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Liquid crystal behavior induced in highly luminescent unsymmetrical borondifluoride β-diketonate materials

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ABSTRACT

Highly luminescent and liquid crystal materials were successfully prepared by the strategic introduction of unsymmetrically alkyloxyphenyl substituted β -diketones, as ligands towards the BF₂ group. So, four families of ligands and their boron derivatives were prepared, each of them containing invariable the alkyl chain at one of the substituents in the 1(3) position, with 12, 14, 16 or 18 carbon atoms, while for the other substituent at the 3(1) position, the number of alkyl carbon atoms was increased from 4 to 18. In this way, the influence of factors as asymmetry or molecular length was evaluated towards the liquid crystal behavior of the compounds.

The photophysical characterization of the boron derivatives was also carried out, showing in all cases a high fluorescent emission in the blue–violet region in solution and in the green region in the solid state, with quantum yields near the unity. In addition, thermal studies by DSC, as well as the analysis by POM and XRD were determinant to characterize the compounds as liquid crystal materials, exhibiting B₁ mesophases, in agreement with the banana molecular shape. In contrast the corresponding β -diketone precursors behave again as liquid crystals showing SmC and N mesophases.

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1. Introduction

Luminescent liquid crystal materials have attracted considerable attention over past decades by their ability to be used in displays, OLEDs and, in general, in devices for new technologies [1–5].

In particular, to combine liquid crystal and luminescent properties in the same material leading to intrinsically luminescent mesogens is a challenge because the molecular self-organization in the mesophase can be exploited to improve device performances for different applications such as linear polarized electroluminescence [6]. They are also interesting because of their carrier high charge mobility, which makes them able to develop defect-free layers [7].

Related with highly luminescent materials it is noticeable the interest up surged in the research of fluorescent organoboron dyes such as 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) as well as borondiketonates for their applications within fields as molecular probes [1], photosensitizers [2] and lasers [3] because they possess large molar extinction coefficients, two-photon absorption cross section, high emission quantum yields and sensitivity to the surrounding medium. Strongly blue-absorbing dyes have recently stirred a growing interest in fluorescent imaging

based on two photon excitation [6]. Borondifluoride β -diketonates containing aromatic moieties in the chelating ring have been suggested as two-photon probes for in vivo studies with the excitation in the transparent window of tissues due to their intense blue-green luminescence [7], giving their absorption wavelengths for their π - π * transitions much shorter than their analogs BF₂-pyrromethenes [8].

On the other hand, in designing metallomesogens (metalcontaining liquid crystals), metal centers and ligands can be used to control the mesomorphism of the materials, so metals can induce mesomorphism when incorporated in non-mesomorphic materials or mesomorphic ligands can suffer dramatic effects in their liquid crystal properties by coordination to a metal centre. However, although the field of metallomesogens based on transition metals has properly expanded, no relevant information is produced by considering the presence of a metalloid such as boron, which offers new opportunities.

With these considerations in mind, our work has been directed towards the research of new luminescent materials based on borondifluoride β -diketonate compounds which are designed to exhibit additional liquid crystal behavior.

In this context, our previous works were directed towards the study of the photophysical properties of compounds of the type $[BF_2(OO^{R(n)})]$ and $[BF_2(OO^{2R(n)})]$ ($OO^{R(n)} = 3-(4-alkyloxyphenyl)$ -





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propane-1,3-dionate and $OO^{2R(n)} = 1,3$ -bis-(4-alkyloxyphenyl)-propane-1,3-dionate, $R(n) = C_6H_4OC_nH_{2n+1}$). All of them were highly luminescent materials, displaying intense green or blue luminescence in the solid state and in solution, but none of them exhibited liquid crystal behavior [9].

Following our interest on boron complexes with accessible mesophases, the structure of the ligands was strategically modified taking into account concepts such as the lowering of the symmetry or the diminution of the lateral interactions that had been successfully used to improve the mesomorphic behavior [10]. In particular, by reducing the symmetry by building unsymmetrical materials, the molecules ought to pack less favourably in the solid state, hence reducing the melting temperatures, and potentially, the clearing temperatures.

On these basis we decided to involve unsymmetrically substituted β -diketonates of the type 1-(4-alkyloxyphenyl)-3-(4-alkyloxyphenyl)-propane-1,3-dionate, $OO^{R(n)R(m)}$ ($R(n) = C_6H_4OC_nH_{2n+1}$, $R(m) = C_6H_4OC_nH_{2m+1}$) as ligands towards BF₂ as a support for liquid crystal behavior. The first results obtained for the compounds [BF₂(OO^{R(12)R(m)})] (m = 14, 16, 18) evidenced the liquid crystal behavior of those materials, which exhibited B₁ mesophases although in a short range of temperatures [11].

Encouraged by these results, we were interested in confirming the above proposal by the study of related boron derivatives for which existed the possibility of varying independently the chain length of the alkyloxyphenyl substituent in each position of the β -diketonate. This systematic variation allows us to analyze the influence of both factors, the asymmetry and the overall molecular length, in the mesomorphism of the compounds.

Thus, the following families of complexes $[BF_2(OO^{R(n)R(m)})]$ with n = 12, 14, 16, 18 and m = 4, 8, 10 have been prepared and their thermal and photophysical studies have been carried out. Throughout this paper the abbreviation $D_{n,m}$ is used for the unsymmetrically 1,3-alkyloxyphenyl substituted β -diketones; n and m indicate the number of carbon atoms in the alkyloxy chains. As well, the related borondifluoride β -diketonate complexes are represented by $B_{n,m}$. Thus, for instance, $D_{12,4}$ is the diketone $[HOO^{R(12)R(4)}]$ and $B_{12,4}$ is the complex $[BF_2(OO^{R(12)R(4)})]$.

Thus, four families of compounds have been prepared and their properties discussed. The strategic introduction of asymmetry in this type of compounds appeared to provide a lateral dipole favouring the mesomorphic properties.

A study and discussion of the liquid crystal behavior of the new β -diketones, as precursors of the β -diketonate ligands, is also included.

2. Experimental

2.1. Materials and physical measurements

All commercial reagents were used as supplied. The synthetic route to unsymmetrical alkyloxyphenyl disubstituted β -diketones was carried out following a similar procedure to that used for the related symmetrical derivatives [9,11–13].

Elemental analyses for carbon and hydrogen were carried out by the Microanalytical Service of Complutense University (validated range: %C 0.50–94.7 and %H 0.50–7.6). IR spectra were recorded on a FTIR Thermo Nicolet 200 spectrophotometer with samples as KBr pellets or in dichloromethane solution in the 4000–400 cm⁻¹ region: vs (very strong), s (strong), m (medium), w (weak).

¹H NMR spectra were performed at room temperature on a Bruker DPX-300 spectrophotometer (NMR Service of Complutense University) from solutions in CDCl₃. Chemical shifts δ are listed relative to Me₄Si using the signal of the deuterated solvent as reference (7.26 ppm), and coupling constants *J* are in hertz. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), m (multiplet). The ¹H chemical shifts and coupling constants are accurate to ± 0.01 ppm and ± 0.3 Hz, respectively.

Phase studies were carried out by optical microscopy using an Olympus BX50 microscope equipped with a Linkam THMS 600 heating stage. The temperatures were assigned on the basis of optic observations with polarized light.

Measurements of the transition temperatures were made using a Perkin–Elmer Pyris 1 differential scanning calorimeter with the sample (1–4 mg) sealed hermetically in aluminum pans and with a heating or cooling rate of 5–10 K min⁻¹.

The X-ray diffractograms at variable temperature were recorded on a Panalytical X'Pert PRO MPD diffractometer in a θ - θ configuration equipped with a Anton Paar HTK1200 heating stage (X-ray Diffraction Service of Complutense University).

Absorption spectra were recorded on a IASCO V-650 spectrophotometer and fluorescence emission on a Horiba-Jobin-Yvon Fluoromax-4 spectrofluorimeter equipped with a ThermoNeslab RTE7 bath. The linearity of the fluorescence emission verses concentration was checked in the concentration range used (10⁻⁴- 10^{-6} M). A correction for the absorbed light was performed when necessary. All spectrofluorimetric studies were performed as follows: the stock solutions of the ligands (*ca.* 10^{-3} M) were prepared by dissolving an appropriate amount of the ligand in a 5 mL volumetric flask and diluting to the mark with dichloromethane HPLC or UVA-sol grades. Fluorescence spectra of solid samples were recorded on the spectrofluorimeter exciting the solid compounds at appropriated λ (nm) using a fiber-optics device connected to the spectrofluorimeter. The emission spectra as a function of the temperature were recorded in the 300-800 nm range, using a fiber optic system connected to the spectrofluorimeter and the solid samples were heated over a hotplate with an external temperature control provided with a digital thermo par.

