Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 06 August 2010

To cite this Article Parra, M. , Hernandez, S. , Alderete, J. and Zuniga, C.(2000) 'New Schiff's bases containing 1,3,4-thiadiazole and 1,3,4-oxadiazole units: a study of the effect of the heterocyclic ring and the position of the lateral alkoxy group on liquid crystalline properties', Liquid Crystals, 27: 8, 995 — 1000
To link to this Article: DOI: 10.1080/02678290050080715
URL: http://dx.doi.org/10.1080/02678290050080715

LIQUID CRYSTALS, 2000, VOL. 27, NO. 8, 995–1000

New Schiff's bases containing 1,3,4-thiadiazole and 1,3,4-oxadiazole units: a study of the effect of the heterocyclic ring and the position of the lateral alkoxy group on liquid crystalline properties

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(*Received 10 October 1999; accepted 20 December 1999*)

The synthesis of novel Schiff's bases incorporating the five-membered 1,3,4-thiadiazole (series **7**, **9**) and 1,3,4-oxadiazole (series **8**, **10**) rings have been prepared and their liquid crystalline properties studied. All compounds of series **7** exhibit an enantiotropic smectic C phase. No liquid crystalline properties were observed for the compounds of series **8**–**10**. A study of the structure/mesomorphic activity relationship is also described.

1. Introduction

Since the studies of Vorländer at the beginning of this century it has been well established that thermotropic calamitic mesomorphism can be achieved by a wide variety of lath-shaped molecules having linear mesogenic cores [1]. Mesomorphic compounds containing heterocyclic units have been synthesized and interest in such structures constantly grows. The introduction of heterocycles within the central core of calamitic molecules strongly influences their mesomorphic behaviour due, in part, to the dipolar moment associated with the heterocyclic ring [2–6].

In a study by Zaschke and co-workers [7] on thiadiazole and oxadiazole derivatives, a suppression of mesomorphic behaviour was found with increasing non-linearity of the mesogenic structure. Compounds having a symmetric structure with an oxadiazole unit in the centre of the mesogen did not exhibit liquid crystalline behaviour. The authors assumed that the bend (134°) associated with the exocyclic bonds in the 2- and 5-positions of the oxadiazole unit was too severe to achieve the requisite ordered packing in mesophases. In this paper we present the synthesis and characterization of new Schiff's bases containing 1,3,4-thiadiazole and 1,3,4-oxadiazole rings (see figure 1) which have been synthesized in order to study the effect of the heterocyclic unit and the position of the substituents on liquid crystalline properties.

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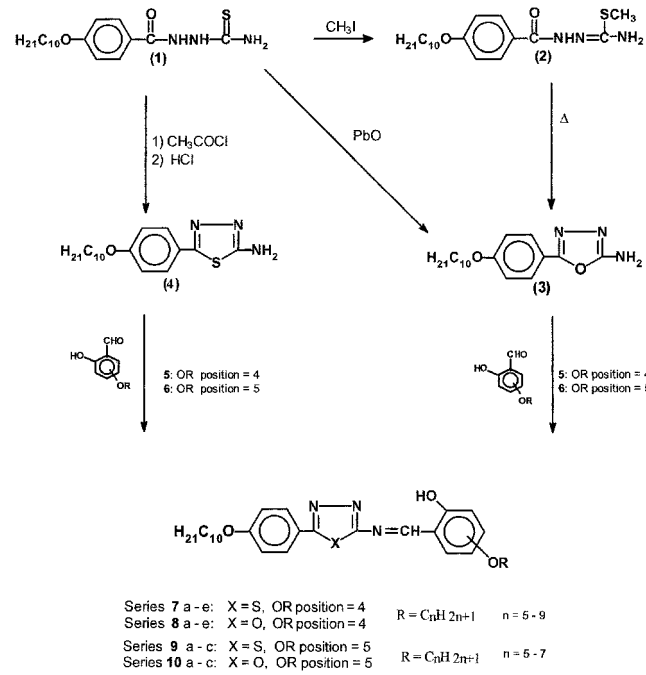
2. Synthesis

The synthesis of the compounds is outlined in the scheme.



