Synthesis and characterization of the photophysical properties of novel heterocyclic imines

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Abstract: As part of an on-going research to develop efficient heterocyclic systems for optical applications (NLO, photochromic, chemosensor, etc) we report in this work the synthesis and the photophysical characterization of novel heterocyclic imines **1a-b** and **2**, functionalized with thiadiazole or benzothiazole as acceptor groups linked to an aryl ring.

Keywords: Schiff bases; Thiadiazole, Benzothiazole, π-Conjugated systems, UV-vis.

1. Introduction

The imine-bridged organics compounds have been target of high interest for the application of photosensitive materials. These compounds are an important group due to the diversity of applications in medicinal, materials and supramolecular chemistry due to their biological properties as well as their ability as chemosensors, photochromic, two-photon absorption and nonlinear optical materials. Schiff bases can be also used as ligands, able to complex with different metals in various oxidation states, showing a great catalytic activity.[1-3]

Additionally, imines having intramolecular hydrogen-bonding are a versatile class of compounds for the design of optical materials since proton transfer in these systems origin the change of their optical properties. Recently, we have showed that the kinetic rate of the thermal *cis-trans* re-isomerization of pyrrolidene Schiff bases, at room temperature, can be controlled through proper substitution at the imine-aryl moiety of the molecule.[4]

Therefore, as part of an on-going research to develop efficient heterocyclic systems for optical applications (NLO, photochromic, chemosensor, etc)[5-8] we report in this communication the synthesis and the photophysical characterization of novel heterocyclic imines **1** and **2** functionalized with thiadiazole or benzothiazole as acceptor groups linked to an aryl ring, having in mind their potential optical (linear and nonlinear) applications.

2. Experimental

2.1 Instruments

NMR spectra were obtained on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for ^{1}H NMR and 75.4 MHz for ^{13}C NMR or a Brucker Avance III 400 at an operating frequency of 400 MHz for ^{1}H NMR and 100.6 MHz for ^{13}C NMR using the solvent peak as internal reference at 25 ºC (δ relative to TMS). All chemical shifts are given in Hz. Assignments were made by comparison of chemical shift, peak multiplicities and *J* values and were supported by spin decoupling-double resonance and bidimensional heteronuclear HMBC and HMQC correlation techniques. IR spectra were determined on a BOMEM MB 104 spectrophotometer. UV-Visible absorption spectra (200-800 nm) were obtained using a Shimadzu UV/2501PC

spectrophotometer. All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected.

2.2 Synthesis

General procedure for the synthesis of imines **1** and **2**: a solution of 2-hydroxy-3-methoxybenzaldehyde (2 mmol), amino derivative (2 mmol), acetic acid (2 drops) in ethanol (15 mL) was heated at reflux and monitored by TLC, which determined the reaction time (9-24 h). After cooling and solvent evaporation, the crude product was recrystallized from light petroleum/dichloromethane or ethanol to afford the pure imines **1** and **2**.

2-(1,3,4-Thiadiazol-2-ylimino)methyl)-6-methoxyphenol **(1a).** Yellow solid (70 %). Mp: 151-152 ºC. ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.84 (s, 3H, OC*H*$_3$), 6.94 (t, 1H, *J*=8 Hz, 4-H), 7.23 (dd, 1H, *J*=8 and *J*=1.2 Hz, 5-H), 7.46 (dd, 1H, *J*=8 and *J*=1.2 Hz, 3-H), 9.25 (s, 1H, 5'-H), 9.46 (s, 1H, C*H*N), 10.98 (s,1H, O*H*). ^{13}C NMR (DMSO-d_6) δ 56.0, 117.0, 119.5, 121.7, 148.2, 150.3, 152.8, 173.5, 191.9. λ_{max} (ethanol)/nm 274 (ε/dm^3 mol^{-1} cm^{-1} 2,240). IR (liquid film): υ 2361, 2341, 1943, 1868, 1864, 1810, 1800, 1792, 1772, 1750, 1684, 1653 cm^{-1}.

2-(5-Phenyl-1,3,4-thiadiazol-2-ylimino)methyl)-6-methoxyphenol (1b). Yellow solid (62 %). Mp: 182-183 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.86 (s, 3H, OC*H*$_3$), 6.96 (t, 1H, *J*=7.8 Hz, 4-H), 7.24 (dd, 1H, *J*=8.4 and *J*=1.5 Hz, 5-H), 7.50 (dd, 1H, *J*=8.4 and *J*=1.5 Hz, 3-H), 7.57-7.59 (m, 3H, 3'-, 4'-, 5'-H), 7.97-8.01 (m, 2H, 2'- and 6'-H), 9.27 (s, 1H, C*H*N), 10.88 (s,1H, O*H*). ^{13}C NMR (DMSO-d_6) δ. 56.1, 117.0, 119.5, 120.0, 121.3 (2 overlapped signals), 127.4, 129.5 (2C), 131.4, 148.2, 150.3, 166.0, 167.2, 173.2, 191.9. λ_{max} (ethanol)/nm 314 (ε/dm^3 mol^{-1} cm^{-1} 16,590). IR (liquid film): υ 2361, 2341, 1945, 1868, 1844, 1830, 1792, 1772, 1750, 1734, 1684, 1653 cm^{-1}.

