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New 1,2,4- and 1,3,4-oxadiazole materials: synthesis, and mesomorphic and luminescence properties

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The synthesis and liquid crystalline properties of new series of 1,2,4- and 1,3,4-oxadiazole derivatives (**2a–f** and **5a–f** respectively) are reported. These compounds contain only one terminal flexible alkoxy chain, the other terminal substituent is a protecting benzyl group. All compounds of series **2** exhibit an enantiotropic nematic phase. The homologue with the longest chain (**2f**) displays an enantiotropic dimorphism smectic A– nematic. None of the compounds of series **5** shows mesomorphism and only crystal–isotropic transitions were observed. The liquid crystalline properties were investigated by differential scanning calorimetry, polarizing optical microscopy and X-ray measurements. Luminescence properties, in chloroform solution, of **2f** and the series **5** compounds were evaluated. Good photoluminescence quantum yields for compounds of series **5** were observed. Compound **2f**, incorporating the 1,2,4-oxadiazole ring shows a very strong reduction in emissive properties.

1. Introduction

Many series of liquid crystalline compounds containing heterocyclic groups have been synthesized due to their pontentially wide range of applications, such as in the optical, electrical and biological medical fields [1–5]. Usually 5- or 6-membered heterocycles are involved, and they form part of the core in rod-shaped, bent-shaped or disc-shaped molecules. Heterocyclic compounds such as five-membered thiadiazole or thiophene rings can be incorporated into the principal structure of calamitic mesogens [6–14].

Some mesogenic compounds containing the 1,3,4-oxadiazole ring have been reported previously [15–24]. Also a variety of mesogenic 1,2,4-oxadiazoles have been synthesized by Torgova *et al*. [25]. These structures have a large dipole moment perpendicular to the molecular axis, a characteristic that influences the mesogenic properties. The electron-accepting property of the oxadiazole ring enables substances incorporating it to be of use as electron transport layers in the development of organic light-emitting devices (OLEDs) [26].

In a continuation of our work on heterocyclic mesogens, we now described the synthesis and characterization of new 1,2,4- and 1,3,4-oxadiazole derivatives (series **2a–f** and **5a–f**, respectively) in which one terminal substituent is an alkoxy group, while the other terminal substituent is a benzyl group. Studies on the effect of the heterocyclic unit on liquid crystalline behaviour and on their photophysical and thermal properties are also reported.

Two points must be noted. First, series **2a–f** and **5a–f** compounds open an interesting possibility for the design of chiral liquid crystalline materials, because the benzyl group is a protecting group; it can be removed leading to the formation of the corresponding phenolic 1,2,4 and 1,3,4-oxadiazole derivatives which can be used as precursors in the preparation of ferroelectric liquid crystals by incorporation of chiral chains in their structures. Indeed, such research with compounds of series **2a–f** and **5a–f** is already in progress. Second, the photoluminescence properties exhibited by series **5** compounds could be of use for OLED design, as will be examined in the future.

2. Results and discussion

2.1. *Synthesis*

The synthesis of the series **2a–f** compounds is outlined in scheme 1. The 1,2,4-oxadiazole derivatives **2a–f** were synthesized starting with the condensation of 4-benzyloxybenzonitrile and hydroxylamine hydrochloride

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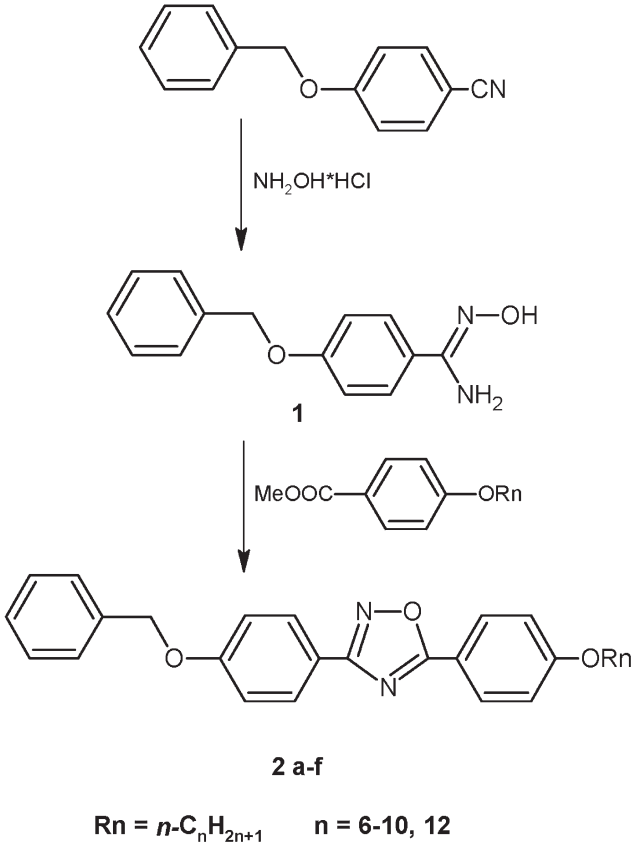


Scheme 1. Synthetic route for oxadiazoles of series **2a–f**.

yielding the corresponding amidoxime **1**. This was reacted with methyl 4-n-alkoxybenzoate (n=6–10, 12) in an ethanolic solution of sodium ethoxide leading to the formation of the 1,2,4-oxadiazoles **2a–f** [27].

Previously, we have reported the synthesis of the non-mesogenic 3-(4-pyridyl)-5-(4-*n*-alkoxy)phenyl-1,2,4-oxadiazoles (see figure 1). In contrast to these compounds, the oxadiazoles reported here (**2a–f**) are mesogenic, which can be attributed to the greater molecular length. The interest in the pyridyl-1,2,4-oxadiazole analogues, previously reported by us, was in their use as proton-acceptors in the formation of mesomorphic H-bonded complexes [27, 28].

