

Reversible *trans*–*cis* photoisomerization of new pyrrolidene heterocyclic imines

Paulo J. Coelho^{a,*}, M. Cidália R. Castro^b, M. Manuela M. Raposo^{b,**}

^a Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal

^b Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

ARTICLE INFO

Article history:

Received 22 November 2012
Received in revised form 4 March 2013
Accepted 9 March 2013
Available online 16 March 2013

Keywords:

Heterocyclic imines
Schiff bases
Photochromism
cis–*trans* isomerization
Molecular switches
Pyrrole

ABSTRACT

A series of novel pyrrolidene imines bearing functionalized aryl or naphthyl moieties was synthesized and their photochromic properties studied by UV spectroscopy. UV irradiation of these heterocyclic Schiff bases at room temperature promotes the *trans*–*cis* photoisomerization of the C=N double bond with formation of a variable amount of the *cis*-isomer that, in the absence of light, returns thermally to the original form in few seconds. The thermal *cis*–*trans* re-isomerization of these molecular switches is much more slower than for the common benzylidene aniline-type imines, allowing the observation of the photochromic phenomena at room temperature. Strong electron-donor substituents in the *para*-position of the aniline part of the molecule decreases even more the kinetics of the thermal *cis*–*trans* re-isomerization leading to a manifest change in the UV spectrum.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The reversible photoinduced *trans*–*cis* isomerization of stilbenes and azo compounds has been extensively studied in the last decades [1–8]. UV or visible irradiation of the thermodynamically more stable *trans*-isomer produces the *cis*-isomer that returns to the initial form either thermally or through irradiation with light of a different wavelength. Usually the differences in the absorption spectrum associated with this process are significant, and the thermal stability of both isomers are sufficiently high to allow easy and accurate measurements of the switching rates and quantum yields. The speed of the thermal switching process is very variable and can take just a few milliseconds or several days, depending on the structure of the compound, temperature, solvent, pH, etc. [9]. This photoinduced molecular rearrangement is also accompanied by important geometrical and physical changes of the molecule that have been exploited in materials chemistry [10–15]. By connecting azo dyes to polymers, the microscopic movements of the azo group induce a macroscopic behaviour of the polymer, creating functional materials that show reversible macroscopic mechanical deformations upon light irradiation [16–19].

The *trans*–*cis* isomerization can also occur in the imino group (C=N), in particular, in imines derived from aniline and aromatic

aldehydes. Notwithstanding the photochromic properties of aromatic imines are much less studied, even though these are rather accessible materials (Scheme 1). The thermo- and photochromic properties of some Schiff bases derived from salicylic aldehydes are well known, but here the isomerization is due to an intramolecular proton transfer, not the *trans*–*cis* around the imino group [20–24].

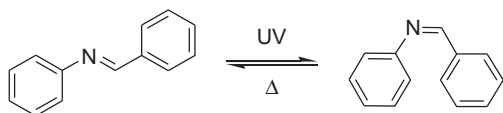
The lack of studies on the *trans*–*cis* photoisomerization of imines is probably associated to the low lifetime of the *cis*-isomer which returns, spontaneously and very quickly, to the *trans* form. Consequently, this phenomena has been detected only at low temperature (–70 °C–100 °C) [25]. The activation energy barrier for the thermal *cis*–*trans* re-isomerization of benzylidene aniline-type compounds is around 70 kJ/mol which is considerable lower than that for azo dyes (ca. 95 kJ/mol) and stilbenes (ca. 175 kJ/mol) and results in a shorter lived *cis*-isomer [26]. On the other hand the UV–vis spectrum of both isomers are typically very similar which difficult the study of the switching process, and these molecules are labile in aqueous acid media what can be a serious limitation for some applications or an opportunity for others.

Most of the studies on the photochromism of imines have been performed with benzylidene aniline-type imines (Scheme 1) [27–29]. The thermodynamically more stable *trans*-isomer is non-planar with torsional angles of the aniline ring 41–55° out of the molecule plane, while the benzylidene moiety is slightly twisted in the opposite direction [27]. Due to the low conjugation between the two aromatic systems these compounds are uncoloured, displaying a strong absorption in the UV spectrum at 264 nm due to the $\sigma \rightarrow \sigma^*$ transition and a less intense band around 311 nm assigned to the $\pi \rightarrow \pi^*$ transition [30,31]. The *cis*-isomer has a quite similar

* Corresponding author. Tel.: +351 259 350284; fax: +351 259 350480.