Scheme.

Compound **1** was synthesized starting with the alkylation of methyl 4-hydroxybenzoate and proceeding with condensation with 80% hydrazine hydrate, yielding 4-*n*-decyloxyphenylhydrazide; this was reacted with

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
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ammonium thiocyanate in concentrated HC1 leading to the formation of the 4-*n*-decyloxybenzoylthiosemicarbazide **1** [8].

The amino-oxadiazole **3** was prepared by two methods [9]. The first consists of the reaction of thiosemicarbazide **1** with methyl iodide to yield the corresponding *p*-*n*-decyloxybenzoyl-*S*-methylisothiosemicarbaz ide **2**, which cyclizes with loss of methanethiol to give 5-(*p*-*n*-decyloxy)-phenyl-2-amino-1,3,4-oxadiazole **3**. This compound also was synthesized by the reaction of **1** with PbO in ethanol; the best yields were obtained for this latter method.

Chudgar *et al.* reported mesogenic amino-oxadiazoles [10]; contrary to this, the amino-oxadiazole **3** synthesized by us is not mesogenic. This can be attributed to the ester centre linkage and three aromatic nuclei, present in the molecules synthesized by Chudgar, which have a larger molecular length than compound **3**.

The amino-thiadiazole **4** was prepared by dehydration of **1** with acetyl chloride followed by hydrolysis of the acetamide compound [11].

The Schiff's bases (series **7–10**) were prepared by condensation of **3** and **4** with an excess of the appropriate aldehydes (**5**, **6**) [12].

3. Results and discussion

3.1. *Mesomorphic properties*

All compounds of series **7** show mesomorphic properties. Contrary to this the compounds in series **8–10** do not show mesomorphic behaviour and only Cr–I transitions are observed.

The optical, thermal and thermodynamic data for the compounds of series **7** are gathered in the table. A graphical representation of the mesomorphic behaviour as a function of the number of carbon atoms in the lateral chain for series **7** is also presented (figure 2).

Compounds in series **7** display nematic and smectic C mesomorphism. The derivatives with $n = 5, 6$ show an enantiotropic nematic and smectic C mesophase. For members with $n \geqslant 7$ the nematic phase is not observed.

The thermal mesomorphic range is similar for all derivatives (*c.* 110°C) and, with the exception of derivatives with $n = 5$ and 6, which have a short nematic range, the members with longer chains display only a smectic C phase. Melting and clearing temperatures are similar in all derivatives and show a similar trend in behaviour.

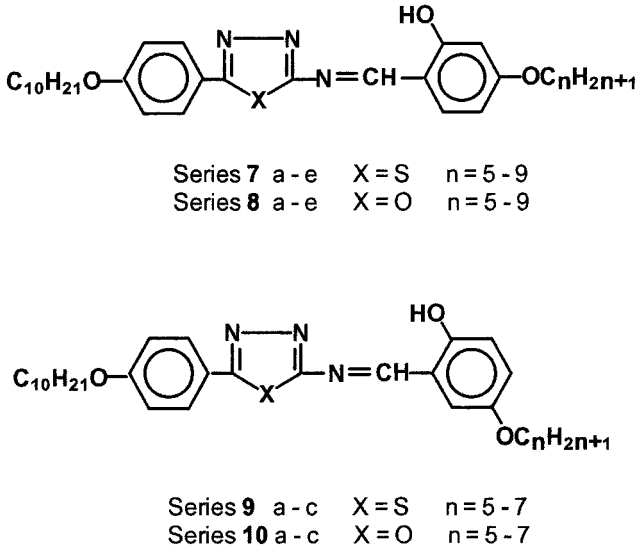
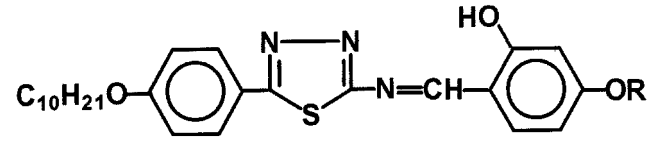


Figure 1. Structures of series **7**, **8**, **9** and **10** compounds.