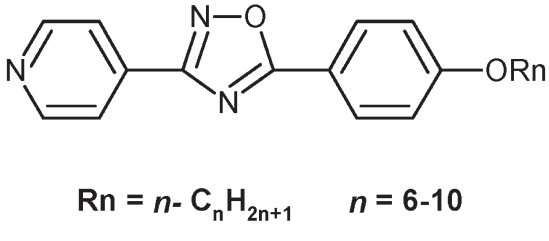
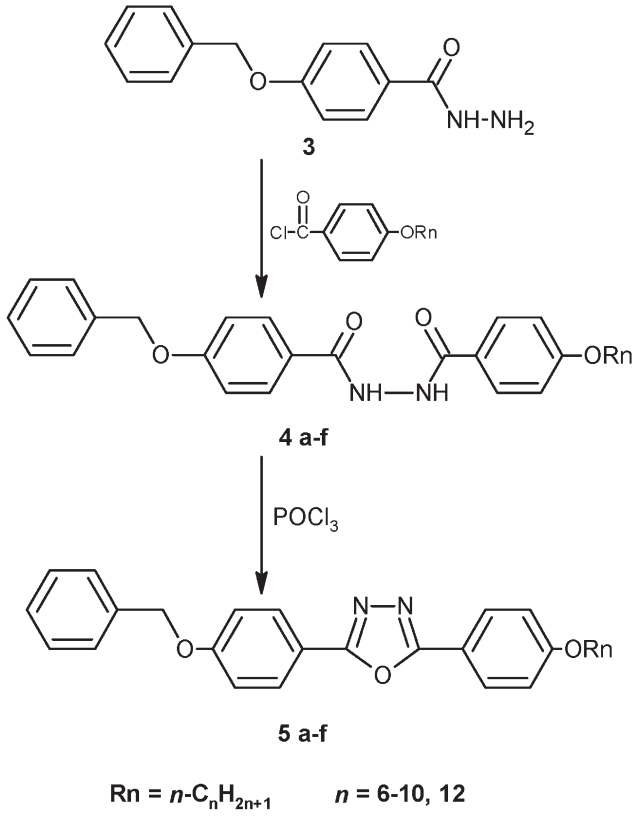


Figure 1. Structure of reported 3-(4-pyridyl)-5-(4-*n*-alkoxy)-phenyl-1,2,4-oxadiazoles.



Scheme 2. Synthetic route for oxadiazoles of series **5a–f**.

The synthetic route to the 1,3,4-oxadiazole derivatives (series **5a–f**) is shown in scheme 2. Compounds **4a–f** were obtained by condensation of compound **3** with 4-*n*-alkoxybenzoyl chloride (n=6–10, 12), according to a procedure reported previously [22, 29]. Reaction of the compounds of series **4a–f** with $POCl_3$ leads to the homologues series of oxadiazoles **5** [22]. It is interesting to note that the diacylhydrazines **4a–f** were previously reported by us. These compounds are mesogenic, displaying smectic C mesomorphism [29].

2.2. *Mesomorphic properties*

All compounds of series **2** show mesomorphic properties. In contrast to this, the compounds of series **5** do not show mesomorphic behaviour and only Cr – I transitions are observed. The optical, thermal and thermodynamic data for compounds **2a–f** are given in table 1. A plot of transition temperature against the number of carbon atoms in the alkoxy chain is shown in figure 2. All the compounds of series **2a–f** display an enantiotropic nematic (N) mesophase. The member with the longest alkoxy chain (**2f**) exhibits an enantiotropic dimorphism smectic A (SmA) – N. These results illustrate the importance of the influence of the terminal

Table 1. Transition temperatures and enthalpies for the compounds of series **2a–f**. Cr=crystal, SmA=smectic A, N=nematic, I=isotropic.

Compound	Transition	Temperature/ °C	ΔH/J g^{-1}
2a (n=6)	Cr – N	102.3	58.0
	N – I	112.2	0.53
	I – N	111.7	−0.61
	N – Cr	101.1	−57.2
2b (n=7)	Cr – N	95.1	77.3
	N – I	108.6	0.43
	I – N	107.7	−0.51
	N – Cr	93.9	−75.4
2c (n=8)	Cr – N	104.2	86.1
	N – I	111.4	0.63
	I – N	110.3	−0.71
	N – Cr	103.9	−84.8
2d (n=9)	Cr – N	102.4	74.4
	N – I	109.2	0.34
	I – N	108.4	−0.41
	N – Cr	101.6	−73.2
2e (n=10)	Cr – N	100.7	94.7
	N – I	110.0	0.79
	I – N	109.6	−0.85
	N – Cr	99.8	−91.2
2f (n=12)	Cr – SmA	98.0	97.4
	SmA – N	105.0	7.9
	N – I	109.3	0.88
	I – N	108.3	−1.2
	N – SmA	103.9	−8.1
	SmA – Cr	91.9	−91.6

chain length on the occurrence of smectic order. It is likely that a lateral interaction giving rise to a layered smectic order is more favoured for the compound **2f** as compared with the homologues **2a–e**, due to the major volume occupied by the longer flexible alkoxy chain.

As mentioned above, the compounds of series **5a–f** do not show liquid crystalline properties, and only a crystalline phase was observed (the melting points of these compunds are given in §3). The same results were obtained with the analogous 1,3,4-oxadiazole derivatives containing a symmetric rigid core, reported by Zaschke *et al*. [30]. The authors assumed that the bend associated with the exocyclic bonds in the 2- and 5-positions of the 1,3,4-oxadiazole unit was too severe to achieve the requisite ordered packing in mesophases.

