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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 (γ_1) (allowing fast switching), birefringence (Δn) 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° and 140°) [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].

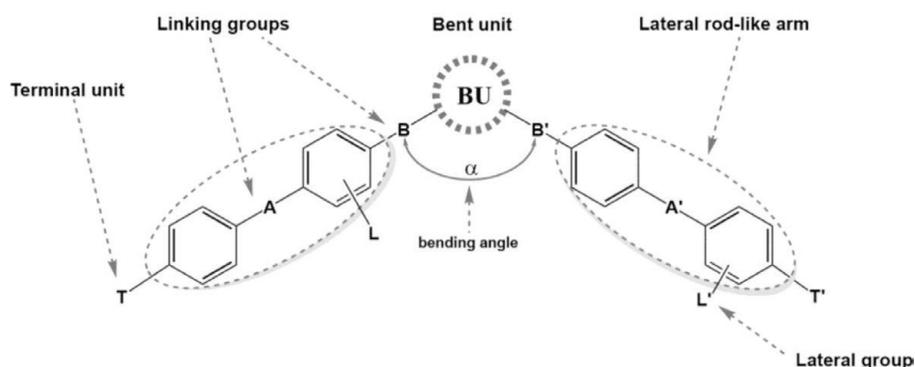


Figure 1.
General structure of banana-type liquid crystals.

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,

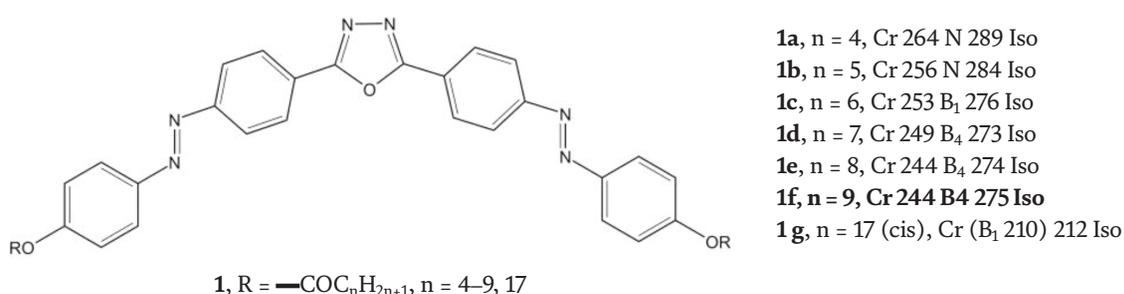
regarding the number of aromatic rings and the nature of linking groups that contribute through polarity, orientation, and flexibility.

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° , larger than the typical value of 120° 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 B₁ phase [39]. Further increase of carbon atoms results in progressive growth of the mesomorphic intervals, with B₄ 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°) position (**Figure 2**). On the other hand, the

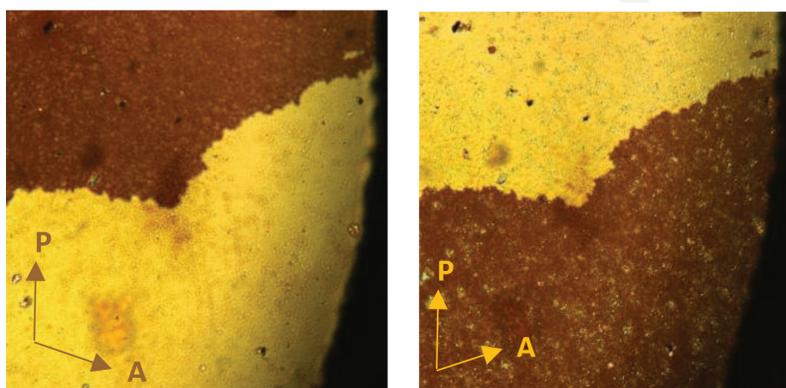
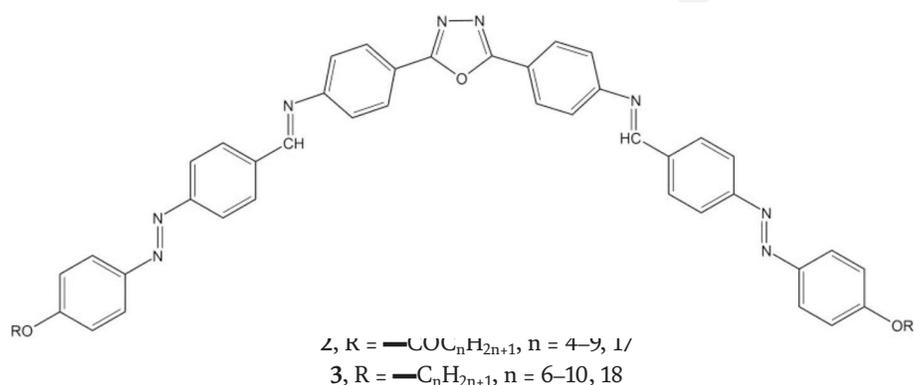