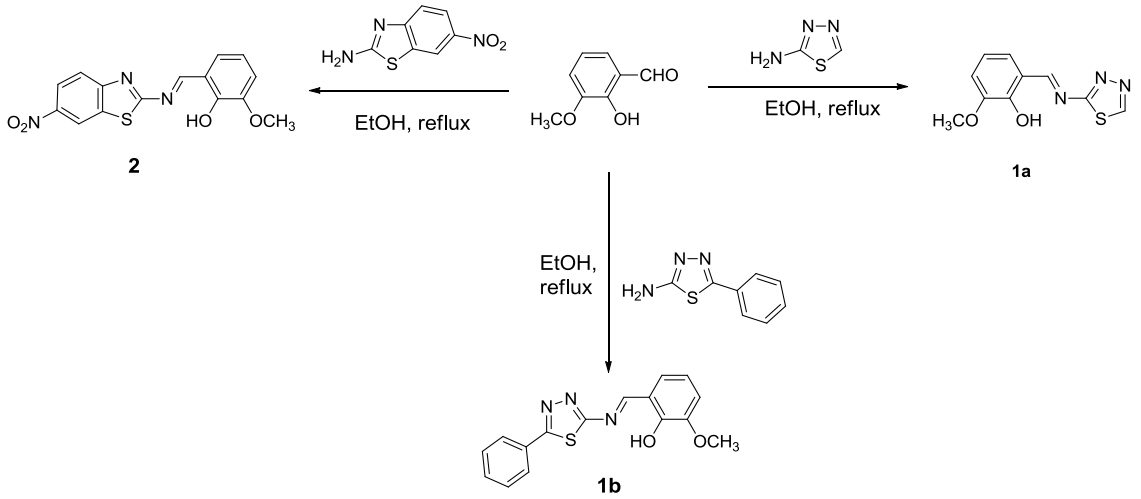
2-(6-Nitrobenzo[d]thiazol-2-ylimino)methyl)-6-methoxyphenol **(2).** Yellow solid (73 %). Mp: 239-241 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.87 (s, 3H, OC*H*$_3$), 6.96 (t, 1H, *J*=8.1 Hz, 4-H), 7.26 (m, 1H, 5-H), 7.54 (dd, 1H, *J*= 7.2 and *J*=0.9 Hz, 3-H), 8.10 (d, 1H, *J*= 9.2 Hz, 4'-H), 8.33 (dd, 1H, *J*= 9.2 and *J*=2.2 Hz, 5'-H), 8.15 (d, 1H, *J*=2.2

Hz, 7'-H), 9.50 (s, 1H, C*H*N), 11.0 (s,1H, O*H*). ^{13}C NMR (DMSO-d_6) δ 56.1, 116.8, 117.6, 117.7, 119.2, 120.1, 122.0, 122.5, 131.6, 140.7, 148.3, 150.7, 158.6, 171.8, 191.9. λ_{max} (ethanol)/nm 358 (ε/dm^3 mol^{-1} cm^{-1} 9,888). IR (liquid film): υ 2361, 2341, 1951, 1870, 1844, 1810, 1800, 1792, 1772, 1734, 1684, 1653, 1559, 1540 cm^{-1}.

3. Results and discussion

3.1. Synthesis

Imines **1** and **2** were synthesized through Schiff-base condensation of commercial available 2-hydroxy-3-methoxybenzaldehyde with amino-thiadiazole or benzothiazole precursors, in ethanol at room temperature (Scheme 1). Purification of the crude products by recrystallization in ethanol gave the pure compounds in moderate to good yields (62-73%) (Table 1). All compounds were characterized by ^{1}H and ^{13}C NMR, UV-Vis and IR, the data obtained are in full agreement with the proposed formulation.



Scheme 1. Synthesis of heterocyclic imines **1-2**.

Table 1. Yields and UV-visible data for compounds **1-2** in ethanol.

Comp.	Yield (%)	Reaction time (h)	λ_{max} (nm)
1a	70	7	274
1b	62	5	314
2	73	6	358

3.2. Optical properties

The UV-visible spectra of imines **1-2** were recorded. in ethanol solutions (10^{-4} M). The position of the absorption bands is influenced by the structure of the compounds, for example, by the different heterocyclic group linked to the aryl-imine moiety (Table 1). Chromophore **2**, which have the benzothiazole heterocycle linked to the aryl ring show a marked bathochromic shift in their charge transfer (CT) band compared with (aryl)thiadiazole imines (**1a**, 84 nm) or (**1b**, 44 nm) due to the stronger electron-acceptor ability of NO_2-benzothiazole heterocycle as well as due to more extensive electron delocalization (Figure 1).