From previous studies reported by Torgova *et al*., it is known that 2,5-disubstituted 1,3,4-oxadiazole and 3,5-disubstituted 1,2,4-oxadiazole derivatives have an exocyclic bond angle of 134° and 140°, respectively [31], indicating that the 1,3,4-oxadiazole in the central rigid core produces a greater distortion of the linearity of the molecules than do the 1,2,4-oxadiazole derivatives. This deviation from the typical rod-like mesogen symmetry towards a non-linear shape, could explain the suppression of mesomorphic behaviour of compounds in series **5**.

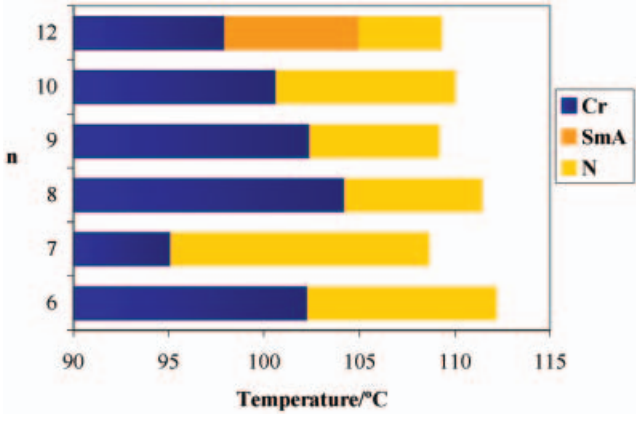


Figure 2. Plot of transition temperature versus the number of carbon atoms in the alkoxy chain for series **2a–f** compounds.

2.3. *Textures observed by polarizing optical microscopy*

The SmA and N phases of the compounds of series **2a–f** were determined from textural observations by thermal microscopy under a polarizing optical microscope using heating and cooling cycles. Phase transition temperatures observed by thermal microscopy were found to be in reasonable agreement with the corresponding DSC thermograms.

The SmA phase of compound **2f** was characterized by formation of a typical focal-conic fan texture (see figure 3). The N phase of series **2a–f** showed a characteristic marble texture.

2.4. *X-ray diffraction studies*

High temperature X-ray diffraction (XRD) experiments were performed on compound **2f** in its SmA mesophase. The results were consistent with the SmA nature of the mesophase assigned on the basis of textures observed by POM. The patterns contain two maxima: (i) a broad, diffuse scattering halo in the large angle region, corresponding to a mean distance of 4.5 Å, which arises from short range lateral interference between neighbouring molecules and confirms the liquid-like order inside each smectic layer characteristic of the SmA mesophase; (ii) a sharp, strong reflection in the small angle region at a distance of 37 Å, which corresponds to the layer thickness. The length of the molecules of **2f**, estimated from Dreiding stereomodels assuming a fully-extended conformation, is 37 Å. The coincidence between the experimental measurement and the theoretical value is consistent with the orthogonal arrangement of the molecules in the layers of a SmA

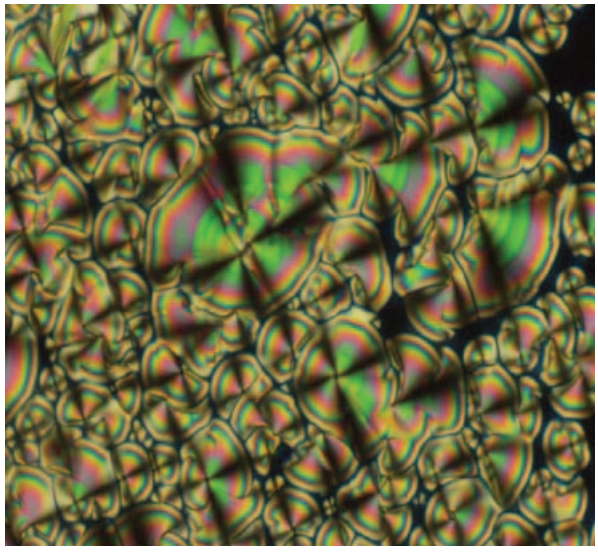


Figure 3. Mesophase textures obtained on cooling. Focal-conic fan texture at 101°C of compound **2f**.

mesophase. Usually, in common SmA mesophases the measured layer thickness is slightly smaller than the estimated molecular length due to conformational disorder of the hydrocarbon chains. However, the agreement of both values for this compound may be accounted for by the greater conformational rigidity compared with classical rod-like mesogens, due to the absence of a hydrocarbon chain at one end of the molecule.

2.5. *UV-visible absorption and photoluminescence spectroscopy*

Representative absorption and emission spectra for compound **5f** in chloroform solutions are shown in figure 4. All the compounds of the series **5a–f** exhibit essentially the same absorption profile. For comparative purposes, we provide the absorption and emission spectra of compound **2f**. Compound **2f** exhibits a unique intense absorption peak at 275 nm while compound **5f** has a small peak at 259 nm and an intense peak at 304.5 nm. Their λ_{max} show a bathochromic shift of 29.5 nm as the nature of the heterocyclic moiety is changed; that is, from 275 nm for the compound containing the 1,2,4-oxadiazole ring (**2f**) to 304.5 nm for the compound containing the 1,3,4-oxadiazole ring (**5f**). The large molar absorption coefficients ($\varepsilon > 30\,000\ M^{-1}\,cm^{-1}$) are indicative of highly π-conjugated systems and their absorption band is attributed to spin-allowed π–π* transitions involving the phenyloxadiazole framework. The emission spectra of all these compounds exhibit two emission peaks at 360.5 and 372.5 nm for **5f** and 349 and 360 nm for **2f**. The emission colours of these compounds are all in the purple region.