** Corresponding author. Tel.: +351 253 604381; fax: +351 253 604382.

E-mail addresses: pcoelho@utad.pt (P.J. Coelho),
mfox@quimica.uminho.pt (M.M.M. Raposo).



Scheme 1. Photochemical and thermal isomerization of benzylidene aniline-type imines.

absorption spectrum, the main difference being a blue shift of the main absorption band to *ca.* 243 nm and the appearance of a weak, low energy band around 343 nm [32]. Therefore, the overall effect of the *trans*–*cis* photoisomerization of these imines is the lowering of the absorption in the 300–350 nm region, reaching a photostationary state constituted by a mixture of both isomers [33]. Because the absorption bands of both isomers are very broad and considerably superposed, light irradiation can not convert completely one isomer into the other, although if the ratio of the extinction coefficients is big enough, rich mixtures of one isomer can be achieved [9].

In the dark, the thermally unstable *cis*-isomer returns spontaneously to the *trans* form which is accompanied by an increase on the absorption in the same region. Accordingly, the photoisomerization process can be followed by UV spectroscopy measuring the absorbance at λ_{\max} of the *trans*-isomer while performing cycles of UV-irradiation/dark (Fig. 1).

The introduction of electron donor/acceptor groups in the aromatic rings of the N-benzylidene anilines led to some tailoring of the photoresponse; in particular, a considerable shift of the λ_{\max} of both isomers was observed when nitro and dimethylamino groups were simultaneously placed in the *para* position of the aromatic rings. Still, the photoisomerization could only be detected at low temperature (-25° to -10°) [33]. In the last years we have studied the photochromic properties of heteroaromatic azo dyes. The use of pyrrole, thiophene, (benzo)thiazole and thiadiazole heterocycles instead of the common phenyl rings led to considerable changes in the colour exhibited by these compounds and in the kinetics of the *trans*–*cis* isomerization reaction. The switching between the *trans* and *cis* isomers of heteroaryl azo dyes can be performed in few seconds at room temperature, in solution [34–38] or in polymeric matrices [39], while the thermal relaxation of the *cis* form of azo benzene derivatives is usually much more slower (from several hours to a few days) [40].

Although some studies on the photochemistry of heteroaryl imines bearing two heteroaromatic rings (furan and thiophene) have been carry out with the objective of performing intramolecular photocyclization [41], to our knowledge, there are no reports on the *trans*–*cis* photoisomerization of heterocyclic imines.

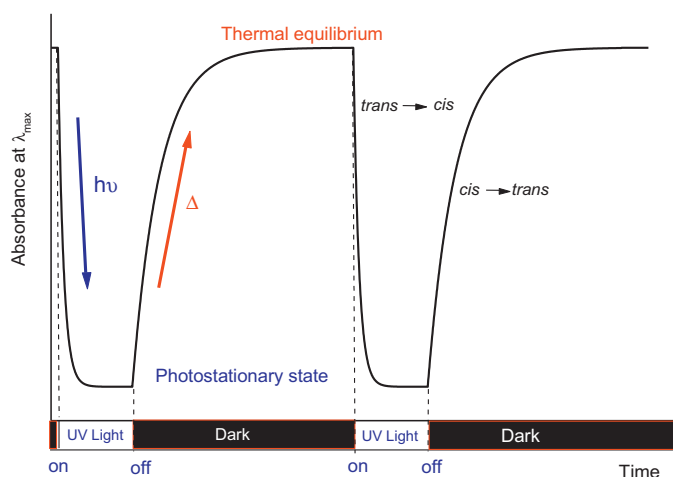


Fig. 1. Photochemical *trans*–*cis* and thermal *cis*–*trans* switching.

Since these compounds are easily accessible and can be very useful, we decided to prepare some simple pyrrole-2-carbaldehyde imine derivatives and test their behaviour under UV irradiation.

