures follow the odd-even effect in accordance with the number of carbon atoms in the terminal alkyl chain, the most stable mesophases being evidenced by compounds with an even number of carbon atoms.



**Figure 6.**  
 Optical micrographs of mesophases: (a) **8b**, 65°C; cooling and (b) **9d**, 43°C, cooling.

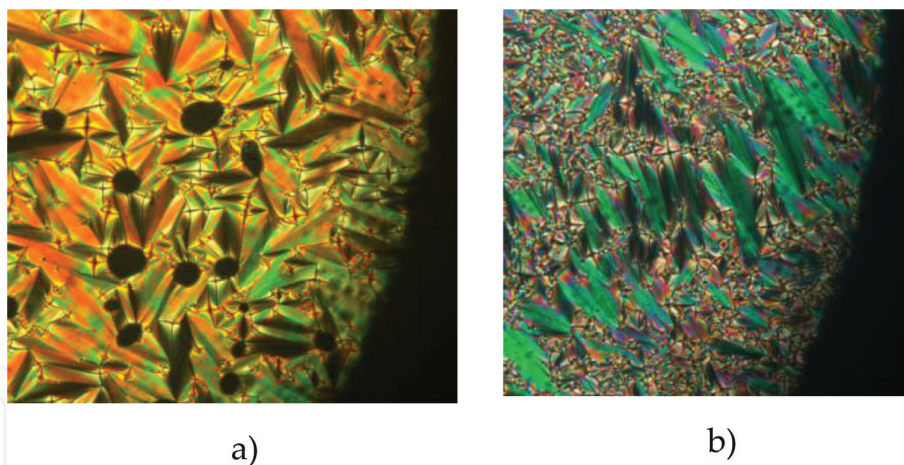
When benzyl unit in compounds **8** and **9** is replaced by a cholesteryl moiety linked by a pentamethylene flexible spacer to resorcinol (compounds **10** and **11**), the liquid crystalline behavior changed significantly [46].



**10a**, n = 6: Cr 59 Sm 146 Iso  
**10b**, n = 7: Cr 83 Sm 142 Iso  
**10c**, n = 8: Cr 77 Sm 133 Iso  
**10d**, n = 9: Cr 78 Sm 133 Iso  
**10e**, n = 10: Cr 80 Sm 122 Iso  
**10f**, n = 12: Cr 82 Sm 97 Iso

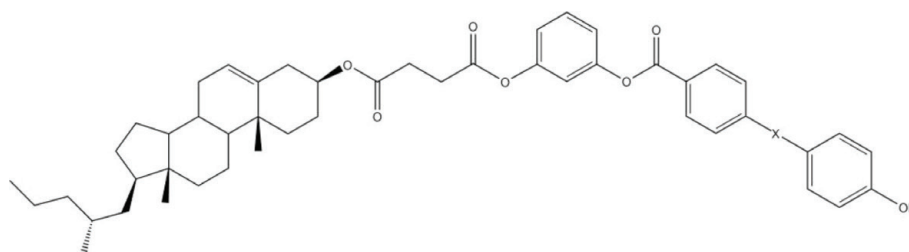
**11a**, n = 6: Cr<sub>1</sub> 33 Cr<sub>2</sub> 52 Cr<sub>3</sub> 91 Sm  
**109 Sm 115 Iso**  
**11b**, n = 7: Cr<sub>1</sub> 50 Cr<sub>2</sub> 70 Cr<sub>3</sub> 87 Sm 102  
 Sm 109 Iso  
**11c**, n = 8: Cr<sub>1</sub> 78 Cr<sub>2</sub> 91 Sm 102 Sm  
 110 Iso  
**11d**, n = 9: Cr<sub>1</sub> 20 Cr<sub>2</sub> 41 Cr<sub>3</sub> 90 Sm 99  
 Sm 107 Iso  
**11e**, n = 10: Cr<sub>1</sub> 21 Cr<sub>2</sub> 45 Cr<sub>3</sub> 80 Sm 85  
 Sm 100 Iso

In the case of compounds **10a–10f**, containing azo linkage between the aromatic cycles, only smectic-type textures were observed, the most stable interval of the mesophase being observed for compound **10a**, with the shorter flexible terminal chain (n = 6). Because of strong polar interactions, all compounds presented high viscosity and crystallized very slowly below room temperature. Compared with compounds **10a–10e**, compounds **11a–11e** presented a rich polymorphism on heating with crystalline-crystalline or liquid crystalline-liquid crystalline transitions, on a narrow range of mesophases. However, neither characteristic cholesteric textures were observed as was the case for compounds with azo linkage in the structure; only smectic phases have been observed (**Figure 7a,b**). As for previous compounds **10a–10e**, on cooling, compounds **11a–11e** presented mesophases much below room temperature.