Photoluminescence is observed for all the compounds in chloroform solutions with quantum yields (Φ_{PL}) ranging from ~15% to ~70% for **2f** and **5a–f**, respectively (see table 2). Compounds **5a–f** have the highest quantum yield, while compound **2f** has the lowest quantum yield. We assume that the other homologues of the series **2** compounds (**2a–e**) have similar photoluminescence behaviour to compound **2f**. The unique difference between compounds **2** and **5** is in their heterocyclic unit. The former have a 1,2,4-oxadiazole unit, the latter have a 1,3,4-oxadiazole instead. Clearly, the nature of the oxadiazole ring plays an important role in the photoluminescence behaviour. Replacement of the 1,3,4-oxadiazole ring (series **5**) by a 1,2,4-oxadiazole ring (series **2**) results in a lower quantum yield. Probably, this is due to the electronic effect, which lowers the LUMO level and reduces the energy gap.

The photoluminescence quantum yield, Φ_{PL}, was calculated according to the equation:

$$\Phi_{PL} \approx \Phi_{std} \times \left(\frac{Abs_{std}}{Abs_{sample}} \times \frac{A_{sample}}{A_{std}} \times \frac{\eta^2_{sample}}{\eta^2_{std}} \right)$$

where Φ_{PL} is the photoluminescence quantum yield of the standard 9,10-diphenylantracene ($\Phi_{std}=0.900$, cyclohexane); Abs_{std} and Abs_{sample} are the absorbance of the standard and sample respectively; A_{sample} and A_{std} are the integrated area of the emission peak of the sample and standard, respectively; and η_{sample} and η_{std} are the refractive indices of the sample and standard solutions. The quantum yields and the Stokes shifts are summarized in table 2.

3. Experimental

3.1. *Characterization*

The structures of the compounds were confirmed by ^1H NMR and ^{13}C NMR (Bruker AC-250P) spectra. Transition temperatures and textures of mesophases were determined by optical microscopy using an Ortholux Pol BK-11 polarizing microscope equipped with a Mettler FP 800 hot stage. Transition temperatures and enthalpies were investigated by differential scanning calorimetry using a Rheometric DSC-V calorimeter. Samples were encapsulated in aluminium pans and observed at scanning rate of $5°C\,min^{-1}$ on heating and cooling. The instrument was calibrated using an indium standard (156.6°C, $28.44\,J\,g^{-1}$). The purity of the final products was evaluated by thin layer chromatography.

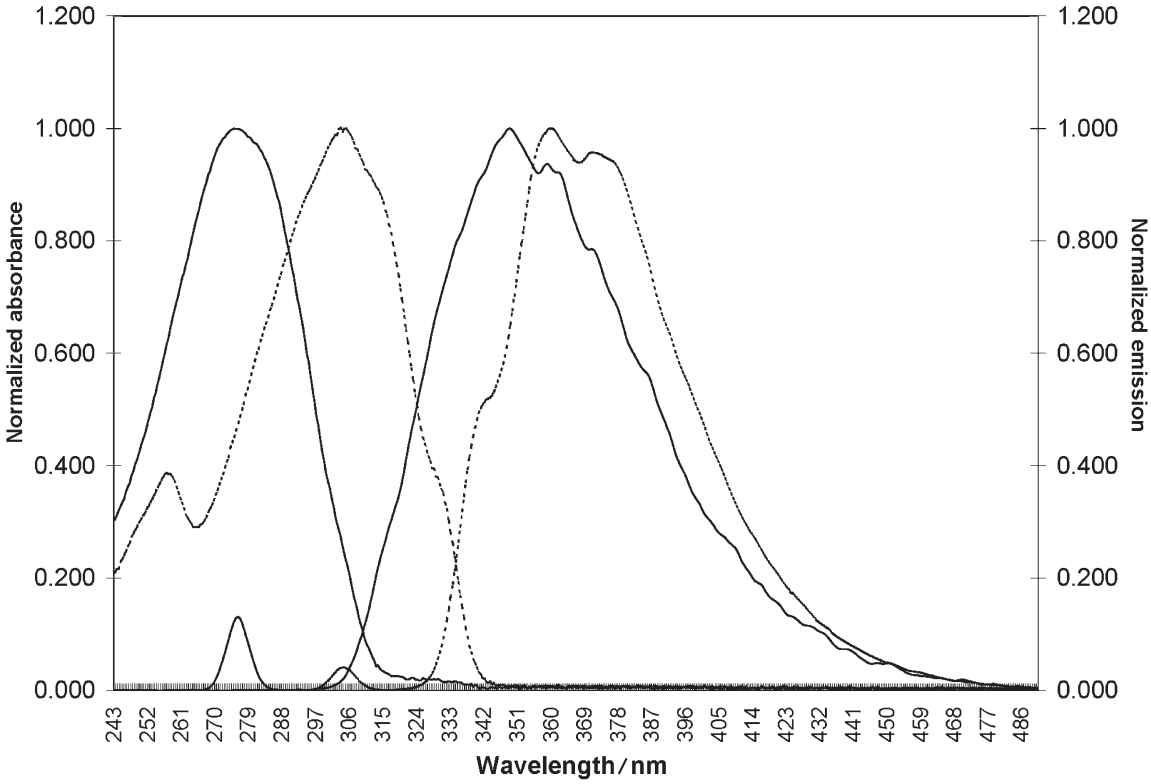


Figure 4. Normalized absorption and emission spectra of **2f** (solid lines) and **5f** (dashed lines) in chloroform solution.