Table. Transition temperatures and enthalpies data of series **7a–e** compounds.



Compound $R = n\text{-}C_nH_{2n+1}$	Transition	Temperature /°C	ΔH /kJ mol^{-1}
7a ($n = 5$)	Cr–Sc	100	29.68
	Sc–N	205	3.24
	N–I	214	1.66
7b ($n = 6$)	Cr–Sc	97	28.90
	Sc–N	209	7.66
	N–I	213	0.07
7c ($n = 7$)	Cr–Sc	96	30.98
	Sc–I	213	6.26
7d ($n = 8$)	Cr–Sc	98	26.60
	Sc–I	213	8.16
7e ($n = 9$)	Cr–Sc	101	26.04
	Sc–I	213	9.42

3.2. *Textures observed by polarizing optical microscopy*

The mesophases exhibited by these compounds were identified according to their optical textures which were

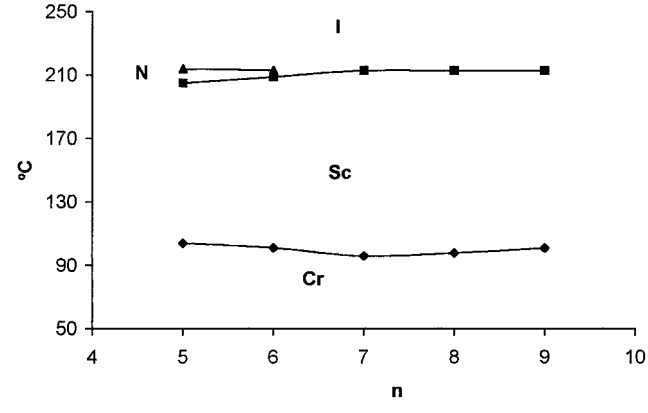


Figure 2. Plot of transition temperatures versus the number of carbon atoms (n) in the alkyl chain (R) of series **7**.

observed by optical microscopy, using the classification systems reported by Sackmann and Demus [13], Gray and Goodby [14].

The nematic phase showed the typical schlieren texture with characteristic two- and four-brush singularities and the typical nematic droplets. On cooling this phase, its colour gradually changed to adopt finally a homeotropic texture before passing into the smectic C phase.

The smectic C mesophase was identified by the appearance of a schlieren texture, with blue zone and only two-brush singularities, on both heating and cooling, showing a strong change of colour with temperature as the tilt angle varied. On cooling, a broken focal-conic texture was also observed for this phase.

The occurrence of a tilted smectic C mesophase in compounds of series **7** opens an interesting possibility for further studies, such as the introduction of a chiral terminal alkyl chain in the calamitic structure in order to obtain chiral mesophases (cholesteric, tilted smectic) which may exhibit interesting electro-optical properties. In addition, these compounds are Schiff's base chelating imines and can be used as ligands in the preparation of mesogenic complexes (metallomesogens). In fact, such research with compounds of series **7** is already in progress.

3.3. *Structure/mesomorphic activity relationship*

Different behaviours are observed in the four series of compounds studied. All compounds of series **7** show mesomorphic properties, whereas compounds of series **8–10** do not exhibit mesomorphic behaviour. These results can be explained by considering the stable conformations of the systems under investigation. In order to obtain structural information we performed semi-empirical calculations at level AM1 [15], implemented on the GAUSSIAN 94W program [16]. We have used the derivatives with an ethoxy terminal chain in the 4-position of the phenyl ring for the model calculations. We see that the most stable conformation in both the thiadiazole and oxadiazole derivatives is that with a coplanar arrangement between the heterocyclic unit and the central bridge.