Figure 2. Textures of B₄ chiral domains' phase of compound **1f** at $T = 175^\circ\text{C}$ between slightly de-crossed polarizers from 90° by about $\pm 5^\circ$.

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, $n = 4$, Cr₁ 228 Cr₂ 244 Sm 264 N 333 Iso (d)
2b, $n = 5$, Cr₁ 214 Cr₂ 232 N 342 Iso (d)
2c, $n = 6$, Cr₁ 80 Cr₂ 134 N 253 Iso (d)
2d, $n = 7$, **Cr₁ 64 Cr₂ 174 Sm 219 N 343 Iso (d)**
2e, $n = 8$, Cr₁ 193 Cr₂ 204 Sm 249 N 321 Iso (d)
2f, $n = 9$, Cr₁ 192 Cr₂ 204 Sm 234 N 332 Iso (d)
2g, $n = 17$, Cr₁ 96 Cr₂ 194 N 335 Iso (d)

3a, $n = 6$, Cr₁ 113 Cr₂ 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**).

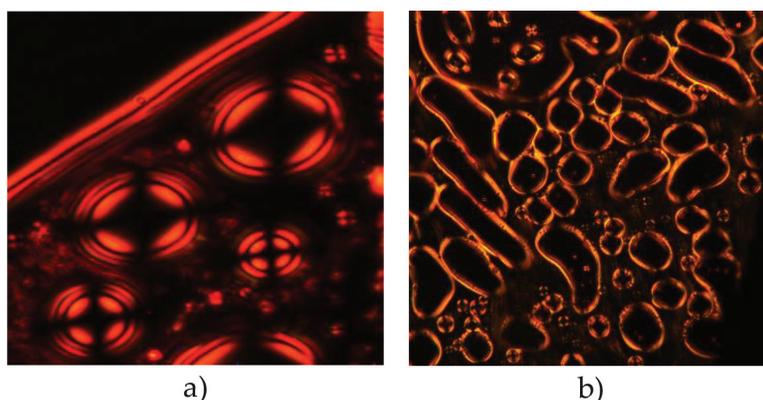
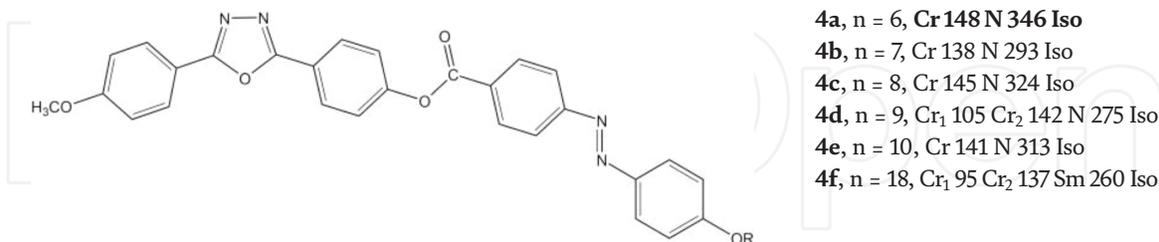


Figure 3.
 Optical micrographs of mesophases: (a) **3a**, 285°C, heating; (b) **3e**, 205°C, cooling.