**Figure 7.**  
Optical micrographs of mesophases: (a) **10d**, 115°C, heating and (b) **11c**, 71°C, cooling.

Compounds **12** and **13** were obtained when the flexible spacer between resorcinol and cholesteryl unit in compounds **10** and **11** was changed to a succinate one [47].



**12**, X = —N=N—, R = —C<sub>n</sub>H<sub>2n+1</sub>, n = 6–10, **12**

**13**, X = —OCO—, R = —C<sub>n</sub>H<sub>2n+1</sub>, n = 6–10

**12a**, n = 6: Cr 105 Sm 155 Iso

**12b**, n = 7: Cr<sub>1</sub> 65 Cr<sub>2</sub> 95 Sm 104 Sm 147 Iso

**12c**, n = 8: Cr<sub>1</sub> 16 Cr<sub>2</sub> 102 Sm 109 Sm 134 Iso

**12d**, n = 9: Cr<sub>1</sub> 80 Cr<sub>2</sub> 113 Sm 134 Iso

**12e**, n = 10: Cr<sub>1</sub> 87 Cr<sub>2</sub> 118 Sm 128 Sm 139 Iso

**12f**, n = 12: Cr 106 Sm 111 Sm 131 Iso

**13a**, n = 6: Cr (Sm 71) 157 Iso

**13b**, n = 7: Cr (Sm 91) 139 Iso

**13c**, n = 8: Cr (Chol 86) 91 Iso

**13d**, n = 9: Cr (Chol 76) 93 Iso

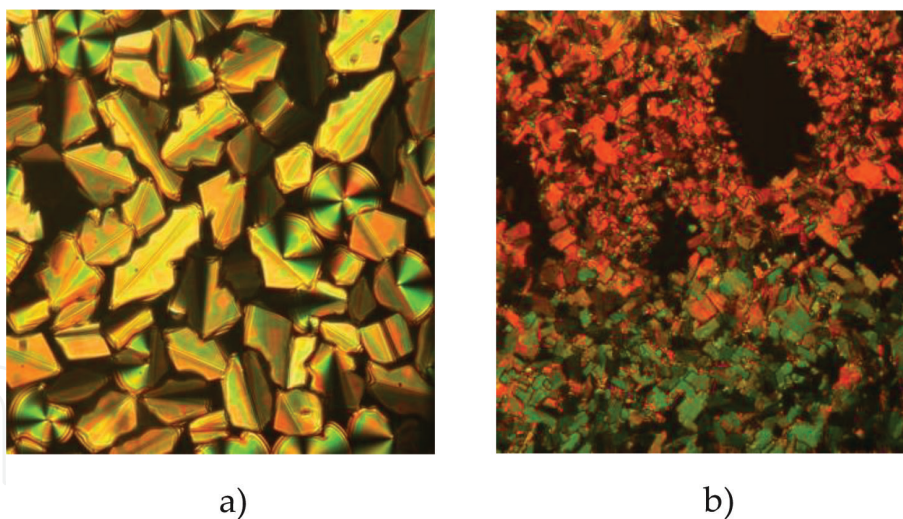
**13e**, n = 10: Cr (Chol 99) 101 Iso

Compounds of type **12** presented wider mesophase domains on heating and cooling (compared with compounds of type **10**), suggesting better interactions when the flexible chain inside one arm is shorter.