We also studied the rotational barrier around the C(heterocyclic)–C(phenyl) bond (ϕ_1) and C(heterocyclic)–N(imine) bond (ϕ_2). Figure 3 shows two conformations adopted by these derivatives. Figure 3 (*a*) corresponds to a conformation for $\phi_2 = 180°$ designated 's-*trans*' by us, and figure 3 (*b*) corresponds to a conformation for $\phi_2 = 0°$ designated as 's-*cis*'. The 's-*cis*' conformation is more linear than the 's-*trans*' conformation both in thiadiazole and oxadiazole derivatives. The significant difference is the degree of stabilization obtained between the extreme values of these conformers. The rotational barrier around the C(heterocyclic)–N(imine) bond (ϕ_2) is approximately

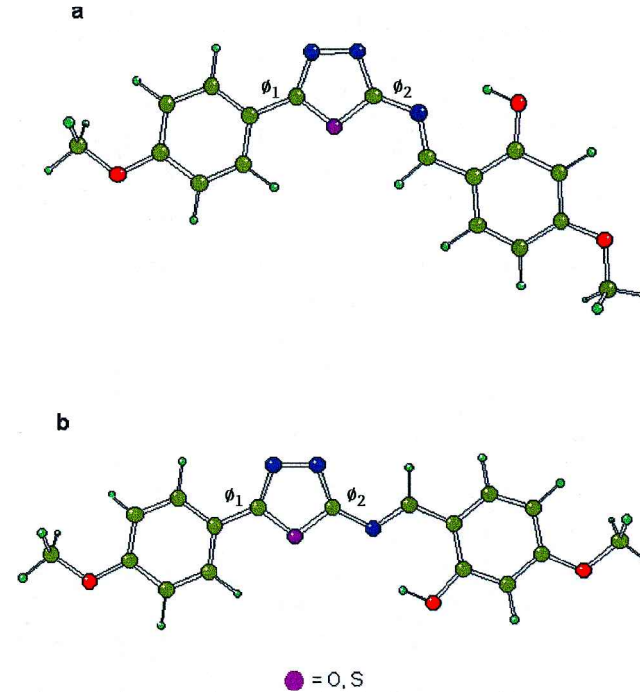


Figure 3. Representation of the two coplanar conformations of the thiadiazole and oxadiazole derivatives with alkoxy chain in 4-position of the benzene ring. (*a*) Conformation of the 's-*trans*' for $\phi_2 = 180°$; (*b*) conformation of the 's-*cis*' for $\phi_2 = 0°$.

6.5 kcal mol^{-1} in the thiadiazole derivatives and three times lower, at approximately 2.5 kcal mol^{-1}, for the oxadiazole derivatives (figure 4). These values correspond to $\phi_2 = 180°$ and 90°, respectively. Another important difference is that the thiadiazole derivatives have only a single minimum in the potential energy curve, corresponding to the 's-*cis*' conformation, whereas the oxadiazole derivatives have two minimal—in this case both 's-*cis*' and 's-*trans*' conformers are favoured.

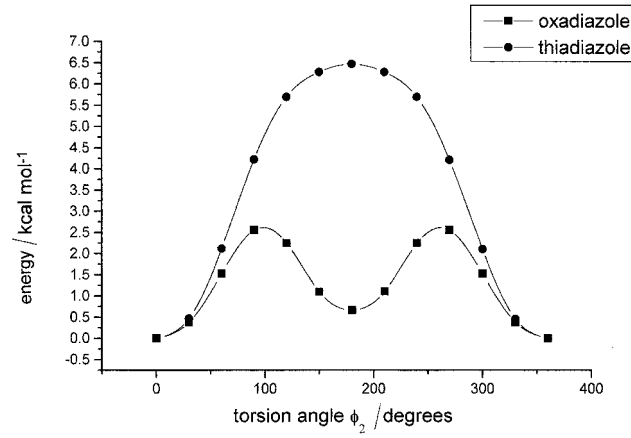


Figure 4. Potential energy curve describing the rotational barrier around the C(heterocyclic)–N(imine) bond (ϕ_2).

From these significant differences we conclude that 's-*cis*' is the most stable conformation for thiadiazole derivatives. These derivatives also show a hindered rotation around the C(heterocyclic)–N(imine) bond (ϕ_2), consequently a major linearity. This could explain the mesomorphic behaviour observed for the compounds in series **7**.