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, Cr₁ 105 Cr₂ 142 N 275 Iso
4e, n = 10, Cr 141 N 313 Iso
4f, n = 18, Cr₁ 95 Cr₂ 137 Sm 260 Iso

4, R = —C_nH_{2n+1}, n = 6–10, 18

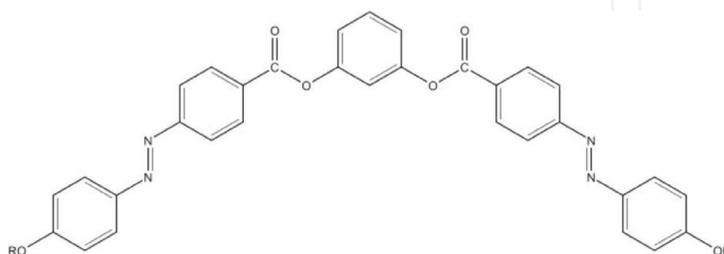
As for previous compounds, the stability of mesophases follows the odd-even effect, because of changing the ability to order into mesophase. Thus, the increase of aliphatic chain to 18 carbon atoms induces changes in supramolecular ordering, which leads to the narrowest mesophase range. All the compounds 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 iminoazo 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 B₁ mosaic one at lower temperature [43].



5, R = —C_nH_{2n+1}, n = 6–10

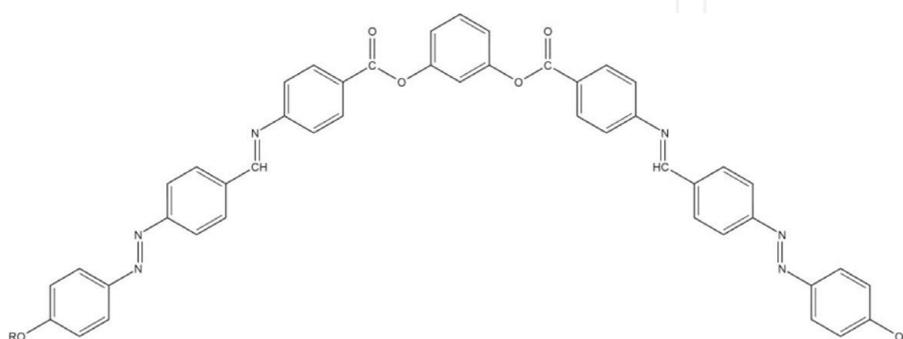
5a, n = 6: Cr₁ 116 Cr₂ (SmB 163) 168 Iso
5b, n = 7: Cr₁ 111 Cr₂ 142 SmB 163 Iso
5c, n = 8: Cr₁ 94 Cr₂ 143 SmB 159 Iso

5d, n = 9: Cr₁ 100 Cr₂ 147 Iso
5e, n = 10: Cr₁ 100 Cr₂ 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, $n = 6$: Cr₁ 159 Cr₂ 181 Cr₃ 215 Sm 294 Iso

6b, $n = 7$: Cr₁ 151 Cr₂ 181 Cr₃ 213 Sm 276 Iso

6c, $n = 8$: Cr₁ 136 Cr₂ 202 B₁ 267 Iso

6d, $n = 9$: Cr 195 B₃ 260 Iso

6e, $n = 10$: Cr₁ 152 Cr₂ 177 B₃ 259 Iso

7a, $n = 5$: Cr₁ 169 Cr₂ 202 Sm 315 Iso

7b, $n = 6$: Cr₁ 164 Cr₂ 209 Sm 304 Iso

7c, $n = 7$: Cr₁ 146 Cr₂ 207 Sm 285 Iso

7d, $n = 8$: Cr₁ 148 Cr₂ 202 Sm 288 Iso

7e, $n = 9$: Cr₁ 148 Cr₂ 195 B₂ 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 B₇ 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**).