XRD patterns were obtained with a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu-K_α beam. The sample was held in a Lindemann glass capillary (diameter 1 mm, wall thickness 0.01 mm) and heated with a variable temperature attachment. The patterns were collected on flat photographic films, perpendicular to the X-ray beam, with a sample–film distance of 80 mm. Spacings were obtained via Bragg's law. Optical absorption spectra in chloroform solution were recorded with a UV-Vis spectrophotometer UV4-200 from ATI-Unicam.

Luminescence measurements were performed using a Perkin-Elmer LS50B spectrofluorimeter. Spectra of the pure compounds were recorded in 10^{-6} M chloroform solution under excitation at the absorption maximum. Fluorescence quantum yields were determined by comparing the integrated photoluminescence of a *c.* 0.035 optical density chloroform solution of the compound with that of a reference with a known quantum yield. 9,10-Diphenylanthracene (99%, Acros Organic) in cyclohexane (quantum yield 0.90) was used as reference.

3.2. *Synthesis*

3.2.1. 4-Benzyloxyphenylamidoxime (1). This compound was synthesized according to the procedure

Table 2. Absorption and photoluminescence spectra of compounds **5a–f** and **2f**.

Compound	$\lambda_{abs\ max}$[a]/nm (ε)[b]	$\lambda_{em\ max}$[c]/nm	Φ_{PL}[d]	Stokes shift/nm
5a $n=6$	304.0 (3.71×10^4)	360.0	0.7086	56
5b $n=7$	304.0 (3.76×10^4)	360.0	0.6945	56
5c $n=8$	304.0 (3.78×10^4)	360.5	0.7368	56.5
5d $n=9$	304.5 (3.61×10^4)	360.5	0.7303	55
5e $n=10$	304.5 (3.81×10^4)	360.5	0.7283	55
5f $n=12$	304.5 (3.64×10^4)	360.5	0.7751	55
2f $n=12$	275.0 (4.11×10^4)	349	0.1546	74

[a]Measured in $CHCl_3$. [b]Units=$M^{-1}\,cm^{-1}$. [c]Excited at absorption maxima. [d]Standard 9,10-diphenylantracene.

previously described [27]. Sodium bicarbonate (5.88 g, 70 mmol) was added in portions to a solution of hydroxylamine hydrochloride (4.86 g, 70 mmol) in water (20 ml). A solution of 4-benzyloxybenzonitrile (7.32 g, 35 mmol) in ethanol (34 ml) was then added and the mixture heated under reflux for 6 h. After cooling, the reaction mixture was filtered and the solid was crystallized from ethanol; yield 92%, m.p. 168°C. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ=5.22 (s, 2H, CH_2 of the benzyl group); 5.85 (s, 2H, NH_2); 7.11 (d, J=8.8 Hz, 2H, 2 arom. H); 7.49 (m, 5H, 5 arom. H); 7.73 (d, J=8.8 Hz, 2H, 2 arom. H); 9.61 (s, 1H, OH of the amidoxime group). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ=69.2 ($\underline{C}H_2$ of the benzyl group); 114.4, 126.8, 127.7, 127.9, 128.5 (arom. C); 126.0 (quaternary C of the amidoxime group); 136.9, 150.6, 158.9 (quaternary arom. C).

3.2.2. 3-(4-Benzyloxyphenyl)-5-(4-*n*-alkoxy)phenyl-1,2,4-oxadiazoles (2a–f). General Method [27]: Amidoxime **1** (1.5 g, 6.2 mmol) and methyl 4-*n*-alkoxybenzoate (12.4 mmol) in anhydrous ethanol (20 ml) was added over 3 min to a stirred solution of sodium ethoxide (0.14 g, 6.2 mmol of sodium in 10 ml of anhydrous ethanol). The mixture was heated under reflux for 8 h. After cooling, the reaction mixture was filtered and the solid washed with ethanol. The solid was then suspended in water, stirred for 20 min, collected by filtration and crystallized from ethanol. Yields: **2a** 74%, **2b** 68%, **2c** 67%, **2d** 85%, **2e** 58%, **2f** 73%.

2a: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ=0.98 (t, J=6.65 Hz, 3H, CH_3); 1.37–1.90 (m, 8H, 4 CH_2); 3.98 (t, J=6.63 Hz, 2H, OCH_2 of the alkoxy chain); 5.11 (s, 2H, OCH_2 of the benzyl group); 7.01 (d, J=8.70 Hz, 2H, 2 arom H); 7.10 (d, J=8.71 Hz, 2H, 2 arom. H); 7.48 (m, 5H, 5 arom. H); 8.10 (d, J=8.83 Hz, 2H, 2 arom. H); 8.10 (d, J=8.85 Hz, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ=13.9, 22.4, 25.8, 28.9, 31.6 (aliph. C); 68.2 ($O\underline{C}H_2$ of the alkoxy chain); 69.9 ($O\underline{C}H_2$ of the benzyl group); 114.7, 115.1, 127.5, 128.2, 128.6, 129.0, 129.9 (arom. C); 116.7, 120.0, 136.2, 161.0, 162.6, 168.4, 175.2 (quaternary arom. C).

2b: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ=0.95 (t, J=6.55 Hz, 3H, CH_3); 1.35–1.85 (m, 10H, 5 CH_2); 3.95 (t, J=6.53 Hz, 2H, OCH_2 of the alkoxy chain); 5.10 (s, 2H, OCH_2 of the benzyl group); 6.96 (d, J=8.78 Hz, 2H, 2 arom H); 7.07 (d, J=8.80 Hz, 2H, 2 arom. H); 7.40 (m, 5H, 5 arom. H); 8.07 (d, J=8.85 Hz, 2H, 2 arom. H); 8.10 (d, J=8.86 Hz, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ=14.0, 22.6, 25.9, 29.0, 29.1, 31.7 (aliph. C); 68.3 ($O\underline{C}H_2$ of the alkoxy chain); 70.0 ($O\underline{C}H_2$ of the benzyl group); 114.8, 115.0, 127.4, 128.1, 128.6, 129.1, 129.9 (arom. C); 116.6, 119.9, 136.4, 160.9, 162.7, 168.4, 175.3 (quaternary arom. C).