2. Results and discussion

2.1. Synthesis and characterization

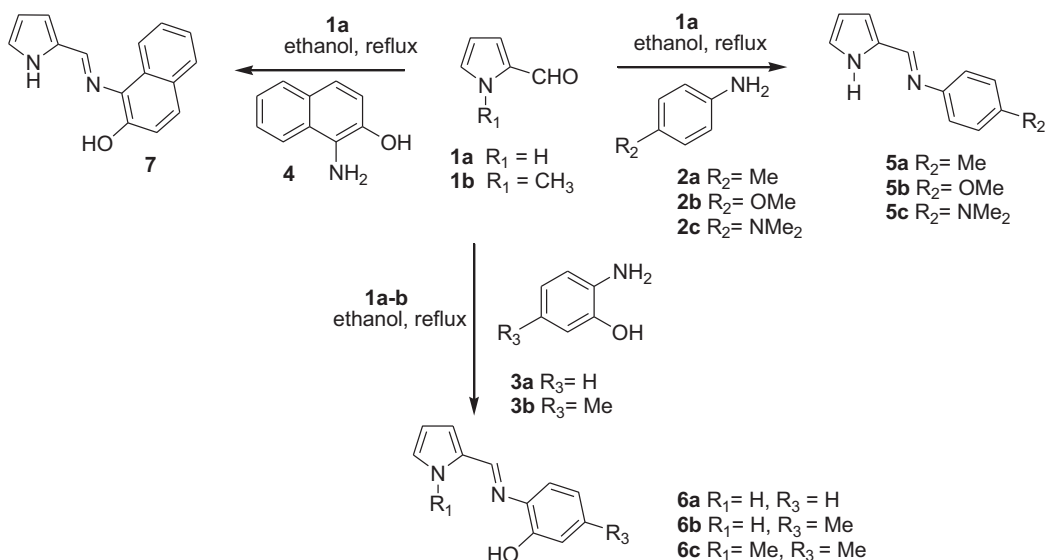
The imines **5**–**7** were synthesized through Schiff-base condensation of pyrrole aldehydes **1a** and **b** with commercial available anilines **2** and **3** or amino-naphthalene **4**, in ethanol at reflux (Scheme 2). Purification of the crude product by recrystallization gave the pure compounds in moderate to good yields (21–86%). All compounds were characterized by ^1H and ^{13}C NMR, IR, MS and HRMS and the data obtained are in full agreement with the proposed formulation (see supplementary information). The most characteristic signals in the ^1H NMR spectra of this family of Schiff bases were those corresponding to the N–H of the pyrrole heterocycle and the CH=N protons. For example, for compounds **5a**–**c** the CH=N protons resonate at 8.28–8.30 ppm, whereas pyrrole N–H protons were found in the 11.56–11.69 ppm interval. Additionally, compounds **6a**–**c** exhibit a broad singlet at 9.53–9.54 ppm due to the O–H proton.

In 5.0×10^{-5} M acetonitrile solutions imines **5**–**7** are near colourless compounds with similar UV spectra characterized by two strong absorption bands at 288–315 nm and 332–373 nm (see supplementary information). In acetone, the simplest imine **5a** with a methyl group on the *para*-position of the aniline moiety has $\lambda_{\max} = 332$ nm. The introduction of the hydroxyl group in the *ortho*-position on the aniline ring (**6a**–**c**) or dimethylamino group in the *para*-position (**5c**) leads to a strong bathochromic shift of the maximum wavelength of absorption (23–34 nm). The imine **7**, derived from 3-hydroxy-2-naphthylamine, exhibits a broad band centred at 373 nm with a significant absorption above 400 nm while imines **5b**, **5c** and **6a** present a second low intensity band centred at 450 nm. As a result, diluted solutions of imines **5c** and **7** are slightly yellow.