For the oxadiazole derivatives the 's-*cis*' and 's-*trans*' conformers have similar stability and co-exist. This should lead to a deviation from the typical rod-like mesogen symmetry towards one with an average non-linear shape, explaining the suppression of mesomorphic behaviour of compounds in series **8**.

With respect to the rotational barrier around the C(heterocyclic)–C(phenyl) bond (ϕ_1), thiadiazole and oxadiazole show the same profile (figure 5), nevertheless oxadiazole derivatives have a higher rotational barrier. Thus thiadiazole derivatives favour the rod-like structure.

From these results we assumed that thiadiazole and oxadiazole derivatives with an alkoxy chain in the 5-position of the phenyl ring (series **9** and **10**), would show the same results with respect to the rigid core. However, the flexible side alkoxy chain in the 5-position, induces a loss of linearity in both the thiadiazole and oxadiazole derivatives, leading to a complete loss of liquid crystalline properties.

4. Experimental

The structures of the compounds were confirmed by ^{1}H NMR, ^{13}C NMR (Bruker AC-250P) and FTIR (Nicolet 550) spectra. The transition temperatures and textures of the mesophases were determined by optical microscopy using an Ortholux Pol BK-11 polarizing microscope equipped with a Mettler FP 800 hot stage. The transition temperatures and enthalpies were investigated by differential scanning calorimetry (DSC) using a Rheometric DSC-V calorimeter with a heating and cooling rate of 10°C min^{-1}. The apparatus was calibrated with indium.

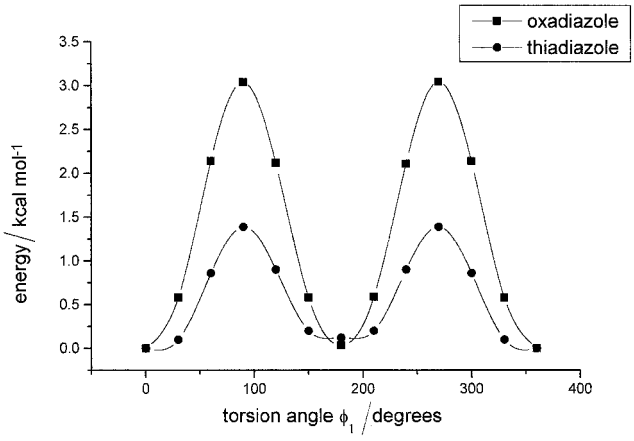


Figure 5. Potential energy curve describing the rotational barrier around the C(heterocyclic)–C(phenyl) bond (ϕ_1).

4.1. *p-n-Decyloxybenzoylthiosemicarbazide (1)*

This compound was synthesized according to reference [8].

4.2. *p-n-Decyloxybenzoyl-S-methylisothiosemicarbazide (2)* [9]

p-n-Decyloxybenzoylthiosemicarbazide **1** (6.0 g, 28 mmol) in 2-ethoxyethanol (400 ml) at 50°C was reacted with methyl iodide (4.44 g, 30 mmol) in ethanol (30 ml) to give the *S*-methylisothiosemicarbazide (**2**); this was crystallized from ethanol in colourless needles (1.71 g, 27% yield), m.p. 220°C (decomp.). ^{1}H NMR (DMSO-d_6, TMS, 250 MHz): δ = 9.85 (s, 1H, NH); 7.55 (d, J = 8.40 Hz, 2H, 2 arom. H); 6.85 (d, J = 8.40 Hz, 2H, 2 arom. H); 6.55 (s, 2H, NH_2); 4.18 (t, J = 6.30 Hz, 2H, OCH_2); 2.45 (s, 3H, SCH_3); 1.83–1.40 (m, 16H, 8 CH_2); 0.94 (t, J = 6.40 Hz, 3H, CH_3). ^{13}C NMR (DMSO-d_6, TMS, 62.9 MHz): δ = 162.5 (C=O); 159.8 (C–S); 154.7; 129.2; 125.2; 114.7 (arom. C); 66.5; 30.5; 28.6; 28.5; 28.4; 28.3; 28.2; 24.9; 21.3; 13.6; 12.8 (aliph. C). IR (KBr disk): cm^{-1} = 3550 (N–H); 3220, 3160 (NH_2); 1650 (C=O); 1600 (benzene ring); 2920 (C_{sp3}–H).