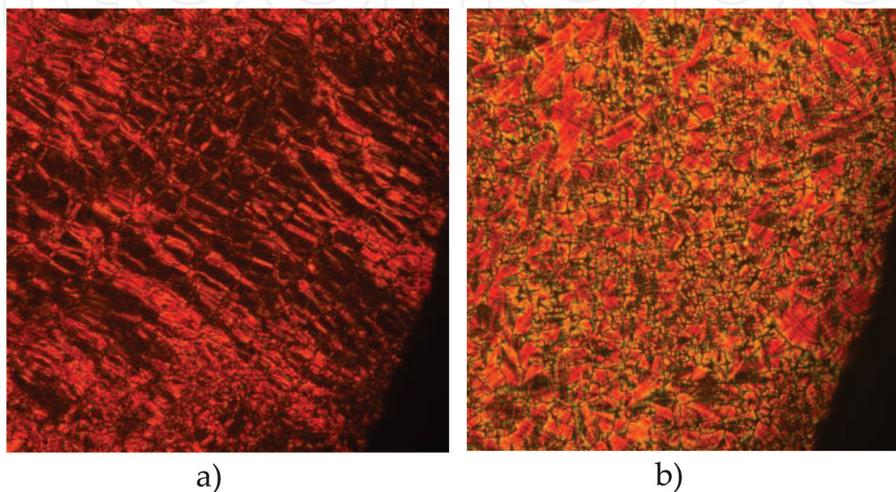


Figure 4.
Optical micrographs of mesophases of compound **6e**, (a) 195°C, heating; (b) 170°C, cooling.

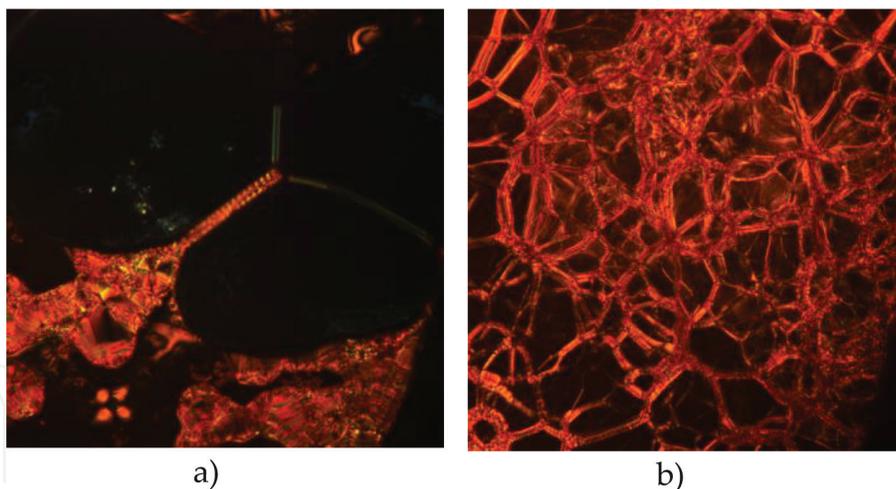
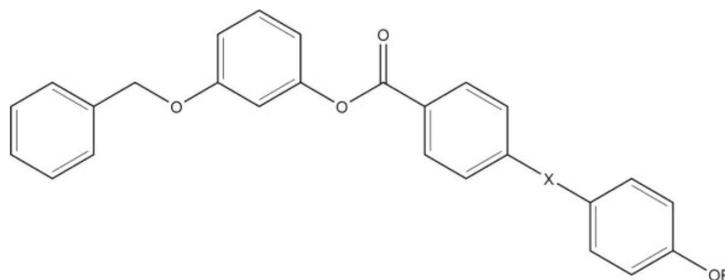


Figure 5.
Optical micrographs of mesophases: (a) **7b**, 280°C, cooling and (b) **7e**, 280°C, heating.