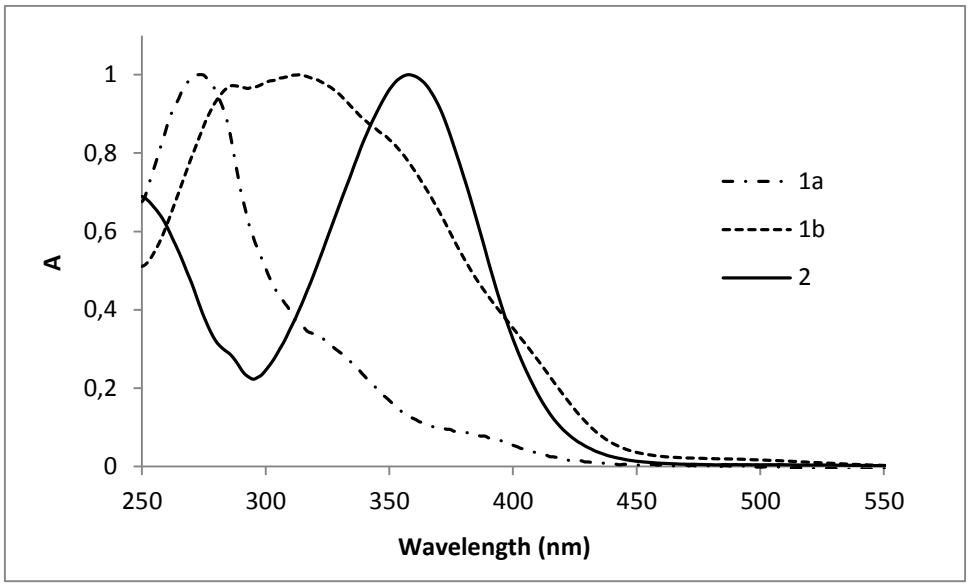


Fig. 1- Comparative absorption spectra of heterocyclic imines **1-2** in ethanol at room temperature.

3.3. Electronic structure analysis

The most characteristic signals in the ^{1}H NMR spectra of this family of Schiff bases is that corresponding to the C*H*=N protons. Compounds **1-2** have the C*H*=N protons resonate at 9.27-9.50 ppm, whereas aryl O*H* protons were found in the 10.80-11.0 ppm interval. All protons in compound **2** exhibits signals that are shifted upfield, compared to the corresponding (aryl)thiadiazole derivatives **1a-b**, due to the strongest electron acceptor ability of the nitro- functionalized benzothiazole electron-deficient heterocycle compared to the (aryl)thiadiazole groups (Table 2).

The ^{1}H NMR chemical shifts reflect a charge separation in the ground state, consequently the analysis of these data in push-pull organic systems such as imines **1**-**2** bearing thiadiazole and benzothiazole electron-deficiente heterocycles as acceptor groups confirms their push-pull character with a significant intramolecular charge transfer (ICT) from the donor aryl-imine moiety to the acceptor groups and a high polarizability of the whole donor-acceptor derivatives.

Table 2. Chemical shifts of protons of compounds **1**-**2** in deuterated DMSO at 300 and 400 MHz, with chemical shift values in ppm.

Comp.	C*H*=N	O*H*	3-H	4-H	5-H
1a	9.46	10.98	7.46	6.94	7.23
1b	9.27	10.88	7.50	6.96	7.24
2	9.50	11.00	7.54	6.96	7.26

4. Conclusions

In summary, we have synthetized in good to excellent yields new heterocyclic imines functionalized with (aryl)thiadiazole or benzothiazole acceptors groups linked to the imne-aryl moiery through position 2 of the thiadiazole or benzothiazole heterocycles, using simple experimental procedures.

Modulation of the electronic and optical properties of compounds **1**-**2**, was achieved through the variation of the electronic acceptor ability of the heterocycle as well as increase of the π-conjugated bridge.

Due to their push-pull character and marked acidity of OH protons the new heterocyclic systems could have potential applications for NLO chromophores and/or as colorimetric chemosensors.

Acknowledgements

Thanks are due to *Fundação para a Ciência e Tecnologia* (FCT-Portugal) and FEDER-COMPETE for financial support through Centro de Química [PEst-C/QUI/UI0686/2011 (F-COMP-01-0124-FEDER-022716)] and a PhD grant to M.C.R. Castro (SFRH/BD/78037/2011). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased with funds from FCT and FEDER. We are

also grateful to the Instituto da Educação of Universidade do Minho for providing the laboratory infrastructure necessary for the development of this work.

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