2c: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ=0.91 (t, J=6.30 Hz, 3H, CH_3); 1.32–1.81 (m, 12H, 6 CH_2); 4.00 (t, J=6.50 Hz, 2H, OCH_2 of the alkoxy chain); 5.11 (s, 2H, OCH_2 of the benzyl group); 7.01 (d, J=8.88 Hz, 2H, 2 arom H); 7.06 (d, J=8.87 Hz, 2H, 2 arom. H); 7.37 (m, 5H, 5 arom. H); 8.10 (d, J=8.89 Hz, 2H, 2 arom. H); 8.13 (d, J=8.90 Hz, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ=14.1, 22.6, 25.9, 29.0, 29.2, 29.3, 31.8 (aliph. C); 68.2 ($O\underline{C}H_2$ of the alkoxy chain); 69.9 ($O\underline{C}H_2$ of the benzyl group); 114.8, 115.0, 127.4, 128.0, 128.6, 129.0, 129.9 (arom. C); 116.6, 119.8, 136.4, 160.9, 162.6, 168.3, 175.3 (quaternary arom. C).

2d: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ=0.86 (t, J=6.10 Hz, 3H, CH_3); 1.28–1.75 (m, 14H, 7 CH_2); 3.99 (t, J=6.50 Hz, 2H, OCH_2 of the alkoxy chain); 5.10 (s, 2H, OCH_2 of the benzyl group); 6.97 (d, J=8.84 Hz, 2H, 2 arom H); 7.04 (d, J=8.83 Hz, 2H, 2 arom. H); 7.38 (m, 5H, 5 arom. H); 8.05 (d, J=8.69 Hz, 2H, 2 arom. H); 8.09 (d, J=8.70 Hz, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ=14.1, 22.7, 25.9, 29.1, 29.2, 29.3, 31.8 (aliph. C); 68.3 ($O\underline{C}H_2$ of the alkoxy chain); 70.1 ($O\underline{C}H_2$ of the benzyl group); 114.9, 115.1, 127.5, 128.1, 128.6, 129.1, 129.9 (arom. C); 116.7, 119.9, 136.5, 160.9, 162.8, 168.4, 175.4 (quaternary arom. C).

2e: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ=0.90 (t, J=6.60 Hz, 3H, CH_3); 1.30–1.83 (m, 16H, 8 CH_2); 4.05 (t, J=6.55 Hz, 2H, OCH_2 of the alkoxy chain); 5.15 (s, 2H, OCH_2 of the benzyl group); 7.02 (d, J=8.95 Hz, 2H, 2 arom H); 7.10 (d, J=8.91 Hz, 2H, 2 arom. H); 7.42 (m, 5H, 5 arom. H); 8.11 (d, J=8.93 Hz, 2H, 2 arom. H); 8.13 (d, J=8.92 Hz, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ=14.1, 22.6, 25.9, 29.0, 29.2, 29.3, 29.4, 31.8 (aliph. C); 68.3 ($O\underline{C}H_2$ of the alkoxy chain); 70.0 ($O\underline{C}H_2$ of the benzyl group); 114.9, 115.0, 127.4, 128.1, 128.6, 129.1, 129.9 (arom. C); 116.5, 120.0, 136.5, 160.9, 162.8, 168.6, 173.6 (quaternary arom. C).

2f: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ=0.89 (t, J=6.60 Hz, 3H, CH_3); 1.28–1.72 (m, 20H, 10 CH_2); 4.04 (t, J=6.55 Hz, 2H, OCH_2 of the alkoxy chain); 5.14 (s, 2H, OCH_2 of the benzyl group); 7.00 (d, J=8.93 Hz, 2H, 2 arom H); 7.07 (d, J=8.90 Hz, 2H, 2 arom. H); 7.41 (m, 5H, 5 arom. H); 8.09 (d, J=8.84 Hz, 2H, 2 arom. H); 8.13 (d, J=8.82 Hz, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ=14.1, 22.6, 25.9, 29.1, 29.3, 29.6, 31.9 (aliph. C); 68.4 ($O\underline{C}H_2$ of the alkoxy chain); 70.1 ($O\underline{C}H_2$ of the benzyl group); 114.8, 115.0, 127.4, 128.1, 128.6, 129.1, 129.9 (arom. C); 117.1, 120.4, 137.1, 161.4, 163.2, 174.6, 175.8 (quaternary arom. C).

3.2.3. 4-Benzyloxyphenyl-2-carboxylic acid hydrazide (3). This compound was synthesized by the method described previously [22, 29].

3.2.4. 4-n-Alkoxybenzoic acid N′-(4-benzyloxyphenyl-2-carbonyl)hydrazide (4a–f). These compounds were synthesized using the procedure described previously [22, 29].

3.2.5. 5-(4-Benzyloxyphenyl)-2-(4-*n*-alkoxy)phenyl-1,3,4-oxadiazoles (5a–f). General method [22]: Compounds of the series **4a–f** (3.77 mmol) were dissolved in $POCl_3$ (18 ml); the mixtures were heated at 130°C overnight, and then cooled to room temperature. Excess $POCl_3$ was removed at reduced pressure and the remaining mixtures poured into water. The products were filtered off and crystallized from ethanol to give white solids. Yields (%), m.p. (°C): **5a** 60, 117; **5b** 56, 109; **5c** 65, 110; **5d** 52, 107; **5e** 63, 113; **5f** 54, 108.