4.3. *5-(p-n-Decyloxy)-phenyl-2-amino-1,3,4-oxadiazole (3)* [9]

Method 1. p-n-Decyloxybenzoyl-*S*-methylisothiosemicarbazide **2** (1.71 g, 4.7 mmol) was heated in an oil bath at 180°C. Methanethiol was rapidly evolved and after 10 min the residue was cooled and then by crystallization from ethanol gave the oxadiazole as colourless needles (0.12 g, 5% yield) m.p. 225°C.

Method 2. p-n-Decyloxybenzoylthiosemicarbazide **1** (10 g, 28 mmol), PbO (40 g, 182 mmol) and ethanol (500 ml) were heated under reflux for 48 h and then filtered. The solid residue was extracted five times with hot ethanol. The solvents were removed in vacuum, and the residue was crystallized from ethanol giving colourless needles (6.52 g, 73% yield) m.p. 226°C. ^{1}H NMR (DMSO-d_6, TMS, 250 MHz): δ = 7.80 (d, J = 8.50 Hz, 2H, 2 arom. H); 7.15 (d, J = 8.50 Hz, 2H, 2 arom. H); 7.08 (s, 2H, NH_2); 4.15 (t, J = 6.30 Hz, 2H, OCH_2); 1.85–1.45 (m, 16H, 8 CH_2); 0.95 (t, J = 6.40 Hz, 3H, CH_3). ^{13}C NMR (DMSO-d_6, TMS, 62.9 MHz): δ = 163.3; 160.1; 157.2; 126.6; 116.7; 114.9 (arom. C); 67.6 ($O\underline{C}H_2$); 31.0; 28.7; 28.6; 28.5; 28.4; 28.3; 25.2; 21.8 (aliph. C); 13.6 ($\underline{C}H_3$). IR (KBr disk): cm^{-1} = 3320; 3120 (NH_2); 1610 (benzene ring); 2920 (C_{sp3}–H).

4.4. *5-(p-n-Decyloxy)-phenyl-2-amino-1,3,4-thiadiazole (**4**)* [11]

Thiosemicarbazide **1** (24 g, 80 mmol) and acetyl chloride (250 ml) were mixed ice-cold and afterwards cautiously heated under reflux. When the vigorous reaction subsided, heating was continued for 15 min, and water added (200 ml). The insoluble material was collected, washed several times with water and recrystallized from 2-ethoxyethanol, yielding 10.6 g of the acetamido compound (41% yield, m.p. 180°C). This compound (10 g, 31 mmol) was mixed with concentrated hydrochloric acid (52 ml) and 2-ethoxyethanol (200 ml) and was then heated under reflux for 18 h. The solvent was evaporated under reduced pressure and the residue poured into concentrated sodium hydroxide solution (80 ml). The resulting solid was filtered, washed several times with water and recrystallized from ethanol/water (4:1) yielding 8.9 g (86% yield) of the compound **4**, m.p. 167°C. ^{1}H NMR (DMSO-d_6, TMS, 250 MHz): δ = 7.66 (d, J = 8.43 Hz, 2H, 2 arom. H); 7.09 (s, 2H, NH_2); 6.94 (d, J = 8.43 Hz, 2H, 2 arom. H); 4.0 (t, J = 6.40 Hz, 2H, OCH_2); 1.74–1.25 (m, 16H, 8 CH_2); 0.86 (t, J = 5.67 Hz, 3H, CH_3). ^{13}C NMR (DMSO-d_6, TMS, 62.9 MHz): δ = 168.0; 159.0; 157.4; 127.8; 123.5; 114.9 (arom. C); 68.5 ($O\underline{C}H_2$); 40.2; 39.8; 39.5; 39.2; 38.8; 28.6; 28.4; 25.5 (aliph. C); 13.9 ($\underline{C}H_3$). IR (KBr disk): cm^{-1} = 3260, 3100 (NH_2); 1600 (benzene ring); 2920 (C_{sp3}–H).