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_nH_{2n+1}, n = 6–10

9, X = —OCO—, R = —C_nH_{2n+1}, n = 6–10

8a, n = 6: Cr (B₁ 95) 113 Iso

8b, n = 7: Cr (B₁ 65) 121 Iso

8c, n = 8: Cr (B₁ 95) 117 Iso

8d, n = 9: Cr (B₁ 86) 100 Iso

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

9a, n = 6: Cr 46 B₁ 105 Iso

9b, n = 7: Cr (B₁ 65) 106 Iso

9c, n = 8: Cr 75 B₁ 94 Iso

9d, n = 9: Cr (B₁ 45) 90 Iso

9e, n = 10: Cr 71 B_x 90 Iso

The mesophase appearance was identified mainly as mosaic textures of the banana B₁ 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.

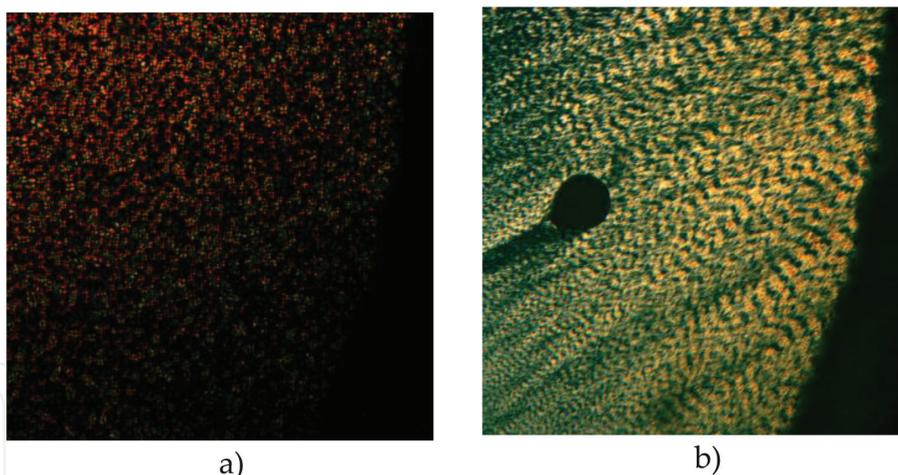
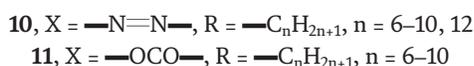
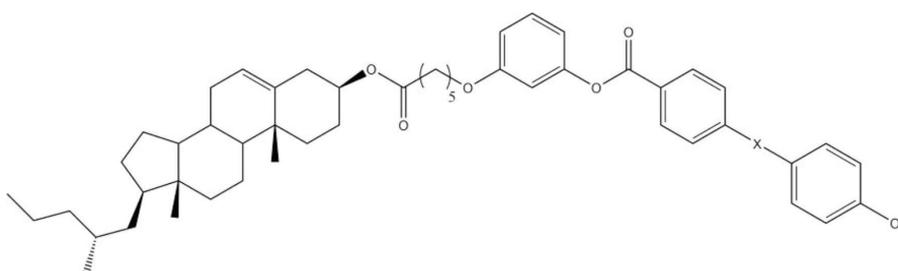


Figure 6.
 Optical micrographs of mesophases: (a) **8b**, 65°C; cooling and (b) **9d**, 43°C, cooling.

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: Cr₁ 33 Cr₂ 52 Cr₃ 91 Sm
109 Sm 115 Iso
11b, n = 7: Cr₁ 50 Cr₂ 70 Cr₃ 87 Sm 102
 Sm 109 Iso
11c, n = 8: Cr₁ 78 Cr₂ 91 Sm 102 Sm
 110 Iso
11d, n = 9: Cr₁ 20 Cr₂ 41 Cr₃ 90 Sm 99
 Sm 107 Iso
11e, n = 10: Cr₁ 21 Cr₂ 45 Cr₃ 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.