5a: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ=0.91 (t, J=6.43 Hz, 3H, CH_3); 1.30–1.82 (m, 8H, 4 CH_2); 3.95 (t, J=6.55 Hz, 2H, OCH_2 of the alkoxy chain); 5.05 (s, 2H, OCH_2 of the benzyl group); 6.94 (d, J=8.84 Hz, 2H, 2 arom H); 7.02 (d, J=8.83 Hz, 2H, 2 arom. H); 7.33 (m, 5H, 5 arom. H); 7.96 (d, J=6.79 Hz, 2H, 2 arom. H); 8.00 (d, J=6.80 Hz, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ=13.9, 22.4, 25.5, 28.9, 31.4 (aliph. C); 68.0 (O$\underline{C}H_2$ of the alkoxy chain); 69.9 (O$\underline{C}H_2$ of the benzyl group); 114.7, 115.1, 127.3, 128.0, 128.3, 128.5, 129.5 (arom. C); 116.1, 116.6, 136.1, 161.1, 161.6, 163.7, 163.9 (quaternary arom. C).

5b: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ=0.89 (t, J=6.80 Hz, 3H, CH_3); 1.30–1.81 (m, 10H, 5 CH_2); 3.93 (t, J=6.55 Hz, 2H, OCH_2 of the alkoxy chain); 5.03 (s, 2H, OCH_2 of the benzyl group); 6.95 (d, J=8.84 Hz, 2H, 2 arom H); 7.00 (d, J=8.86 Hz, 2H, 2 arom. H); 7.31 (m, 5H, 5 arom. H); 7.95 (d, J=6.80 Hz, 2H, 2 arom. H); 7.99 (d, J=6.81 Hz, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ=13.9, 22.4, 25.7, 28.8, 28.9, 31.6 (aliph. C); 68.0 (O$\underline{C}H_2$ of the alkoxy chain); 69.8 (O$\underline{C}H_2$ of the benzyl group); 114.6, 115.0, 127.2, 127.9, 128.2, 128.4, 129.2 (arom. C); 116.0, 116.6, 136.0, 161.0, 161.6, 163.7, 163.8 (quaternary arom. C).

5c: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ=0.89 (t, J=6.30 Hz, 3H, CH_3); 1.28–1.84 (m, 12H, 6 CH_2); 4.01 (t, J=6.54 Hz, 2H, OCH_2 of the alkoxy chain); 5.14 (s, 2H, OCH_2 of the benzyl group); 6.98 (d, J=8.89 Hz, 2H, 2 arom H); 7.07 (d, J=8.89 Hz, 2H, 2 arom. H); 7.37 (m, 5H, 5 arom. H); 8.01 (d, J=6.78 Hz, 2H, 2 arom. H); 8.06 (d, J=6.79 Hz, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ=14.1, 22.6, 26.0, 29.1, 29.4, 29.5, 31.8 (aliph. C); 68.5 (O$\underline{C}H_2$ of the alkoxy chain); 69.9 (O$\underline{C}H_2$ of the benzyl group); 114.9, 115.3, 127.5, 128.5, 128.7, 128.9, 129.6 (arom. C); 116.0, 116.8, 136.1, 161.4, 161.8, 163.9, 164.2 (quaternary arom. C).

5d: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ=0.89 (t, J=6.61 Hz, 3H, CH_3); 1.20–1.82 (m, 14H, 7 CH_2); 3.95 (t, J=6.52 Hz, 2H, OCH_2 of the alkoxy chain); 5.05 (s, 2H, OCH_2 of the benzyl group); 6.93 (d, J=8.82 Hz, 2H, 2 arom H); 7.02 (d, J=8.83 Hz, 2H, 2 arom. H); 7.33 (m, 5H, 5 arom. H); 7.96 (d, J=6.79 Hz, 2H, 2 arom. H); 8.01 (d, J=6.81 Hz, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ=14.0, 22.5, 25.9, 29.1, 29.2, 31.7 (aliph. C); 68.1 (O$\underline{C}H_2$ of the alkoxy chain); 69.9 (O$\underline{C}H_2$ of the benzyl group); 114.7, 115.1, 127.3, 128.0, 128.3, 128.5, 129.5 (arom. C); 116.1, 116.6, 136.1, 161.1, 161.6, 163.7, 163.9 (quaternary arom. C).

5e: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ=0.89 (t, J=6.55 Hz, 3H, CH_3); 1.20–1.75 (m, 16H, 8 CH_2); 4.03 (t, J=6.51 Hz, 2H, OCH_2 of the alkoxy chain); 5.15 (s, 2H, OCH_2 of the benzyl group); 7.03 (d, J=8.88 Hz, 2H, 2 arom H); 7.09 (d, J=8.87 Hz, 2H, 2 arom. H); 7.30 (m, 5H, 5 arom. H); 7.90 (d, J=6.98 Hz, 2H, 2 arom. H); 8.05 (d, J=7.00 Hz, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ=14.1, 22.6, 26.0, 29.3, 29.5, 29.6, 31.8 (aliph. C); 68.2 (O$\underline{C}H_2$ of the alkoxy chain); 70.1 (O$\underline{C}H_2$ of the benzyl group); 114.8, 115.3, 127.4, 128.2, 128.5, 128.6, 129.3 (arom. C); 116.2, 116.8, 136.2, 161.3, 161.8, 164.0, 164.1 (quaternary arom. C).