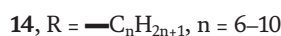
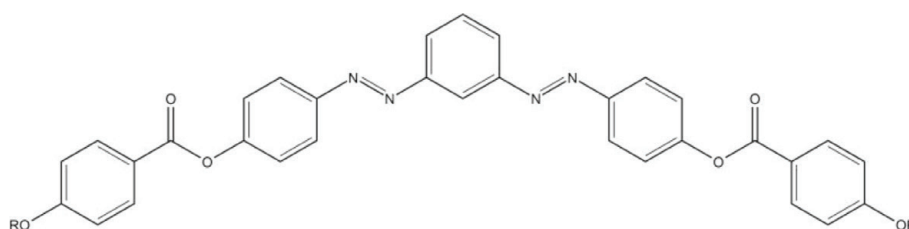
While compounds **12a–e** showed enantiotropic behavior with smectic-type textures, when switching the azo unit with an ester the mesophases are destabilized, with compounds **13a–e** presenting only monotropic behavior. Whereas the first two compounds, **13a** and **13b**, showed smectic phases, the next homologous compound presented cholesteric phases.

### 2.2.2. 1,3-Diaminobenzene central core

Symmetric derivatives **14a–14d** presented focal-conic and fan-shaped textures, which are characteristic of the banana B<sub>6</sub> phase (**Figure 8**) (compound **14e** (n = 10) is non mesomorphic) [48]. The mesophase stability ranges decrease with the number of the carbon atoms in the alkyl chain, and the variation of transition temperature follows the odd/even effect, derivatives with an even number of carbon atoms present a larger domain of mesophase.



**Figure 8.**  
 Optical micrographs of mesophases: (a) **14c**, 151°C cooling and (b) **18c**, 151°C cooling.



**14a**, n = 6: Cr **141** B<sub>6</sub> **171** Iso

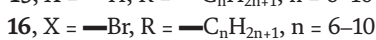
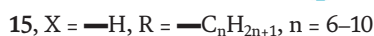
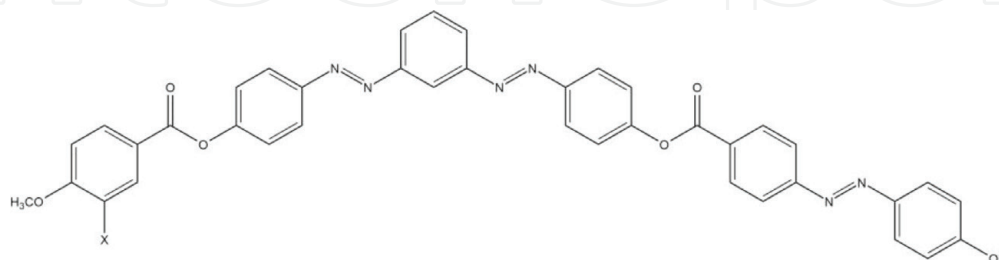
**14b**, n = 7: Cr **148** B<sub>6</sub> **158** Iso

**14c**, n = 8: Cr **135** B<sub>6</sub> **155** Iso

**14d**, n = 9: Cr **140** B<sub>6</sub> **148** Iso

**14e**, n = 10: Cr **141** Iso

The liquid crystalline properties of asymmetric bent-core derivatives **15** and **16** depend on the nature of the X substituent [49]. Thus, for X = -H, compounds **15a–15e** showed an enantiotropic behavior with fan-shaped texture characteristic of the banana B<sub>6</sub> phase while replacement of hydrogen atom with  $\text{---Br}$  decreased the mesophase stability, so compounds **16a–16d** presented only monotropic behavior with narrow intervals of mesophases.