2.2. Synthesis of the compounds $[HOO^{R(n)R(m)}]$ (n = 12, 14, 16, 18; m = 4, 6, 8, 10, 14, 16) ($D_{n,m}$)

The compounds $D_{n,m}$ were obtained by Claysen synthesis between a 4-alkyloxyacetophenone and an ethyl 4-alkyloxybenzoate. The general procedure is described as follows: To a solution of 12 mmol of the 4-alkyloxyacetophenone and 30 mmol of NaH (60 wt.% dispersion in mineral oil) in dimethoxyethane (250 mL), 15 mmol of the corresponding ethyl 4-alkyloxybenzoate were slowly added. The solution was refluxed for 24 h. The resulting suspension was left to cool at room temperature and then added to water (600 mL). By addition of a hydrochloric acid solution (*spec. grav.* 1.19) until pH 2 a brown precipitate was obtained. The mixture was stirred for 24 h at room temperature and then the brown precipitate was filtered off and washed repeatedly with 50 mL hexane portions to yield a white solid which was dried *in vacuo*.

The compounds $D_{18,12}$, $D_{16,12}$ and $D_{14,12}$, which will be used in the discussion for comparative purposes, have been reported in our previous work [11]. Yields, elemental analysis and spectroscopic IR and ¹H NMR are given for all the β -diketones prepared.

2.2.1. [HOO^{R(12)R(4)}] (D_{12,4})

Yield: 3.12 g (52%). *Anal.* Calc. for C₃₁H₄₄O₄·H₂O (498.7 g mol⁻¹): C, 74.66; H, 9.30. Found: C, 75.00; H, 9.18%. IR (KBr, cm⁻¹): 3431w (OH), 1673s (C=O enol form) and 1606s (C=C)_{*θ*}. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³J 6.6, CH₃ R(12)), 0.99 (t, ³J 7.4, CH₃ R(4)), 1.27 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³J 6.6, OCH₂), 4.52 (s CH₂ keto form), 6.73 (s, CH enol form), 6.93 (d, ³J 8.7, H_m), 6.96 (d, ³J 8.7, H_{m'}), 7.94 (d, ³J 8.7, H_o), 8.05 (d, ³J 8.7, H_{o'}).

2.2.2. $[HOO^{R(12)R(8)}]$ (D_{12.8})

Yield: 3.37 g (49%). *Anal.* Calc. for $C_{35}H_{52}O_4 \cdot 2H_2O$ (572.8 g mol⁻¹): C, 73.39; H, 8.85. Found: C, 73.35; H, 8.86%. IR (KBr, cm⁻¹): 3431w (OH), 1672s (C=O enol form) and 1607s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³J 6.7, CH₃), 1.26 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³J 6.7, OCH₂), 4.52 (s CH₂ keto form), 6.73 (s, CH enol form), 6.92 (d, ³J 8.9, H_m), 6.95 (d, ³J 8.9, H_m'), 7.94 (d, ³J 8.9, H_o), 8.04 (d, ³J 8.9, H_{o'}).

2.2.3. $[HOO^{R(12)R(10)}](D_{12,10})$

Yield: 4.08 g (57%). *Anal.* Calc. for $C_{37}H_{56}O_{4}$ ·1.75H₂O (596.4 g mol⁻¹): C, 74.52; H, 10.06. Found: C, 74.55; H, 9.26%. IR (KBr, cm⁻¹): 3432w (OH), 1686s (C=O enol form) and 1606s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³*J* 6.6, CH₃), 1.27 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³*J* 6.6, OCH₂), 4.52 (s CH₂ keto form), 6.73 (s, CH enol form), 6.93 (d, ³*J* 8.9, H_m), 6.96 (d, ³*J* 8.9, H_m), 7.94 (d, ³*J* 8.9, H₀), 8.05 (d, ³*J* 8.9, H_{o'}).

2.2.4. $[HOO^{R(14)R(4)}]$ (D_{14.4})

Yield: 5.02 g (79%). Anal. Calc. for $C_{33}H_{48}O_4 \cdot H_2O$ (526.8 g mol⁻¹): C, 75.25; H, 9.57. Found: C, 75.08; H, 9.51%. IR (KBr, cm⁻¹): 3429w (OH), 1672s (C=O enol form) and 1606s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³J 6.7, CH₃ R(14)), 0.99 (t, ³J 7.4, CH₃ R(4)), 1.26 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³J 6.7, OCH₂), 4.52 (s CH₂ keto form), 6.73 (s, CH enol form), 6.93 (d, ³J 8.9, H_m), 6.96 (d, ³J 8.9, H_{m'}), 7.94 (d, ³J 8.9, H_o), 8.04 (d, ³J 8.9, H_{o'}).

2.2.5. $[HOO^{R(14)R(6)}]$ (D_{14.6})

Yield: 4.52 g (65%). Anal. Calc. for $C_{35}H_{52}O_4 \cdot 2.5H_2O$ (581.4 g mol⁻¹): C, 72.25; H, 9.87. Found: C, 72.66; H, 8.56%. IR (KBr, cm⁻¹): 3445w (OH), 1685s (C=O enol form) and 1606s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.91 (t, ³J 6.5, CH₃), 1.26 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³J 6.5, OCH₂), 4.53 (s CH₂ keto form), 6.73 (s, CH enol form), 6.93 (d, ³J 8.9, H_m), 6.96 (d, ³J 8.9, H_m'), 7.94 (d, ³J 8.9, H₀), 8.05 (d, ³J 8.9, H₀').

2.2.6. [HOO^{R(14)R(8)}] (D_{14.8})

Yield: 6.15 g (88%). *Anal.* Calc. for $C_{37}H_{56}O_4 \cdot H_2O$ (582.9 g mol⁻¹): C, 76.25; H, 10.03. Found: C, 75.99; H, 9.79%. IR (KBr, cm⁻¹): 3431w (OH), 1672s (C=O enol form) and 1607s (C=C)₀. IR (CH₂Cl₂, cm⁻¹) 1724 m (C=O keto form), 1686 m (C=O enol form) and 1604s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³J 6.7, CH₃), 1.26 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³J 6.7, OCH₂), 4.52 (s CH₂ keto form), 6.73 (s, CH enol form), 6.92 (d, ³J 8.9, H_m), 6.95 (d, ³J 8.9, H_{m'}), 7.94 (d, ³J 8.9, H_o), 8.04 (d, ³J 8.9, H_{o'}).

2.2.7. $[HOO^{R(14)R(10)}](D_{14,10})$

Yield: 5.77 g (79%). Anal. Calc. for $C_{39}H_{60}O_4$ ·H₂O (610.9 g mol⁻¹): C, 76.68; H, 10.23. Found: C, 76.85; H, 9.83%. IR (KBr, cm⁻¹): 3438w (OH), 1672s (C=O enol form) and 1606s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³J 6.7, CH₃), 1.26 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³J 6.7, OCH₂), 4.52 (s CH₂ keto form), 6.73 (s, CH enol form), 6.93 (d, ³J 8.9, H_m), 6.96 (d, ³J 8.9, H_{m'}), 7.94 (d, ³J 8.9, H₀), 8.04 (d, ³J 8.9, H_{o'}).

2.2.8. $[HOO^{R(16)R(4)}]$ (D_{16.4})

Yield: 4.98 g (75%). Anal. Calc. for $C_{35}H_{52}O_4\cdot H_2O$ (554.8 g mol⁻¹): C, 75.77; H, 9.81. Found: C, 76.04; H, 9.60%. IR (KBr, cm⁻¹): 3420w (OH), 1673s (C=O enol form) and 1607s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.87 (t, ³J 6.6, CH₃ R(16)), 0.99 (t, ³J 7.4, CH₃ R(4)), 1.25 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³J 6.6, OCH₂), 4.52 (s CH₂ keto form), 6.73 (s, CH enol form), 6.92 (d, ³J 8.9, H_m), 6.96 (d, ³J 8.9, H_{m'}), 7.94 (d, ³J 8.9, H_o), 8.04 (d, ³J 8.9, H_{o'}).