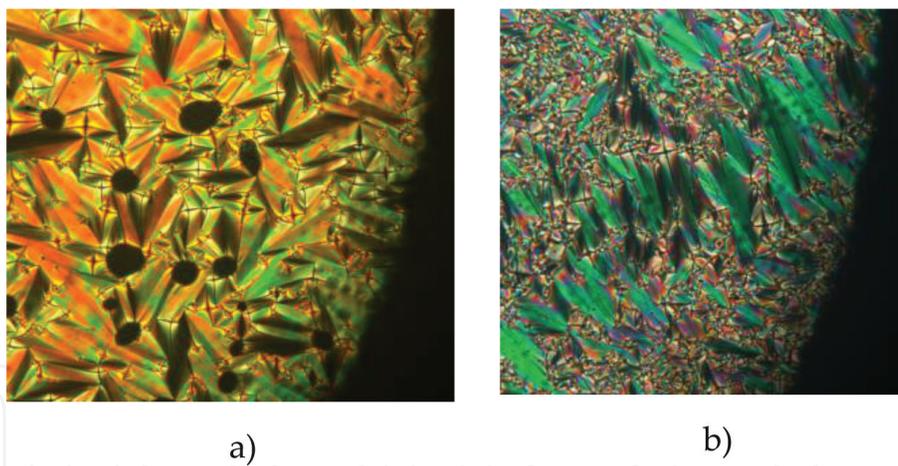
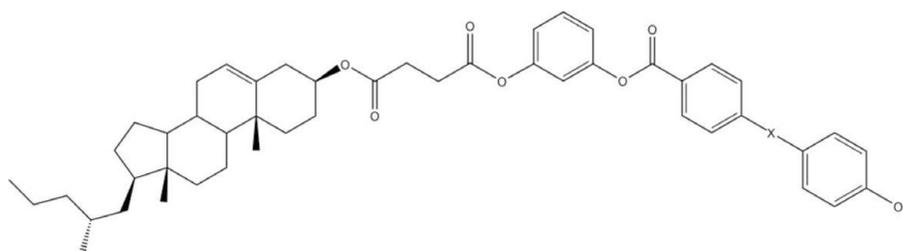


Figure 7.
Optical micrographs of mesophases: (a) **10d**, 115°C, heating and (b) **11c**, 71°C, cooling.

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_nH_{2n+1}, n = 6–10, **12**

13, X = —OCO—, R = —C_nH_{2n+1}, n = 6–10

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

12b, n = 7: Cr₁ 65 Cr₂ 95 Sm 104 Sm 147 Iso

12c, n = 8: Cr₁ 16 Cr₂ 102 Sm 109 Sm 134 Iso

12d, n = 9: Cr₁ 80 Cr₂ 113 Sm 134 Iso

12e, n = 10: Cr₁ 87 Cr₂ 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 B₆ 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.

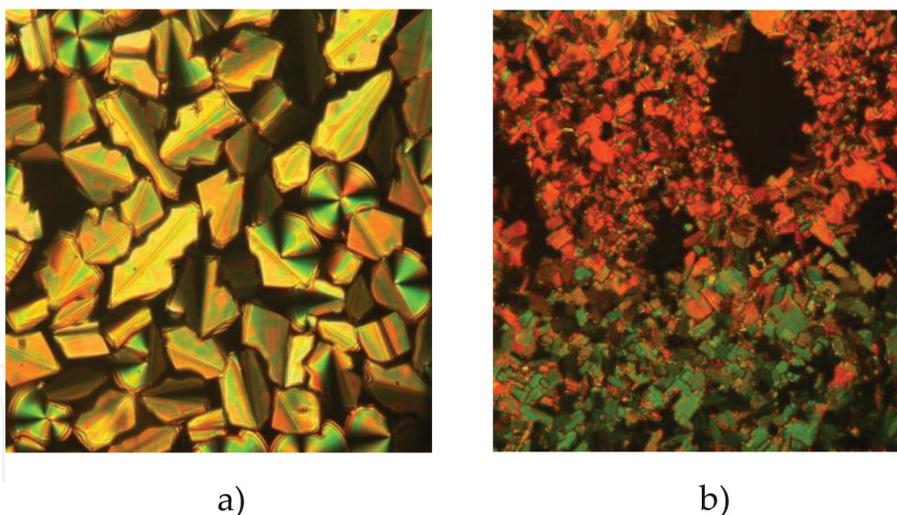
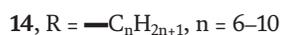
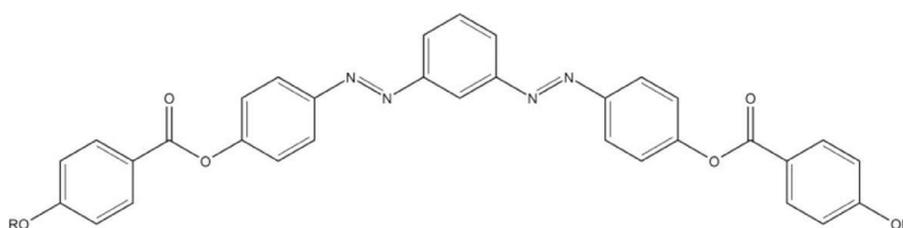