**15a**, n = 6: Cr<sub>1</sub> **113** Cr<sub>2</sub> **156** B<sub>6</sub> **183** Iso

**15b**, n = 7: Cr<sub>1</sub> **125** Cr<sub>2</sub> **146** B<sub>6</sub> **205** Iso

**15c**, n = 8: Cr<sub>1</sub> **131** Cr<sub>2</sub> **158** B<sub>6</sub> **181** Iso

**15d**, n = 9: Cr<sub>1</sub> **133** B<sub>6</sub> **159** Iso

**15e**, n = 10: Cr<sub>1</sub> **128** B<sub>6</sub> **142** Iso

**16a**, n = 6: Cr (166) B<sub>6</sub> **175** Iso

**16b**, n = 7: Cr (179) B<sub>6</sub> **172** Iso

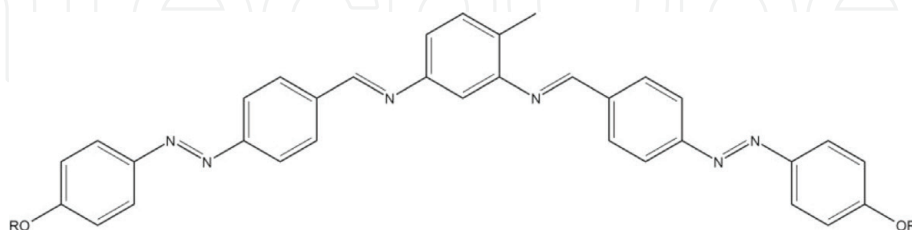
**16c**, n = 8: Cr (166) B<sub>6</sub> **176** Iso

**16d**, n = 9: Cr (159) B<sub>6</sub> **166** Iso

**16e**, n = 10: Cr **168** Iso

Compounds of type **17** and **18** were obtained by condensing 4-methylbenzene-1,3-diamine with 4'-alkyloxy-4-formylazobenzene and 4'-acyloxy-4-formylazobenzene, respectively [50].

Compounds with alkyloxy terminal flexible chain (compounds **17a–17f**) evidenced nematic phases on heating and smectic textures on cooling. Introduction of an acyl group as terminal chain (compounds **18a–18f**) has as result the slight increase of the transition temperatures but a decrease of meso-phase stability, such that only compounds **18c–18f** showed mesomorphic behavior.



**17**, R =  $\text{—C}_n\text{H}_{2n+1}$ , n = 6–10, **18**

**18**, R =  $\text{—COC}_n\text{H}_{2n+1}$ , n = 5–9, **17**

**17a**, n = 6: Cr 154 N 172 Iso

**17b**, n = 7: Cr 158 N 164 Iso

**17c**, n = 8: Cr<sub>1</sub> 72 Cr<sub>2</sub> 155 N 160 Iso

**17d**, n = 9: Cr<sub>1</sub> 112 Cr<sub>2</sub> 145 N 164 Iso

**17e**, n = 10: Cr 155 N 165 Iso

**17f**, n = 18: Cr 120 N 137 Iso

**18a**, n = 5: Cr<sub>1</sub> 146 Cr<sub>2</sub> 177 Iso

**18b**, n = 6: Cr<sub>1</sub> 128 Cr<sub>2</sub> 172 Iso

**18c**, n = 7: Cr<sub>1</sub> 135 Cr<sub>2</sub> 158 Sm 166 Iso

**18d**, n = 8: Cr<sub>1</sub> 123 Cr<sub>2</sub> 151 Sm 159 Iso

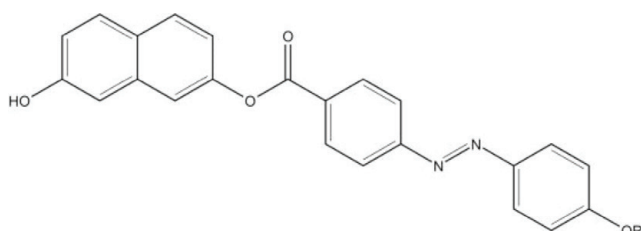
**18e**, n = 9: Cr<sub>1</sub> 122 Cr<sub>2</sub> 147 Sm 156 Iso

**18f**, n = 17: Cr 128 Sm 150 Iso

However, the optical microscope observations revealed focal-conic or fan-like textures for compounds **18c–18f** on cooling, characteristic of the banana B<sub>2</sub> phase, with striations across individual fans which on further cooling transform into mosaic textures (**Figure 8**).

### 2.3. Bent-core compounds based on 2,7-dihydroxynaphthalene core

The presence of a naphthalene unit in banana-shaped compounds is characterized by increased temperature transitions, compared to previous compounds with a benzene central core. Hence, the nematic mesophase domains of compounds **19a–19e** are situated between 175 and 214°C. The nematic phases were identified by characteristic Schlieren textures and nematic droplets or ribbon-like textures [51].