2.2.9. $[HOO^{R(16)R(6)}]$ (D_{16.6})

Yield: 5.24 g (75%). *Anal.* Calc. for $C_{37}H_{56}O_4 \cdot 1.25H_2O$ (587.4 g mol⁻¹): C, 75.66; H, 10.03. Found: C, 75.70; H, 9.64%. IR (KBr, cm⁻¹): 3422w (OH), 1673s (C=O enol form) and 1607s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.90 (t, ³J 6.5, CH₃), 1.26 (m, CH₂), 1.81 (m, CH₂), 4.03 (t, ³J 6.5, OCH₂), 4.52 (s CH₂ keto form), 6.72 (s, CH enol form), 6.92 (d, ³J 8.9, H_m), 6.95 (d, ³J 8.9, H_m), 7.94 (d, ³J 8.9, H_o), 8.04 (d, ³J 8.9, H_{o'}).

2.2.10. [HOO^{R(16)R(8)}] (D_{16.8})

Yield: 5.16 g (70%). Anal. Calc. for $C_{39}H_{60}O_4$ ·H₂O (610.9 g mol⁻¹): C, 76.68; H, 10.23. Found: C, 76.81; H, 9.98%. IR (KBr, cm⁻¹): 3431w (OH), 1673s (C=O enol form) and 1607s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³J 6.7, CH₃), 1.26 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³J 6.7, OCH₂), 4.52 (s CH₂ keto form), 6.73 (s, CH enol form), 6.92 (d, ³J 8.9, H_m), 6.95 (d, ³J 8.9, H_{m'}), 7.94 (d, ³J 8.9, H_o), 8.04 (d, ³J 8.9, H_{o'}).

2.2.11. $[HOO^{R(16)R(10)}]$ (D_{16,10})

Yield: 5.65 g (73%). Anal. Calc. for $C_{41}H_{64}O_4 \cdot 1.5H_2O$ (648.0 g mol⁻¹): C, 76.00; H, 10.42. Found: C, 76.35; H, 9.69%. IR (KBr, cm⁻¹): 3434w (OH), 1673s (C=O enol form) and 1606s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³J 6.7, CH₃), 1.26 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³J 6.7, OCH₂), 4.52 (s CH₂ keto form), 6.73 (s, CH enol form), 6.93 (d, ³J 8.9, H_m), 6.96 (d, ³J 8.9, H_{m'}), 7.94 (d, ³J 8.9, H_o), 8.04 (d, ³J 8.9, H_{o'}).

2.2.12. $[HOO^{R(16)R(14)}]$ (D_{16.14})

Yield: 5.70 g (67%). Anal. Calc. for $C_{45}H_{72}O_4 \cdot 1.5H_2O$ (704.1 g mol⁻¹): C, 76.77; H, 10.74. Found: C, 76.35; H, 9.98%. IR (KBr, cm⁻¹): 3427w (OH), 1680s (C=O enol form) and 1606s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³*J* 6.5, CH₃), 1.27 (m, CH₂), 1.80 (m, CH₂), 4.02 (t, ³*J* 6.5, OCH₂), 4.52 (s CH₂ keto form), 6.72 (s, CH enol form), 6.93 (d, ³*J* 8.9, H_m), 6.96 (d, ³*J* 8.9, H_m), 7.94 (d, ³*J* 8.9, H_o), 8.04 (d, ³*J* 8.9, H_{o'}).

2.2.13. [HOO^{R(18)R(4)}] (D_{18.4})

Yield: 4.62 g (67%). Anal. Calc. for $C_{37}H_{56}O_4 \cdot 0.5H_2O$ (573.9 g mol⁻¹): C, 77.44; H, 10.01. Found: C, 77.15; H, 10.05%. IR (KBr, cm⁻¹): 3431w (OH), 1687s (C=O enol form) and 1608s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.87 (t, ³J 6.8, CH₃ R(18)), 0.99 (t, ³J 7.4, CH₃ R(4)), 1.25 (m, CH₂), 1.80 (m, CH₂), 4.02 (t, ³J 6.8, OCH₂), 4.52 (s CH₂ keto form), 6.73 (s, CH enol form), 6.93 (d, ³J 8.9, H_m), 6.96 (d, ³J 8.9, H_{m'}), 7.94 (d, ³J 8.9, H_o), 8.04 (d, ³J 8.9, H_{o'}).

2.2.14. [HOO^{R(18)R(6)}] (D_{18.6})

Yield: 4.98 g (67%). Anal. Calc. for $C_{39}H_{60}O_4 \cdot 1.5H_2O$ (619.9 g mol⁻¹): C, 75.56; H, 10.24. Found: C, 75.92; H, 9.93%. IR (KBr, cm⁻¹): 3417w (OH), 1687s (C=O enol form) and 1608s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³J 6.5, CH₃), 1.26 (m, CH₂), 1.81 (m, CH₂), 4.03 (t, ³J 6.5, OCH₂), 4.52 (s CH₂ keto form), 6.72 (s, CH enol form), 6.92 (d, ³J 8.9, H_m), 6.95 (d, ³J 8.9, H_m), 7.94 (d, ³J 8.9, H_o), 8.04 (d, ³J 8.9, H_o).

2.2.15. $[HOO^{R(18)R(8)}]$ (D_{18.8})

Yield: 4.13 g (51%). *Anal.* Calc. for $C_{41}H_{64}O_4 \cdot 3H_{2}O$ (675.0 g mol⁻¹): C, 72.96; H, 9.45. Found: C, 73.30; H, 9.33%. IR (KBr, cm⁻¹): 3445w (OH), 1673s (C=O enol form) and 1606s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³*J* 6.7, CH₃), 1.25 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³*J* 6.7, OCH₂), 4.52 (s CH₂ keto form), 6.73 (s, CH enol form), 6.92 (d, ³*J* 8.9, H_m), 6.95 (d, ³*J* 8.9, H_m'), 7.94 (d, ³*J* 8.9, H_o), 8.04 (d, ³*J* 8.9, H_{o'}).

2.2.16. $[HOO^{R(18)R(10)}]$ (D_{18,10})

Yield: 5.14 g (63%). Anal. Calc. for $C_{43}H_{68}O_4 \cdot 1.5H_2O$ (676.0 gmol⁻¹): C, 76.40; H, 10.59. Found: C, 76.11; H, 9.72%. IR (KBr, cm⁻¹): 3427w (OH), 1672s (C=O enol form) and 1606s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³J 6.7, CH₃), 1.26 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³J 6.7, OCH₂), 4.52 (s CH₂ keto form), 6.73 (s, CH enol form), 6.92 (d, ³J 8.9, H_m), 6.95 (d, ³J 8.9, H_{m'}), 7.94 (d, ³J 8.9, H₀), 8.04 (d, ³J 8.9, H_{o'}).

2.2.17. $[HOO^{R(18)R(14)}]$ (D_{18.14})

Yield: 7.25 g (78%). *Anal.* Calc. for $C_{47}H_{76}O_4 \cdot 4H_2O$ (777.2 g mol⁻¹): C, 72.64; H, 10.89. Found: C, 72.77; H, 10.06%. IR (KBr, cm⁻¹): 3427w (OH), 1687s (C=O enol form) and 1607s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³J 6.4, CH₃), 1.26 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³J 6.4, OCH₂), 4.52 (s CH₂ keto form), 6.72 (s, CH enol form), 6.92 (d, ³J 8.9, H_m), 6.95 (d, ³J 8.9, H_m'), 7.94 (d, ³J 8.9, H_o), 8.04 (d, ³J 8.9, H_{o'}).

2.2.18. $[HOO^{R(18)R(16)}]$ (D_{18.16})

Yield: 7.12 g (77%). *Anal.* Calc. for $C_{49}H_{80}O_4 \cdot 2H_2O$ (769.2 gmol⁻¹): C, 76.51; H, 11.01. Found: C, 76.49; H, 10.17%. IR (KBr, cm⁻¹): 3444w (OH), 1679s (C=O enol form) and 1607s (C=C)₀. ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (t, ³*J* 6.4, CH₃), 1.26 (m, CH₂), 1.81 (m, CH₂), 4.02 (t, ³*J* 6.4, OCH₂), 4.52 (s CH₂ keto form), 6.72 (s, CH enol form), 6.92 (d, ³*J* 8.9, H_m), 6.95 (d, ³*J* 8.9, H_{m'}), 7.94 (d, ³*J* 8.9, H₀), 8.04 (d, ³*J* 8.9, H_{o'}).