4.5. *2-Hydroxy-4-n-alkoxybenzaldehydes (**5**) and 2-hydroxy-5-n-alkoxybenzaldehydes (**6**)*

These compounds were prepared from 2,4- and 2,5-dihydroxybenzaldehyde according to the reported procedure [17] as follows. A solution of 4.04 g (72 mmol) of KOH, (10 g, 72 mmol) of 2,4- or 2,5-dihydroxybenzaldehyde and 0.11 mol of *n*-alkylbromide in 60 ml of ethanol was heated under reflux for 6 h. It was allowed to cool and the organic product was extracted with ether. The ethereal phase was extracted several times with 10% NaOH. The combined aqueous layers were acidified with concentrated HCl and then extracted with ether and dried with anhydrous Na_2SO_4. The solvent was evaporated and the residue purified by column chromatography on silica (*n*-hexane/ethyl acetate = 7:3 as eluent). Products in oil-form were obtained. The oil solidified on standing at room temperature for several days but it had no sharp melting point. Yield 40–60% for series **5** and 10–14% for series **6** compounds.

4.6. *5-(4-n-Decyloxy)-phenyl-2-(2-hydroxy-4-n-alkoxy)-benzylideneamino-1,3,4-thiadiazoles (**7a–e**)*

A general method was used for these compounds [12]. A mixture of **4** (0.4 g, 0.6 mmol) and 2.4 mmol of 2-hydroxy-4-*n*-alkoxybenzaldehyde (**6**) was heated in an oil bath at 140°C for 1 h. The residue was cooled and crystallized from ethanol; the following yields were obtained:

n	5	6	7	8	9
yield/%	87	75	76	32	94.

*Spectroscopic characterization of homologue **7b** with n = 6.* ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ = 12.36 (s, 1H, OH); 8.99 (s, 1H, N=CH); 7.86 (d, J = 8.7 Hz, 2H, arom. H); 7.34 (d, J = 8.7 Hz, 1H, arom. H); 6.96 (d, J = 8.7, 2H, arom. H); 6.51 (m, 2H, arom. H); 4.0 (t, J = 6.5 Hz, 4H, 2 OCH_2); 1.83–1.28 (m, 24H, 12 CH_2); 0.88 (t, J = 6.8, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ = 170.7 (N=$\underline{C}$H); 166.5; 165.5; 164.4; 161.5; 122.8; 112.1 (quaternary arom. C); 135.3; 129.0; 114.9; 109.1; 101.5; (arom. C); 68.5; 68.3 (2 $O\underline{C}H_2$); 31.9; 31.5; 29.5; 29.3; 26.0; 25.6; 22.6; 14.0 (aliph. C). IR (KBr disk): cm^{-1} = 3423 (OH); 3020 (C_{sp2}–H); 2925 (C_{sp3}–H); 1605 (C=C and C=N).

4.7. *5-(4-n-Decyloxy)-phenyl-2-(2-hydroxy-5-n-alkoxy)-benzylideneamino-1,3,4-oxadiazoles (**8a–e**)*

These compounds were synthesized using the same procedure as described for series **7a–e**. Yields were as follows:

n	5	6	7	8	9
yield/%	87	79	71	66	34
m.p./°C	141	134	139	141	142.