**19**, R =  $\text{—C}_n\text{H}_{2n+1}$ , n = 6–10

**19a**, n = 6: Cr **190** N **214** Iso

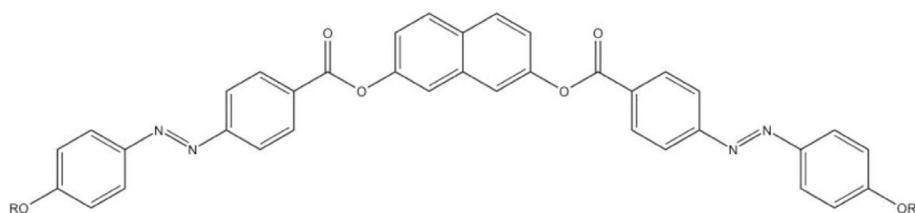
**19b**, n = 6: Cr 178 N 190 Iso

**19c**, n = 6: Cr 183 N 198 Iso

**19d**, n = 6: Cr 177 N 197 Iso

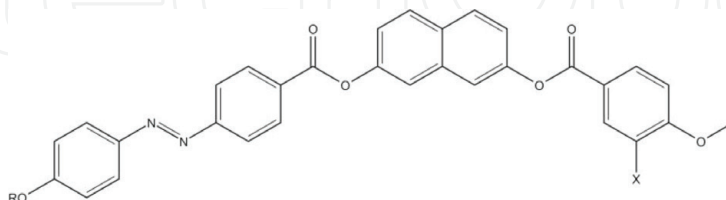
**19e**, n = 6: Cr 175 N 196 Iso

The symmetric disubstitution of compounds of type **19** gave compounds of type **20**, which are non mesomorphic [51].



20, R =  $\text{---C}_n\text{H}_{2n+1}$ , n = 6–10

The asymmetric disubstituted compounds **21** and **22** that differ only by X substituent showed similar monotropic behavior, mainly with nematic textures [52].



21, X = -H, R =  $\text{---C}_n\text{H}_{2n+1}$ , n = 6–10

22, X = -Br, R =  $\text{---C}_n\text{H}_{2n+1}$ , n = 6–10

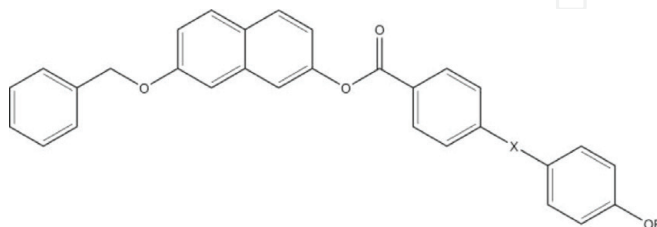
21a, n = 6: Cr (N 137) 140 Iso  
 21b, n = 7: Cr (N 130) 133 Iso  
 21c, n = 8: Cr (N 135) 140 Iso  
 21d, n = 9: Cr (N 146) 150 Iso  
 21e, n = 10: Cr (N 142) 146 Iso

22a, n = 6: Cr (N 99) 149 Iso  
 22b, n = 7: Cr (N 108) 159 Iso  
 22c, n = 8: Cr (N 109) 147 Iso  
 22d, n = 9: Cr (B<sub>6</sub> 106) 129 Iso  
 22e, n = 10: Cr 130 N 146 Iso

If compared with previous naphthalene derivatives, transition temperatures were relatively low, something higher in brominated derivatives **22a–22e**. While the mesophase ranges on cooling for compounds **21a–21e** are larger, the mesophase domains of derivatives **22a–22e** are much narrower, proving the destabilizing effect of the bulky bromine atom.

Anyway, compound **22e** showed enantiotropic behavior, meaning that a length of 10 carbon atoms on the alkyl terminal chain compensated the negative effect of bromine and stabilized the liquid crystalline character. Only the last two compounds of this series showed fan-shaped textures of banana B<sub>6</sub> growing from the isotropic melt on cooling.

The introduction of benzyl unit to compounds **19a–19e** led to compounds **23a–23e**, where only the last three compounds of the series showed enantiotropic behavior [53]. It was noted that though the melting and isotropization transition temperatures were lower, considering the hydrogen bonding interaction in compounds **19a–19e**, but at the same time, the mesophase domains were larger, up to 35°C in compound **23e**.