2.3. Synthesis of the compounds $[BF_2(OO^{R(n)R(m)})]$ (n = 12, 14, 16, 18; m = 4, 8, 10) (B_{n,m})

To a solution in dichloromethane (50 mL) of 1 mmol of the corresponding sodium β -diketonate (prepared *in situ* from 1 mmol of the β -diketone and 1.5 mmol of NaH 60% dispersion in mineral oil), 5 mmol of HBF₄·Et₂O were added. The mixture was stirred at room temperature for 24 and then cooled down at -18 °C. The yellow solid formed was filtered off *in vacuo* and purified by chromatography using dichloromethane as eluent. The compounds B_{18,12}, B_{16,12} and B_{14,12}, reported by us [11] will be used in this work in the discussion. Elemental analysis and spectroscopic data are given as follows.

2.3.1. $[BF_2OO^{R(12)R(4)}]$ (B_{12.4})

Anal. Calc. for $C_{31}H_{43}O_4BF_2 \cdot 0.3(CH_2Cl_2)$ (554.0 g mol⁻¹): C, 67.86; H, 7.93. Found: C, 67.85; H, 7.71%. IR (KBr, cm⁻¹): 1548vs (C=O), 1502s (C=C)₀, 1378 m (BO) and 1038s (BF). ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (3H, t, ³J 6.7, CH₃ R(12)), 0.99 (3H, t, ³J 7.4, CH₃ R(4)), 1.27 (20H, m, CH₂), 1.83 (4H, m, CH₂), 4.07 (4H, t, ³J 6.7, OCH₂), 7.00 (1H, s, CH), 7.00 (4H, d, ³J 9.0, H_m), 8.11 (4H, d, ³J 9.0, H_o).

2.3.2. $[BF_2OO^{R(12)R(8)}]$ (B_{12.8})

Anal. Calc. for C₃₅H₅₁O₄BF₂·0.15(CH₂Cl₂) (597.3 g mol⁻¹): C, 70.68; H, 8.66. Found: C, 70.63; H, 8.35%. IR (KBr, cm⁻¹): 1556vs (C=O), 1502s (C=C)_Ø, 1376 m (BO) and 1036s (BF). ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.90 (6H, t, ³*J* 6.7, CH₃), 1.28 (28H, m, CH₂), 1.83 (4H, m, CH₂), 4.08 (4H, t, ³*J* 6.7, OCH₂), 6.99 (1H, s, CH), 7.00 (4H, d, ³*J* 9.0, H_m), 8.11 (4H, d, ³*J* 9.0, H_o).

2.3.3. $[BF_2OO^{R(12)R(10)}]$ $(B_{12,10})$

Anal. Calc. for C₃₇H₅₅O₄BF₂ (612.7 g mol⁻¹): C, 72.54; H, 9.05. Found: C, 72.02; H, 8.67%. IR (KBr, cm⁻¹): 1562vs (C=O), 1504s (C=C)_φ, 1378 m (BO) and 1036s (BF). ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.89 (6H, t, ³J 6.7, CH₃), 1.27 (32H, m, CH₂), 1.83 (4H, m, CH₂), 4.07 (4H, t, ³J 6.7, OCH₂), 6.99 (1H, s, CH), 7.00 (4H, d, ³J 9.0, H_m), 8.10 (4H, d, ³J 9.0, H_o).

2.3.4. $[BF_2OO^{R(14)R(4)}]$ (B_{14.4})

Anal. Calc. for $C_{33}H_{47}O_4BF_2$ (556.6 g mol⁻¹): C, 71.22; H, 8.51. Found: C, 70.88; H, 8.31%. IR (KBr, cm⁻¹): 1561vs (C=O), 1503s (C=C)₀, 1378 m (BO) and 1033s (BF). ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (3H, t, ³J 6.7, CH₃ R(14)), 0.99 (3H, t, ³J 7.4, CH₃ R(4)), 1.26 (24H, m, CH₂), 1.83 (4H, m, CH₂), 4.07 (4H, t, ³J 6.7, OCH₂), 7.00 (1H, s, CH), 7.00 (4H, d, ³J 9.0, H_m), 8.11 (4H, d, ³J 9.0, H₀).

2.3.5. $[BF_2OO^{R(14)R(8)}]$ (B_{14.8})

Anal. Calc. for $C_{37}H_{55}O_4BF_2 \cdot 0.05(CH_2Cl_2)$ (616.9 g mol⁻¹): C, 72.14; H, 8.99. Found: C, 72.05; H, 8.59%. IR (KBr, cm⁻¹): 1561vs (C=O), 1503s (C=C)_Ø, 1376 m (BO) and 1036s (BF). ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (6H, t, ³J 6.7, CH₃), 1.27 (32H, m, CH₂), 1.83 (4H, m, CH₂), 4.08 (4H, t, ³J 6.7, OCH₂), 6.99 (1H, s, CH), 7.00 (4H, d, ³J 9.0, H_m), 8.11 (4H, d, ³J 9.0, H_o).

2.3.6. $[BF_2OO^{R(16)R(4)}]$ (B_{16.4})

Anal. Calc. for $C_{35}H_{51}O_4BF_2 \cdot 0.15(CH_2Cl_2)$ (597.3 g mol⁻¹): C, 70.68; H, 8.66. Found: C, 70.56; H, 8.40%. IR (KBr, cm⁻¹): 1562vs (C=O), 1503s (C=C)₀, 1378 m (BO) and 1030s (BF). ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (3H, t, ³J 6.7, CH₃ R(16)), 0.99 (3H, t, ³J 7.4, CH₃ R(4)), 1.26 (28H, m, CH₂), 1.83 (4H, m, CH₂), 4.07 (4H, t, ³J 6.7, OCH₂), 7.00 (1H, s, CH), 7.00 (4H, d, ³J 9.0, H_m), 8.11 (4H, d, ³J 9.0, H_o).

2.3.7. $[BF_2OO^{R(16)R(8)}]$ (B_{16.8})

Anal. Calc. for $C_{39}H_{59}O_4BF_2$ (640.7 g mol⁻¹): C, 73.11; H, 9.28. Found: C, 73.27; H, 9.00%. IR (KBr, cm⁻¹): 1561vs (C=O), 1504s (C=C)₀, 1378 m (BO) and 1036s (BF). ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (6H, t, ³J 6.7, CH₃), 1.27 (36H, m, CH₂), 1.83 (4H, m, CH₂), 4.07 (4H, t, ³J 6.7, OCH₂), 6.99 (1H, s, CH), 7.00 (4H, d, ³J 9.0, H_m), 8.11 (4H, d, ³J 9.0, H_o).

2.3.8. $[BF_2OO^{R(18)R(4)}]$ (B_{18.4})

Anal. Calc. for $C_{37}H_{55}O_4BF_2 \cdot 0.15(CH_2Cl_2)$ (625.4 g mol⁻¹): C, 71.35; H, 8.91. Found: C, 71.36; H, 8.59%. IR (KBr, cm⁻¹): 1549vs (C=O), 1498s (C=C)_Ø, 1374 m (BO) and 1033s (BF). ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (3H, t, ³J 6.7, CH₃ R(18)), 0.99 (3H, t, ³J 7.4, CH₃ R(4)), 1.26 (32H, m, CH₂), 1.82 (4H, m, CH₂), 4.07 (4H, t, ³J 6.7, OCH₂), 7.00 (1H, s, CH), 7.00 (4H, d, ³J 9.0, H_m), 8.11 (4H, d, ³J 9.0, H_o).

2.3.9. $[BF_2OO^{R(18)R(8)}]$ (B_{18.8})

Anal. Calc. for $C_{41}H_{63}O_4BF_2$ (668.8 g mol⁻¹): C, 73.64; H, 9.50. Found: C, 73.39; H, 9.18%. IR (KBr, cm⁻¹): 1562vs (C=O), 1504s (C=C)₀, 1378 m (BO) and 1035s (BF). ¹H NMR (300 MHz; CDCl₃; Me₄Si) δ (ppm): 0.88 (6H, t, ³J 6.7, CH₃), 1.26 (40H, m, CH₂), 1.82 (4H, m, CH₂), 4.07 (4H, t, ³J 6.7, OCH₂), 7.00 (1H, s, CH), 7.00 (4H, d, ³J 9.0, H_m), 8.11 (4H, d, ³J 9.0, H_o).