Figure 8.
 Optical micrographs of mesophases: (a) **14c**, 151°C cooling and (b) **18c**, 151°C cooling.



14a, n = 6: Cr **141** B₆ **171** Iso

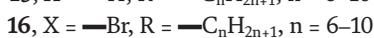
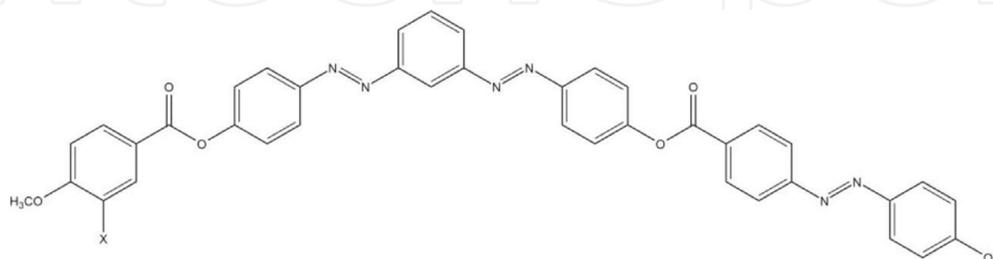
14b, n = 7: Cr **148** B₆ **158** Iso

14c, n = 8: Cr **135** B₆ **155** Iso

14d, n = 9: Cr **140** B₆ **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 B₆ phase while replacement of hydrogen atom with ---Br decreased the mesophase stability, so compounds **16a–16d** presented only monotropic behavior with narrow intervals of mesophases.



15a, n = 6: Cr₁ **113** Cr₂ **156** B₆ **183** Iso

15b, n = 7: Cr₁ **125** Cr₂ **146** B₆ **205** Iso

15c, n = 8: Cr₁ **131** Cr₂ **158** B₆ **181** Iso

15d, n = 9: Cr₁ **133** B₆ **159** Iso

15e, n = 10: Cr₁ **128** B₆ **142** Iso

16a, n = 6: Cr (166) B₆ **175** Iso

16b, n = 7: Cr (179) B₆ **172** Iso

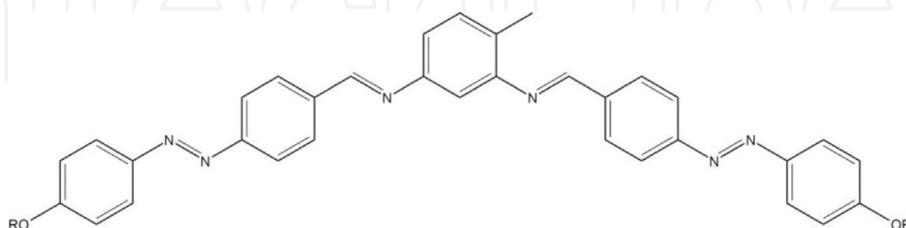
16c, n = 8: Cr (166) B₆ **176** Iso

16d, n = 9: Cr (159) B₆ **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: Cr₁ 72 Cr₂ 155 N 160 Iso