5f: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ=0.81 (t, J=6.50 Hz, 3H, CH_3); 1.19–1.71 (m, 20H, 10 CH_2); 3.92 (t, J=6.53 Hz, 2H, OCH_2 of the alkoxy chain); 5.07 (s, 2H, OCH_2 of the benzyl group); 6.93 (d, J=8.90 Hz, 2H, 2 arom H); 7.03 (d, J=8.87 Hz, 2H, 2 arom. H); 7.32 (m, 5H, 5 arom. H); 7.94 (d, J=6.81 Hz, 2H, 2 arom. H); 7.99 (d, J=6.80 Hz, 2H, 2 arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ=14.1, 22.7, 26.0, 29.1, 29.4, 29.6, 31.9 (aliph. C); 68.3 (O$\underline{C}H_2$ of the alkoxy chain); 70.2 (O$\underline{C}H_2$ of the benzyl group); 114.8, 115.4, 127.5, 128.2, 128.4, 128.6, 129.5 (arom. C); 116.1, 116.7, 136.1, 161.3, 161.8, 163.8, 164.1 (quaternary arom. C).

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References

[1] K. Pantalone, A.J. Seed. *Liq. Cryst.*, **29**, 945 (2002).
[2] M. Eich, J. Wendorff. *Macromol. Chem. rapid Commun.*, **8**, 467 (1987).
[3] L.L. Chapoy. *Advances in Liquid Crystalline Polymers*, Chapoy (Eds), Elsevier, London (1985).
[4] E. Meyer, A.C. Joussef, H. Gallardo, A.J. Bortoluzzi. *J. mol. Struct.*, **655**, 361 (2003).

[5] S.J. Melo, A.D. Sobral, H. Lopes, R.M. Srivastava. *J. Braz. chem. Soc.*, **9**, 465 (1998).
[6] M. Parra, J. Belmar, H. Zunza, C. Zúñiga, Sh. Villouta, R. Martínez. *J. prakt. Chem.*, **337**, 325 (1995).
[7] M. Parra, Sh. Villouta, V. Vera, J. Belmar, C. Zúñiga, H. Zunza. *Z. Naturforsch.*, **52b**, 1533 (1997).
[8] M. Parra, J. Belmar, Sh. Villouta, R. Martínez, C. Zúñiga, H. Zunza. *Bol. Soc. Chil. Quím.*, **40**, 175 (1995).
[9] M. Parra, J. Belmar, H. Zunza, C. Zúñiga, Sh. Villouta, R. Martínez. *Bol. Soc. Chil. Quím.*, **38**, 325 (1993).
[10] M. Parra, J. Alderete, C. Zúñiga, H. Gallardo, P. Hidalgo, J. Vergara, S. Hernández. *Liq. Cryst.*, **28**, 1659 (2001).
[11] M. Parra, S. Hernández, J. Alderete, C. Zúñiga. *Liq. Cryst.*, **27**, 995 (2000).
[12] M. Parra, J. Alderete, C. Zúñiga, S. Hernández. *Liq. Cryst.*, **29**, 647 (2002).
[13] M. Parra, J. Alderete, C. Zúñiga, V. Jiménez, P. Hidalgo. *Liq. Cryst.*, **30**, 297 (2003).
[14] M. Parra, J. Vergara, J. Alderete, C. Zúñiga. *Liq. Cryst.*, **31**, 1531 (2004).
[15] M. Parra, J. Belmar, H. Zunza, C. Zúñiga, C. Fuentes, R. Martínez. *J. prakt. Chem.*, **337**, 239 (1995).
[16] C. Aguilera, M. Parra, C. Fuentes. *Z. Naturforsch.*, **53b**, 367 (1997).
[17] M. Parra, S. Hernández, J. Belmar, C. Zúñiga. *Bol. Soc. Chil. Quím.*, **42**, 507 (1997).
[18] M. Parra, J. Alderete, C. Zúñiga, P. Hidalgo, J. Vergara, G. Fuentes. *Liq. Cryst.*, **29**, 1375 (2002).
[19] M. Parra, G. Fuentes, V. Vera, Sh. Villouta, S. Hernández. *Bol. Soc. Chil. Quím.*, **40**, 455 (1995).
[20] D. Girdziunaite, C. Tschierske, E. Novotna, H. Kresse, A. Hetzheim. *Liq. Cryst.*, **10**, 397 (1991).
[21] K. Dimitrowa, J. Hauschild, H. Zaschke, H. Schubert. *J. prakt. Chem.*, **331**, 631 (1980).
[22] H-H. Sung, H-Ch. Lin. *Liq. Cryst.*, **31**, 831 (2004).
[23] T.J. Dingemans, E.T. Samulski. *Liq. Cryst.*, **27**, 131 (2000).
[24] L.A. Karamysheva, S.T. Torgova, I.F. Agafonova, V.F. Petrov. *Liq. Cryst.*, **27**, 393 (2000).
[25] S. Torgova, L. Karamysheva, A. Strigazzi. *Braz. J. Phys.*, **32, 2B**, 593 (2002).
[26] G. Hughes, M.R. Bryce. *J. Mater. Chem.*, **15**, 94 (1980).
[27] M. Parra, P. Hidalgo, J. Alderete. *Liq. Cryst.*, **32**, 449 (2005).
[28] M. Parra, P. Hidalgo, J. Barberá, J. Alderete. *Liq. Cryst.*, **32**, 573 (2005).
[29] M. Parra, P. Hidalgo, E. Carrasco, J. Barberá, C. Saavedra. *Liq. Cryst.*, **33**, 391 (2006).
[30] K. Dimitrowa, J. Hauschild, H. Zaschke, H. Schubert. *J. prakt. Chem.*, **322**, 933 (1980).
[31] S. Torgova, T. Geivandova, O. Francescangeli, A. Strigazzi. *Pranama-J. Phys.*, **61**, 239 (2003).