3. Results and discussion

3.1. Characterization and thermal studies of the β -diketones [HOO^{R(n)R(m)}]

The ligands play a key role in determining the mesomorphic behavior, since they can control the molecular shape and polarization by using suitable substituents. Before discussing the mesomorphism of the new β -diketones described in this work we consider of interest the data reported for previous related compounds.

The symmetrically 1,3-alkyloxyphenyl substituted β -diketone ligands, [HOO^{2R(n)}], D_{n,n}, *n* = 8, 9 and 10, have been previously reported by Ohta and col. as mesomorphic compounds [13,14]



Fig. 1. β-Diketones studied.

exhibiting a mesophase which was described by Serrano and coworkers. as a crystalline smectic phase [15].

Related β -diketones with longer n = 12, 14, 16 and 18 carbon atoms in the alkyl chains, D_{12,12}, D_{14,14}, D_{16,16} and D_{18,18} were studied in our lab and clearly determined as mesomorphic materials showing SmC phases in the temperature range of 94–130 °C [16].

Moreover, unsymmetrically substituted β -diketones of the type [HOO^{*R*(*n*)*R*(*m*)], D_{*n*,*m*}, were also reported for *n* = 7 and *m* = 9, 10 carbon atoms in the alkyl chains of the substituents at 1(3) and 3(1) positions. D_{7,9} did not show mesomorphic behavior, but the longer D_{7,10} exhibited a monotropic smectic phase [17].}

On the other hand, some other β -diketones with three or four alkyl chains in the aromatic substituents, such as 1-(3,4-dialkyl-oxyphenyl)-3-(4-alkyloxyphenyl)-propane-1,3-dione and 1-(3,4-dialkyloxyphenyl)-3-(3,4-dialkyloxyphenyl)-propane-1,3-dione have been also reported as non-liquid crystal materials [17]. In those compounds, the absence of mesomorphism has been explained on the basis that the increased number of terminal chains on these ligands disrupts the calamitic mesomorphism [15].

In this work, four new series of unsymmetrically substituted β diketones have been prepared and structurally characterized (Fig. 1). Their thermal behavior has been studied by differential scanning calorimetry (DSC), polarized-light optical microscopy (POM) and low angle temperature-dependent X-ray diffraction (XRD).

The solution ¹H NMR spectra in CDCl₃ of all new compounds $D_{n,m}$ show well defined signals for the β -diketone core and the alkyloxyphenyl substituents. The singlets at *ca*. 6.73 ppm from CH proton and 4.52 ppm from CH₂ protons of the central carbon of the diketone core confirm the existence of keto and enol tautomers in solution (Fig. 2), being the enol form the major one (>90%) as deduced from the signal intensity ratio of the CH/CH₂ protons. However, in the NMR time-scale it was not possible to distinguish between the two different possible enol forms (Fig. 2a and 2c). Duplicated doublets at *ca*. 8.04, 7.94 and 6.96, 6.93 ppm

correspond to the *ortho* and *meta* protons of the phenyl rings, of the two tautomeric keto and enol forms.

The IR spectrum of $D_{14,8}$, as a representative example, in CH_2CI_2 solution shows two bands in the carbonyl region at 1724 and 1683 cm⁻¹ assigned to the v(CO) absorption frequencies of the keto and enol forms, respectively. By contrast, the IR spectra in the solid state of all the compounds exhibit only one band in this region at *ca*. 1671 cm⁻¹. This fact is in agreement with the presence of the enol form as the unique tautomer in the solid state. Bands at *ca*. 1607 and 3431 cm⁻¹ assigned to the $v(C=C)_{\emptyset}$ and v(OH) absorptions are also observed.

The new β -diketones studied exhibit mesomorphic behavior (Table 1), showing SmC mesophases in all cases (Fig. 3a, b and d) and N mesophases in some of them (Fig. 3c and d). Several solid-solid phase transitions are observed as well.

The Cr \rightarrow SmC phase transition typically varies between 81 and 105 °C. In general terms, it was observed that the variation on the number of carbon atoms in both alkyl chains, n and m, decreased or increased the stability of the crystalline phase, being this fact reflected by the lowering or the increasing of the melting point as it is commented as follows.

An analysis of the thermal behavior of the four families of compounds allows us to observe two tendencies in the variation of the melting temperatures in each family, depending on the chain length with $m \ge 10$ or $m \le 10$ carbon atoms, I and II, respectively.

On one hand, for compounds of the families $D_{14,m}$, $D_{16,m}$ and $D_{18,m}$ with a full length of the alkyl chains of $L = m + n \ge 24$, 26 and 28 carbon atoms, respectively (I), the melting temperatures decrease by increasing the asymmetry |m - n| which is consistent with an increasing of the molecular length. Therefore, for each kind of family, the best results were obtained for compounds with the shortest chains, $D_{14,10}$, $D_{16,10}$ and $D_{18,10}$, respectively. However, in the family $D_{12,m}$ with L > 22 (I), although a decreasing the asymmetry, in this case the lowest melting temperature was found for the longest compound, $D_{12,18}$.

On the other hand, for the compounds of all the above families, but with shorter chains, $L \leq 22$, 24, 26 and 28 for $D_{12,m}$, $D_{14,m}$, $D_{16,m}$ and $D_{18,m}$, respectively (II), the melting temperatures decrease by increasing the full molecular length, being this fact related to the concomitant decreasing of the asymmetry. As a consequence, those with L = 22, 24, 26 and 28 for $D_{12,m}$, $D_{14,m}$, $D_{16,m}$ and $D_{18,m}$, respectively, are the compounds with lower melting points.

These variations are summarized, for the families $D_{12,m}$ and $D_{18,m}$, as representative examples in the Fig. 4a and b, respectively.

As a conclusion we can deduce that for compounds with longer chains, $m \ge 10$, an increasing in the asymmetry is determining to get lower transition temperatures. By contrast, the compounds of all families having shorter chains, $m \le 10$, require the presence of alkyl chains in both substituents with closer lengths to get a lower melting temperature (Table 2).

Temperature-dependent powder X-ray diffraction experiments for some selected compounds confirmed the SmC mesophases