*Spectroscopic characterization of **8b** with n = 6.* ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ = 12.28 (s, 1H, OH); 9.16 (s, 1H, N=CH); 7.99 (d, J = 8.8 Hz, 2H, arom. H); 7.37 (d, J = 8.6 Hz, 1H, arom. H); 6.99 (d, J = 8.8 Hz, 2H, arom. H); 6.53 (m, 2H, arom. H); 4.03 (t, J = 6.5 Hz, 4H, 2 OCH_2); 1.83–1.28 (m, 24H, 12 CH_2); 0.88 (t, J = 6.8 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ = 167.9 (N=$\underline{C}$H); 166.1; 165.4; 163.8; 161.9 (quaternary arom. C); 135.8; 128.4; 115.0; 109.4; 101.6 (arom. C); 68.6; 68.3 (2 $O\underline{C}H_2$); 31.5; 29.3; 26.0; 22.6; 14.0 (aliph. C). IR (KBr disk): cm^{-1} = 3440 (OH); 3020 (C_{sp2}–H); 2925 (C_{sp3}–H); 1604 (C=C and C=N).

4.8. *5-(4-n-Decyloxy)-phenyl-2-(2-hydroxy-4-n-alkoxy)-benzylideneamino-1,3,4-thiadiazoles (**9a–c**)*

These compounds were synthesized using the same procedure as described for series **7a–e**. Yields were as follows:

n	5	6	7
yields/%	20	90	21
m.p./°C	97	100	102.

Spectroscopic characterization of compound ***9a*** *with* $n = 5$. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): $\delta = 11.53$ (s, 1H, OH); 9.04 (s, 1H, N=CH); 7.81 (d, $J = 8.8$ Hz, 2H, arom. H); 7.04 (dd, $J = 8.8$ Hz, $J = 3.0$ Hz, 1H, arom. H); 6.93 (d, $J = 8.8$ Hz, 3H, arom. H); 6.88 (d, $J = 2.9$ Hz, 1H, arom. H); 3.96 (t, $J = 6.5$ Hz, 2H, OCH_2); 3.91 (t, $J = 6.5$ Hz, 2H, OCH_2); 1.78–1.21 (m, 22H, 11 CH_2); 0.88 (t, $J = 6.8$ Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): $\delta = 167.5$ (N=CH); 170.4; 167.5; 161.7; 156.4; 152.2 (quaternary arom. C); 129.1; 124.4; 122.7; 118.6; 117.5; 116.6; 115.1 (arom. C); 68.9; 68.3; (2 OCH_2); 31.7; 29.5; 29.3; 25.8; 22.6; 14.0 (aliph. C). IR (KBr disk) cm^{-1}: 3500 (OH); 3015 (C_{sp2}–H); 2920 (C_{sp3}–H); 1602 (C=C and C=N).

4.9. *5-(4-n-Decyloxy)-phenyl-2-(2-hydroxy-5-n-alkoxy)-benzylideneamino-1,3,4-oxadiazoles (**10a–c**)*

These compounds were synthesized using the same procedure as described for series **7a–e**. Yields are as follows:

n	5	6	7
yields/%	27	65	44
m.p./°C	109	136	98.

Spectroscopic characterization of compound ***10a*** *with* $n = 5$. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): $\delta = 11.49$ (s, 1H, OH); 9.25 (s, 1H, N=CH); 8.03 (d, $J = 8.8$ Hz, 2H, arom. H); 7.16 (dd, $J = 8.8$ Hz, $J = 3.0$ Hz, 1H, arom. H); 7.01 (m, 4H, arom. H); 4.03 (t, $J = 6.5$ Hz, 2H, OCH_2); 3.95 (t, $J = 6.5$ Hz, 2H, OCH_2); 1.82–1.28 (m, 22H, 11 CH_2); 0.94 (t, $J = 6.9$ Hz, 3H, CH_3); 0.88 (t, $J = 6.9$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): $\delta = 191.1$ (N=CH); 163.5; 162.9; 156.8; 155.2; 151.6 (quaternary arom. C); 126.8; 124.8; 122.1; 118.6; 116.8; 115.1; 114.2 (arom. C); 68.6; 68.3 (2 OCH_2); 31.3; 29.0; 28.7; 27.7; 25.5; 21.9; 13.9 (aliph. C). IR (KBr disk): cm^{-1} = 3450 (OH); 3020 (C_{sp2}–H); 2930 (C_{sp3}–H); 1609 (C=C and C=N).

This work was supported by 'Dirección de Investigación' of the University of Concepción (Grant 98.023.021-1.0).

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