17d, n = 9: Cr₁ 112 Cr₂ 145 N 164 Iso

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

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

18a, n = 5: Cr₁ 146 Cr₂ 177 Iso

18b, n = 6: Cr₁ 128 Cr₂ 172 Iso

18c, n = 7: Cr₁ 135 Cr₂ 158 Sm 166 Iso

18d, n = 8: Cr₁ 123 Cr₂ 151 Sm 159 Iso

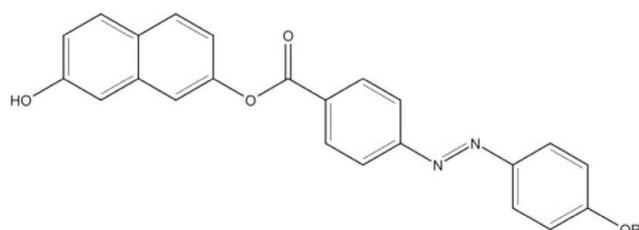
18e, n = 9: Cr₁ 122 Cr₂ 147 Sm 156 Iso

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 B₂ 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

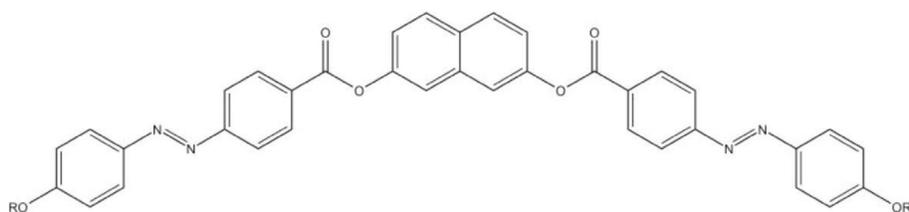
19b, n = 6: Cr 178 N 190 Iso

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

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

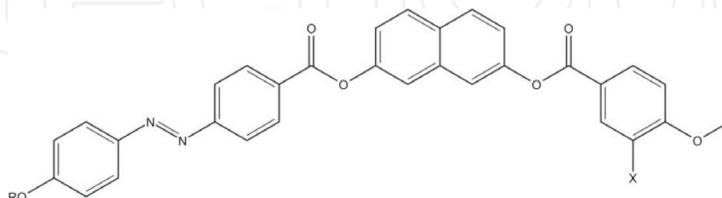
19e, n = 6: Cr 175 N 196 Iso

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

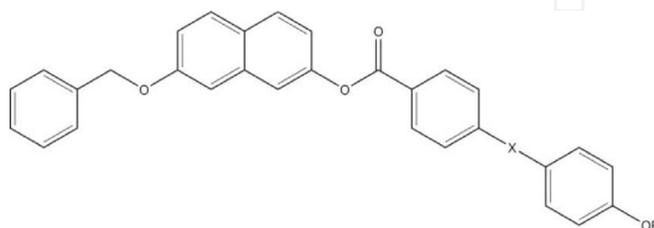
21a, n = 6: Cr (N 137) 140 Iso
 21b, n = 7: Cr (N 130) 133 Iso
 21c, n = 8: Cr (N 135) 140 Iso
 21d, n = 9: Cr (N 146) 150 Iso
 21e, n = 10: Cr (N 142) 146 Iso

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 (B₆ 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 B₆ 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 = ---N=N--- , R = $\text{---C}_n\text{H}_{2n+1}$, n = 6–10

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

23a, n = 6: Cr (B₁ 126) 155 Iso
 23b, n = 7: Cr (N 118) 143 Iso
 23c, n = 8: Cr₁ 107 Cr₂ 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 B₁ 144 Iso
 24b, n = 7: Cr₁ 109 Cr₂ 116 B₁ 129 Iso
 24c, n = 8: Cr 127 B₁ 148 Iso
 24d, n = 9: Cr (B₁ 108) 146 Iso
 24e, n = 10: Cr (B₁ 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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