 $R = OC_nH_{2n+1}; R' = OC_mH_{2m+1}$

Table 1
Thermal behavior of compounds $D_{n,m}$.
$T = C (A \cup J = mol^{-1})$

1/ C()										
FAMIL	Y COMPOUN	D Cr →	Cr' →	Cr" →	SmO	$2 \rightarrow 1$	$N \rightarrow$	$I \rightarrow$	$N \rightarrow$	$SmC \rightarrow$	$Cr \rightarrow$	Cr'
D12 m	D124	• 73 (18.3)	•	91 (32.0)	•		113 (0.4)	•	106 (-0.4)	• 70 (-11.6)	 49 (-13.5) 	•
12,11	D12.4	• 72 (43.7)	•	86 (7.4)	•	$116^{a}(2.8)$	• 116^{a} (2.8)	• 118 ^a (-1.5	$\bullet 118^{a}(-1.5)$) • 79 (-5.5)	 55^b 	•
	D _{12,0}	• 62 (5.4)	• $79^{a}(50.8)$	• $84^{a,b}$ (50.8)	•	116 (2.7)	• 118 ^b	• 117 (-1.7)	• 94 (-0.3)	• 74 (-6.8)	 67 (-19.6) 	•
	D12.14	• 74 (7.2)	• 83 ^a (56 3)	• 93 ^{a,b} (56.3)	•		113 (2.9)	•	108(-14)	• 68 (-29 0)	• 63 (-2.1)	
	D12.14	• 64 (6 5)	• $78^{a,b}$ (50.5	$1 \bullet 89^{a}(505)$	•		119(37)	•	115 (-5.1)	• 69 (-9 8)	• 60 (-8.8)	
	D12.10	• 74 (21.3)	• 81 ^a (45.7)	 86^{a,b} (45.7) 	•		118 ^b	•	114 (-4.4)	• 79 (-24 7)	• 74 (-15.2)	
D14 m	D144	• 77 (15.7)	•	95 (42.4)	•		118 (2.6)	•	114 (-2.2)	• 76 (-20.1)	• 56 (-10.4)	•
- 14,11	D14,4	• 60 (18.4)	 81 (8.1) 	• 94(43.0)	•	$115^{a}(2.1)$	 115^a (2.1) 	• 116 (-1.1)	• 71 ^a (-7.3)	• 62 ^b	•	
	D14.8	• 71 (14.9)	•	93 (43.5)	•	112 (3.9)	• 124 ^b	• 114 (-2.9)	• 94 ^b	• 72 (-20.1)	 59 (-8.0) 	•
	D14.10	• 70 (12.6)	• 81 ^a (57.7)	• $92^{a,b}(57.7)$	•		98 (0.2)	•	95 (-0.9)	• 68 (-37.8)	•	
	D14.12	• 74 (7.2)	• 83 ^a (56.3)	• $93^{a,b}$ (56.3)	•		113 (2.9)	•	108 (-1.4)	• 68 (-29.0)	• 63 (-2.1)	•
	D14.16	• 65 (-13.1)	• 87 (12.6)	• 97 (42.2)	•		118 (3.2)	•	111 (-1.9)	• 76 (-39.6)	•	
	D14.18	• 83 ^b	•	94(43.9)	•		113 (4.4)	•	104 (-2.1)	• 83 (-22.4)	• 75 (-8.2)	•
D ₁₆ m	D ₁₆₄	 81 (29.4) 	•	99 (30.1)	•		105 (0.9)	•	102 (-0.4)	• 82 (-17.1)	 65 (-26.1) 	•
10,11	D ₁₆₆	• 58 ^b	•	99 (50.6)	•	114 (2.2)	• 123 (2.0)	 129^b 	• 109 (-4.9)	• 84 (-29.1)	•	
	D _{16.8}	 76 (29.5) 	•	96 (39.4)	•	. ,	109 (3.2)	•	107 (-1.5)	• 76 (-18.8)	 64 (-18.4) 	•
	D _{16 10}	• 60 ^b	 75^a (49.3) 	• 81 ^{a,b} (49.3)	•		98 (1.2)	•	88 (-0.6)	• 63 ^{a,b} (-26.4) • $57^{a}(-26.4)$	•
	D _{16 12} *	 64 (6.5) 	• 78 ^{a,b} (50.5) • $89^{a}(50.5)$	•		119 (3.7)	•	115 (-5.1)	 69 (-9.8) 	• 60 (-8.8)	•
	D _{16 14}	• 65 (-13.1)	• 87 (12.6)	• 97 (42.2)	•		118 (3.2)	•	111 (-1.9)	• 76 (-39.6)	•	
	D _{16.18}	• 87 (15.6)	• 93 ^a (61.0)	• 100 ^{a,b} (61.0)) •		107 ^b	•	96 (-1.0)	• 82 ^{a,b} (-57.8) • 79^{a} (-57.8)	•
D _{18.m}	D _{18.4}	• 71 (10.8)	• 85 (8.1)	 105 (50.1) 	· •		116 (1.2)	•	111 (-1.4)	• 90 (-28.4)	• 73 (-20.6)	•
	D _{18.6}	• 73 ^a (10.9)	• 77 ^{a,b} (10.9) • 100 (56.2)	•		126 (9.6)	•	120 (-7.8)	• 80 (-31.4)	• 65 (-7.4)	•
	D _{18.8}	• 65 ^{a,b} (54.8) • $75^{a}(54.8)$	• 89 ^b	•		112 ^b	•	96 (-0.7)	• 59 (-32.7)	•	
	D _{18.10}	• 53 ^b	• 78 ^{a,b} (50.0) • $81^{a}(50.0)$	•		97 (1.5)	•	92 (-1.0)	• 57 (-27.3)	•	
	D _{18.12} *	• 74 (21.3)	• 81 ^a (45.7)	• 86 ^{a,b} (45.7)	•		118 ^b	•	114 (-4.4)	• 79 (-24.7)	• 74 (-15.2)	•
	D _{18,14}	• 83 ^b	•	94 (43.9)	•		113 (4.4)	•	104 (-2.1)	• 83 (-22.4)	• 75 (-8.2)	•
	D _{18,16}	• 87 (15.6)	• 93 ^a (61.0)	• 100 ^{a,b} (61.0)) •		107 ^b	•	96 (-1.0)	• 82 ^{a,b} (-57.8) • 79 ^a (-57.8)	•

^a Overlapped processes.

^b Temperature determined by POM.

* Ref. [11].



Fig. 3. Photomicrographs of the mesophases observed by POM: (a) SmC mesophase of $D_{12,8}$ at 90 °C on heating; (b) SmC mesophase of $D_{14,8}$ at 110 °C on heating; (c) N mesophase of $D_{14,8}$ at 120 °C on heating; and (d) SmC and N mesophases of $D_{14,8}$ at 95 °C on cooling.

assigned by POM (Table 3). The pattern shows two or three maxima in the low-angle region. The reciprocal spacing ratio of 1:2:3 indicates the existence of a lamellar mesophase. The peaks are so assigned to the $(0\ 0\ 1)$, $(0\ 0\ 2)$ and $(0\ 0\ 3)$ reflections of the smectic phase. Also, the diffuse halo due to the fluid movement of the alkyl chains appears in the medium angle region of the diffractograms.

For these compounds, the layer spacing, d, was smaller than the molecular length in the full extended conformation, l, deduced by



Fig. 4. Melting temperatures of compounds $D_{12,m}$ (a) and $D_{18,m}$ (b) as a function of the molecular length.



		II			Ι						
D _{12,m}	← D _{12,4} 91 ←		D _{12,8} 86	D _{12,10} 84		D _{12,14} 93 ≮	D _{12,16} 89	D _{12,18} 86			
D _{14,m}	← D _{14,4} 95 ←	D _{14,6} 94	D _{14,8} 93	D _{14,10} 92	D _{14,12} 93		D _{14,16} 97	> D _{14,18} 94			
D _{16,m}	← D _{16,4} 99	D _{16,6} 99	D _{16,8} 96	D _{16,10} 81	D _{16,12} 89	D _{16,14} 97		D _{16,18} 100			
D _{18,m}	← D _{18,4} 105 ←	D _{18,6} 100	D _{18,8} 89	D _{18,10} 81	D _{18,12} 86	D _{18,14} 94	D _{18,16} 100				
Lenght L = r	n + n										
Asymmetry Melting Terr	m - n	\rightarrow									

extrapolation from that found in the single-crystal X-ray diffraction of the related $D_{4,4}$ [12]. This fact indicates that in this mesophase the molecules are inclined related to the layer.

the shortest ones of the series $D_{12,m}$, $D_{14,m}$ and $D_{16,m}$ (m = 6, 8, 10) with the exception of those with m = 4.

Nematic enantiotropic phases were also observed for compounds with L = 20 or 22 carbon atoms. Interestingly, those are It seems that in the long chained β -diketones ($L \ge 24$), the higher interchain interactions due to the presence of longer alkyl chains do not allow the characteristic disorder of the N phase.

Table 3		
X-ray diffraction	data for selected	D _{n,m} compounds.

Compound	<i>T</i> (°C)	Phase	Position 2θ (°)	d-spacing (Å)	Miller indexes (hkl)	Lattice parameters (Å)	Estimated length (Å)
D _{12,10}	85 (cooling)	35 (cooling) SmC 2.7 32.2		001	<i>c</i> = 32.2	<i>l</i> = 38.7	
			5.5	16.2	0 0 2		
			18.6	4.8	a		
	115 (cooling)	Ν	3.7	24.1			
			18.5	4.8	a		
D _{14,8}	100 (cooling)	SmC	2.4	36.8	001	<i>c</i> = 36.8	<i>l</i> = 38.7
			4.7	18.7	0 0 2		
			18.3	4.9	a		
D _{16,8}	100 (heating)	SmC	2.4	37.1	001	<i>c</i> = 37.1	<i>l</i> = 41.2
			4.5	17.6	0 0 2		
			19.7	4.6	a		
D _{16,10}	70 (cooling)	SmC	2.3	38.7	001	<i>c</i> = 38.7	<i>l</i> = 43.7
			4.6	19.2	0 0 2		
			19.5	4.6	a		
D _{16,14}	90 (cooling)	SmC	2.2	40.5	001	<i>c</i> = 40.5	<i>l</i> = 48.7
			4.2	20.9	0 0 2		
			18.2	4.9	a		
D _{18,4}	85 (cooling)	SmC	2.4	36.6	001	<i>c</i> = 36.6	<i>l</i> = 38.7
			4.7	18.7	0 0 2		
			7.1	12.5	003		
			18.3	4.9	a		
D _{18,10}	70 (cooling)	SmC	2.2	40.1	001	<i>c</i> = 40.1	<i>l</i> = 46.2
			4.6	19.4	002		
			19.8	4.5	a		

a: Halo of the molten alkyl chains.