23, X =  $\text{---N=N---}$ , R =  $\text{---C}_n\text{H}_{2n+1}$ , n = 6–10

24, X =  $\text{---OCO---}$ , R =  $\text{---C}_n\text{H}_{2n+1}$ , n = 6–10

23a, n = 6: Cr (B<sub>1</sub> 126) 155 Iso  
 23b, n = 7: Cr (N 118) 143 Iso  
 23c, n = 8: Cr<sub>1</sub> 107 Cr<sub>2</sub> 120 N 150 Iso  
 23d, n = 9: Cr 110 N 137 Iso  
 23e, n = 10: Cr 113 N 148 Iso

24a, n = 6: Cr 122 B<sub>1</sub> 144 Iso  
 24b, n = 7: Cr<sub>1</sub> 109 Cr<sub>2</sub> 116 B<sub>1</sub> 129 Iso  
 24c, n = 8: Cr 127 B<sub>1</sub> 148 Iso  
 24d, n = 9: Cr (B<sub>1</sub> 108) 146 Iso  
 24e, n = 10: Cr (B<sub>1</sub> 108) 136 Iso

Comparing this series with compounds **8a–8e**, where the central core derived from resorcinol, the favorable effect of naphthalene as central core was observed, since compounds **8a–8e** showed only a monotropic behavior.

Changing the azo linkage in compounds **23a–23e** with ester results in compounds **24a–24e**, where only the first three homologous compounds, with shorter alkyl chains, presented enantiotropic behavior [53]. The presence of ester linkage increases the transition temperatures but decreases the mesophase range, if one considers compound **24c** (21°C), compared with **23c** (30°C).

### 3. Conclusions

We have presented here, in brief, a part of the work carried out by our group over a period of 16 years, from the standpoint of relationship between the structure and mesomorphic properties on some banana-shaped compounds. Our purpose was to investigate a variety of new compounds in order to design bent-shaped liquid crystals with large mesophase intervals at low transition temperatures, which might expand the field of electro-optical applications. It was found that the mesomorphic behavior depends upon the type of the bent unit, the number of aromatic units in the calamitic substituents, the nature of the linkages, the lateral substitution, and the length as well as the type of the terminal flexible chains. Hence, biaxial nematic, smectic, and cholesteric banana phases as well as less conventional mesophases were identified. The use of resorcinol as central bent unit had proved to be very useful in inducing various mesophases, with some transitions being evidenced even at low temperatures. Derivatives with the smallest length of terminal chains (especially  $n = 6$ ) presented the widest mesophase interval. In terms of symmetrical derivatives, while the presence only of two aromatic cycles on each arm was not enough to stabilize or to induce the mesophase, the introduction of a third aromatic cycle has substantially improved the liquid crystalline properties. In asymmetrical derivatives, the presence of ester and azo linkages between aromatic rings influenced better the mesophase behavior or stability, compared with the situation when only ester linkages were present, except for derivatives with benzyl unit on the shorter arm. Moreover, the introduction of a cholesteryl hexanoate moiety on the second asymmetric arm led to mesophase transitions much below room temperature. In 1,3-diaminobenzene derivatives, the presence of bromine atom as lateral substituent on a calamitic arm destabilized or suppressed the mesophase. However, compared with resorcinol symmetrical derivatives with two aromatic cycles on each arm, just switching the places of ester and azo linkages between cycles had a better influence on liquid crystalline properties. Of the oxadiazole compounds, the hockey-stick derivatives showed the widest nematic ranges, particularly for the homologous compound with smallest number of carbon atoms in the terminal chain ( $n = 6$ ). In symmetrical derivatives, the presence of three aromatic cycles on each arm and of acyloxy linkage on terminal chain induced better interactions and favorable packing, especially for compounds with higher number of carbon atoms in terminal flexible chain ( $n = 9–11$ ), but increased too much the isotropization temperatures up to the beginning of the degradation processes. The presence of 2,7-disubstituted naphthalene as central core in bent-core compounds mainly destabilized the mesophases, compared with 1,3-disubstituted benzene derivatives.

Overall, considering the high impact of liquid crystal displays in everyday life and the multiple possibilities that bent-core compounds offer to vary the properties of materials, it is expected that the present study will contribute to future research directions, hopefully not only in fundamental or theoretical research but also in practical applications.

## **Conflict of interest**

No potential conflict of interest was reported by the authors.

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