Then, we can establish that the type of mesophase obtained is directly linked to the length of the alkyl chains attached to the phenyl rings of the substituents at the 1,3 positions of the β -diketone.

The variation of the clearing temperatures of compounds of the families $D_{14,m}$, $D_{16,m}$, $D_{18,m}$ follows the same sequence that those observed in the melting temperatures By contrast, for the family $D_{12,m}$, the clearing temperatures exhibit an opposite variation to that of the melting temperatures.

From the above comments we determine that for each family, the compound exhibiting the lower melting temperature is that with m = 10 carbon atoms, as shown in green in Table 2. Taking into account this result, and also by considering the compound that exhibits the highest range of the liquid crystal existence, including SmC and N phases, we can conclude that the best results correspond to the compound D_{12,10}, showing phase transition temperatures to the SmC and N phases of 84 and 116 °C, respectively, and a clearing point of 118 °C (Table 2).

3.2. Characterization and thermal studies of the complexes $[BF_2(OO^{R(n)R(m)})]$

We have previously reported that the strategic design of unsymmetrically 1,3-alkyloxyphenyl substituted borondifluoride β -diketonates of the type [BF₂(OO^{R(12)R(m)})] (m = 14, 16 and 18) was successfully used in order to obtain liquid crystal behavior in addition to a high photoluminescent quantum yield [11]. We were interested in proving if this behavior follows a regular pattern so allowing to get the desired bifunctional materials.

Thus, following these precedents and taking into account the thermal study of the new related β -diketones above described, we now propose to extend the thermal and luminescent studies to new families of unsymmetrical boron derivatives using as ligands the asymmetric 1,3-alkyloxyphenyl substituted diketones maintaining one of the lateral chains with 4, 8 or 10 carbon atoms while the other one is increased from 12 to 18 carbon atoms each series (Fig. 5). Those ligands have been selected due to they exhibited the best liquid crystal behavior, related with the melting temperature and the mesophase stability range, and additionally because they are adequate to compare the effect of the molecular

length and the asymmetry in the mesomorphism of the new boron derivatives as well as to study the photoluminescent behavior.

The ¹H NMR spectra in CDCl₃ solution of all complexes $B_{n,m}$ show the characteristic signals of the alkyloxyphenyl substituted β -diketonate ligand [11]. In all cases it is observed a singlet at ca. 7.00 ppm, which corresponds to the central proton of the diketonate core (CH). This fact is consistent with the coordination of the ligand as enolate form. Also, two doublets observed at *ca*. 8.11 and 7.00 ppm, respectively correspond to the *ortho* and *meta* protons of the phenyl rings.

The IR spectra in KBr show an absorption band of the v(CO) frequency at *ca*. 1561 cm⁻¹, bathocromically shifted with respect to the free diketone, in agreement with that of the diketonate form. Also the presence of the v(BO) band at *ca*. 1376 cm⁻¹ and the lack of the v(OH) band from the enol tautomer of the β -diketone indicate the coordination of the carbonyl groups to the boron atom. A band at *ca*. 1036 cm⁻¹, assigned to the v(BF) absorption is also observed.

The thermal behavior of the boron derivatives is shown in Table 4. All the compounds behave as liquid crystals, showing an



D _{12,m}	n = 12	m = 4, 8, 10
$B_{14,m}$	n = 14	m = 4, 8
$B_{16,m}$	n = 16	m = 4, 8
$B_{18,m}$	n = 18	m = 4, 8

Fig. 5. Borondifluoride complexes studied.

Table 4				
Thermal	behavior	of	compounds	B _{n,m}

	T (°C) (ΔH/ł	kJ mo	(l^{-1})															
Family	Compound	Cr	\rightarrow	Cr'	\rightarrow	Cr"	\rightarrow	B_1	\rightarrow	Ι	\rightarrow	B_1	\rightarrow	Cr	\rightarrow	Cr'	\rightarrow	Cr"
B ₁₂ , _m	B ₁₂₄ B _{12,8}	•	109 (10.6) 118 (11.3)	•			132 ^a (22.9) 142 ^a (21.8)	•	$132^{a}(22.9)$ $142^{a}(21.8)$	•	132 ^a (-22.2) 142 ^a (-23.6)	•	132 ^a (-22.9) 142 ^a (-23.6)	•	109 (-3.0)		75 (4 4)	
B _{14,m}	B _{12,10} B _{14,4} B _{14,8}	•	102 (4.6) 109 (14.0)	•			143 (27.4) 131 ^a (24.3) 139 ^a (24.2)	•	143 (27.4) 131 ^a (24.3) 139 ^a (24.2)	•	142 (-26.5) 128 ^a (-21.4) 139 ^a (-24.3)	•	142 (-26.5) 128 ^a (-21.4) 139 ^a (-24.3)	•	87 (-16.0) 70 ^b	•	75 (-4.4)	•
B _{16,m}	B _{16,4} B _{16,8}	•	45 (8.5) 112 (24.1)	•	86 (11.7)	•	120 (25.1) 135 ^a (22.4)	•	130 (12.2) 135 ^a (22.4)	•	128 ^a (-18.9) 135 ^a (-23.6)	:	128 ^a (-18.9) 135 ^a (-23.6)	•	109 (-3.4) 79 (-2.8)	•		
B _{18,m}	B _{18,4} B _{18,8}	•	98 (58.3) 116 (29.7)	•	110 (2.7)	•	133 ^a (26.7) 134 ^a (21.1)	•	133 ^a (26.7) 134 ^a (21.1)	•	122 ^a (-21.6) 133 ^a (-22.4)	•	122 ^a (-21.6) 133 ^a (-22.4)	•	110 (-4.0) 68 ^b	•		

^a Overlapped processes.

^b Temperature determined by POM.

enantiotropic mesophase at temperature close to the clearing. Thus, a crystalline phase, the mesophase and the isotropic liquid are almost observed at the same temperature. In agreement with these features, the DSC thermograms show in the heating, in addition to a first peak due to a solid–solid transition, one wide peak corresponding to the overlapped solid–mesophase–isotropic liquid processes. On cooling, two peaks corresponding to the reverse processes to those appearing on heating are observed. A first wide peak is related to the mesophase growth as well as its crystallization. The second peak is associated to a solid–solid phase transition.

In order to identify the mesophase nature, a careful and precise control of the temperature was carried out by a slow POM observation, maintaining the temperature for several minutes each $0.1 \,^{\circ}$ C increasing or decreasing stage, both on heating and on cooling. In this way, we were able to achieve the mesophase without the pres-

ence of crystals or the quick appearance of the isotropic liquid. The mesophase was identified as a B_1 mesophase. The phase transition temperatures for our compounds are in a similar range to that found for organic compounds exhibiting bent-core mesophases of the B_1 type [18–21].

The B_1 phase is one of the so-called banana phases, formed by bent-core mesogens. This phase seems to exhibit a fluid smectic structure and, in general is observed as having a mosaic texture. When cooling from the isotropic liquid, a dendritic growth of the mesophase is observed with dendrites coalescing to form a mosaic texture [22]. In our compounds, the mosaic texture could be clearly observed in all cases (Fig. 6) both on heating and cooling, as well as the dendritic growth (Fig. 6a) through a very slow decreasing of temperature from the isotropic phase.

By comparing the phase transition temperatures of compounds $B_{n,4}$ and $B_{n,8}$ from their DSC thermograms, we can deduce that, in



Fig. 6. Textures observed by POM of the B₁ mesophase of B_{12,10} at 145.6 °C on cooling (a) and (b), and B_{14.8} at 140.5 °C on cooling (c) and (d).

general terms, the melting temperatures decrease as the difference between the length of both alkyl chains of the substituents increases, therefore, indicating that an increase of the asymmetry gives rise to lower transition temperatures (Table 5).

So, for instance, taken the series $B_{n,4}$, melting temperatures are moved from 132 to 120 °C when n is increased from 12 to 16 carbon atoms and a similar decrease from 142 to 134 °C is observed in $B_{n,8}$ compounds (Table 5b). Related derivatives previously reported [11] are also included here for comparative purposes (Table 5a).

The same behavior was also observed for the compounds with both chains longer than 10 carbon atoms ($B_{12,m}$ with m = 14, 16 and 18 carbon atoms), although for those compounds the increased asymmetry is consistent with a higher full molecular length. Therefore, by considering all the $B_{12,n}$ derivatives (Table 5a and

b) here described, with m + n varying from 16 (B_{12,4}) until 30 (B_{12,18}) carbon atoms in length, it is evident that the lowest melting temperatures are obtained for the longest and shortest compounds, both showing the highest asymmetry.

Taking into account these results, we can conclude that the molecular asymmetry is a determining factor to obtain lower transition temperatures in this type of boron derivatives (Fig. 7).

On the other hand, in order to establish a complete identification of the mesophase, temperature-dependent XRD studies were carried out. Due to the narrow range of existence of the mesophase, diffractograms were taken at different stages at temperatures close to the clearing process, maintaining the temperature for several minutes in each stage, as the same way used on the POM observation. Several registers were taken at each stage after different





Fig. 7. Melting temperature of the compounds $B_{12,m}$ as a function of the molecular length.

lapses of time. Due to this careful control, we were able to obtain diffractograms, which allow us to establish the presence of a B_1 phase. In these cases, the two or three reflection peaks, in the small angle region, indexed as (1 0 1), (2 0 2) and (0 0 2), indicate a rectangular columnar arrangement (Table 6). The intensity of the second peak is much higher than the first peak, as reported for B_1 phases [19].

3.3. Photophysical studies of the compounds $[BF_2(OO^{R(n)R(m)})]$

Electronic absorption spectra in dichloromethane solution and emission spectra in the solid state and in dilute dichloromethane solution were recorded for the complexes of the families $B_{12,m}$, $B_{14,m}$, $B_{16,m}$ and $B_{18,m}$. Due to their similarity, only data of representative examples are depicted in Table 7. Those of the related complex $B_{16,12}$, previously reported by us [11], are also included for comparative purposes.

All of the boron derivatives fluoresce at *ca*. 480 nm in the solid state and at *ca*. 438 nm in dichloromethane solution (Fig. 8). The chain length of the aryl substituents at the 1,3-positions of the β -diketonate ligand has virtually no effect on the spectroscopic properties of these compounds.

3.3.1. Solution studies

The UV–Vis absorption spectra of dilute solutions (*ca.* 2.0– 4.0×10^{-6} M) in dichloromethane of the compounds exhibit two absorption bands, being the strongest one centred at *ca.* 412 nm (Table 7, Fig. 9), characteristic of the electronic π – π * transition of chelating β -diketonate ligands [23].

The fluorescence spectra display a broad band with an unresolved vibronic substructure in the blue region with a maximum at *ca*. 438 nm. The emission shows an excellent photoluminescence relative quantum yield (*ca*. 0.95, with an estimated error of \pm 5%) using a solution of anthracene as standard ($\Phi = 0.27$) [24]. The emissive nature of these compounds was markedly higher than that of our previously reported boron difluoride β-diketonates [9] as well as that of several boron difluoride diaroylmethanato with different substituents [7].

The high quantum yield, close to the unity, in addition to the observed absorption in the yellow region and emission in the blue-violet range, make these compounds to be good candidates as fluorescent biological probes.

3.3.2. Solid state studies

The photophysical properties of the compounds $B_{16,m}$ were also studied in the solid state in order to establish their influence on the fluorescent behavior. The emission spectra exhibit a similar pattern consistent with a broad band centred at *ca*. 480 nm (Table 7, Fig. 9) assigned to a ligand-centred transition (LCT) which is redshifted with respect to that observed in solution.

Table 6

Compound	T (°C)	Phase	Position 2θ (°)	d- spacing (Å)	Miller Indexes (hkl)	Lattice parameters (Å)
B _{12,4}	129 (cooling)	B ₁	4.6 4.8 9.3 18.8	19.1 18.3 9.5 4.7	1 0 1 0 0 2 2 0 2 a	a = 22.4 c = 36.6
B _{18,4}	133 (heating)	B ₁	3.5 4.2 18.6	25.1 21.3 4.8	1 0 1 0 0 2 a	a = 31.1 c = 42.5

a: Halo of the molten alkyl chains.

Table 7

Photophysical characterization of selected compounds of the $B_{n,m}$ type. (Absorption and emission maxima in solution in the solid state in nm, molar absorption coefficient $Lmol^{-1}cm^{-1}$ and fluorescence quantum yields in 2.0×10^{-6} M dichloromethane solution)

Complex	λ_{abs}^{max} solution ^a	$\epsilon/10^4$	λ_{em}^{max} solution ^b	Φ_{f}^{c}	λ_{em}^{max} solid ^d
B _{16,4}	412	7.9	439	0.95	474
B _{16,8}	412	5.4	438	0.92	488
B _{16,12}	412	6.8	437	0.95	486

^a Estimated error: ±1 nm.

^b λ_{ex} = 412 nm; estimated error: ±1 nm.

^c λ_{ex} = 412 nm; estimated error: ±5%.

^d λ_{ex} = 412 nm; estimated error: ±1 nm.

3.3.3. Variable-temperature studies

In order to prove the luminescence of the compounds at the liquid crystal state, the luminescent behavior of the compounds $B_{16,4}$ and $B_{16,8}$ was studied at different temperatures from the solid state to the isotropic liquid. The fluorescence spectra were also registered on cooling from the isotropic liquid until room temperature (Fig. 10).

In general, the behavior of the emission band on heating shows that the intensity of fluorescence is almost unaffected until *ca*. 120-130 °C and then it decreases by increasing the temperature. It almost disappears at temperature of the isotropic liquid, when a quenching on the fluorescence is observed due to the increase of non radiative decay processes. The maximum of the fluorescence emission was not totally recovered upon cooling, being restored until 40% in some cases.

The above results allow us to establish that the mesophase aggregation state does not quench the emission. It is also remarkable that the emission maximum is maintained in the heating/ cooling cycle, indicating that the excited state is not modified.

4. Conclusions

Four new families of unsymmetrically substituted β -diketones [HOO^{R(n)R(m)}] as well as their borondifluoride derivatives [BF₂(OO^{R(n)R(m)})] were prepared and structurally characterized. The thermal study indicates a mesomorphic behavior in all cases, showing SmC and N mesophases for the β -diketones and bent-core B₁ mesophases for the boron derivatives.

It appears that the coordination of the diketonate ligand to the borondifluoride fragment generates a bent-core molecular shape involving three bonded cycles, in contrast with the open structure



Fig. 8. $B_{10,12}$ in the solid state (left) and 10^{-5} M dichloromethane solution (right). ($\lambda_{exc.}$ = 365 nm).



Fig. 9. UV–Vis and normalized emission spectra in 2.0×10^{-6} M dichloromethane solution and in the solid state of (a) $B_{16,4}$ and (b) $B_{16,8}$ at room temperature (λ_{ex} = 412 nm).



Fig. 10. Fluorescence spectra of (a) $B_{16,4}$ and (b) $B_{16,8}$ in the solid state as a function of temperature. Inset: intensity of emission as a function of the temperature ($\lambda_{ex} = 412 \text{ nm}$).

of the free β -diketone. In agreement with this proposal a B₁ mesophase is observed only in the boron derivatives, being the molecular asymmetry a determinant requirement to attain liquid crystal behavior. New studies are in progress in order to extend the mesophase range.

The development of liquid crystal compounds based on achiral bent-shaped molecules has recently attracted much attention due to their potential application as materials with ferroelectric and antiferroelectric properties. Taking into account that molecules described for these purposes are typically organic, the consecution of B_1 mesophases with a central core of the borondifluoride β -diketonate type opens new opportunities in the field of bent-core liquid crystals.

From the photophysical studies of the boron derivatives, a high quantum yield close to the unity was observed in all cases. In addition, the absorption located in the yellow region and their emission in the blue-violet range make these new compounds to be good candidates as fluorescent biological probes.

This type of compounds is one of the few examples of bent-core mesogens with highly luminescent properties.

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