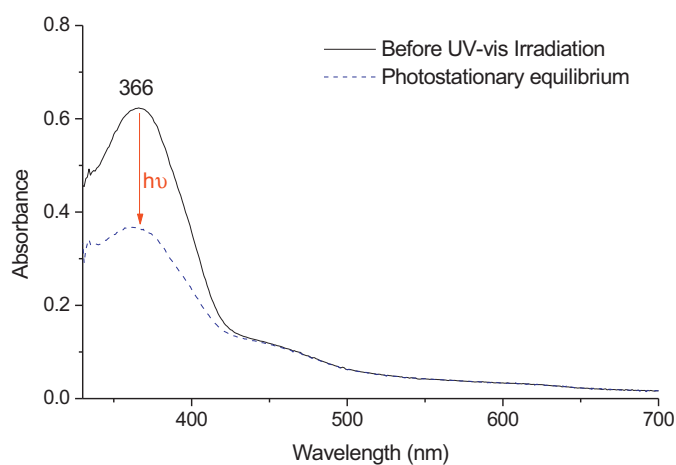
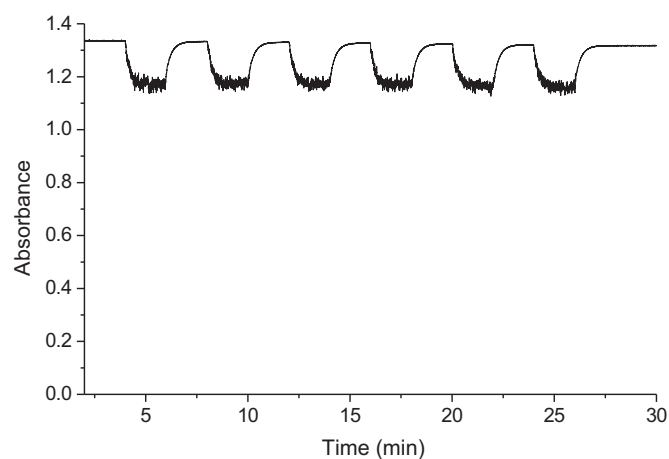
2.2. Trans–cis photochemical isomerization

The photochemical isomerization of the *trans*-isomer of imines **5**–**7** involves three phenomena which occur at the same time upon exposure to the UV/Vis-light: (i) the photochemical *trans*–*cis* conversion; (ii) the photochemical *cis*–*trans* conversion and (iii) the thermal *cis*–*trans* conversion. After a few minutes of light exposure a photostationary state, constituted by a mixture of both isomers, is attained. When the illumination is switch off, only the thermal back *cis*–*trans* conversion takes place. Continuous UV–vis irradiation experiments were carried out at 20°C using a Cary 50 Varian spectrometer equipped with a 150 W ozone free Xenon lamp. The irradiation was extended for until a photostationary state was attained (0.2–2 min), and then the light source was switch off and the changes in the absorption spectra were followed in time.

UV light irradiation of all imines led to a fast decrease of the absorption at λ_{\max} (Fig. 2) which means that the *cis*-isomer has, as expected, a smaller extinction coefficient than the *trans* but similar λ_{\max} . This change in the absorption spectra corresponds however to a limited conversion of the *trans*-isomer into the *cis* (Scheme 3). Curiously, for compound **5c** the long-wavelength band above 450 nm does not decrease upon irradiation which indicates that both isomers should have similar absorption in this region. When the light source was removed the absorption increased in few seconds/minutes to the initial value. At 20°C the time-scale for achievement of the photostationary state was shorter than that required for the thermal process. The kinetic rate of the thermal



Scheme 2. Synthesis of pyrrolidene imines 5–7.

Fig. 2. Absorption spectra of imine **5c** measured before and after UV-vis irradiation.Fig. 3. UV-vis irradiation/dark cycles for imine **6b** at 359 nm.

cis–*trans* reaction can thus be calculated measuring the absorbance at λ_{max} after switching off the illumination (Fig. 3).

Since both *trans*- and *cis*-isomers absorb considerably at the same wavelength, the kinetic curve observed during the photochemical isomerization is the result of two contributions: the absorbance of the *trans*-isomer which decreases in time and the absorbance of the *cis* which increases (Fig. 4). Throughout the thermal *cis*–*trans* isomerization the inverse situation occurs. The thermal process follows a first order kinetics and hence the *cis*–*trans* re-isomerization curve can be fitted to the monoexponential model:

$$\text{Abs}(t) = A_1 e^{-kt} + A_0$$

where $\text{Abs}(t)$ is the absorbance at λ_{max} at any instant t and k the kinetic rate of the thermal reaction. This monoexponential model

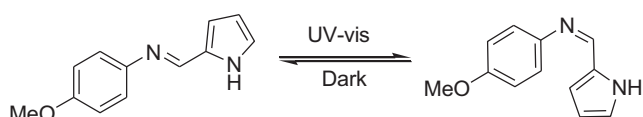
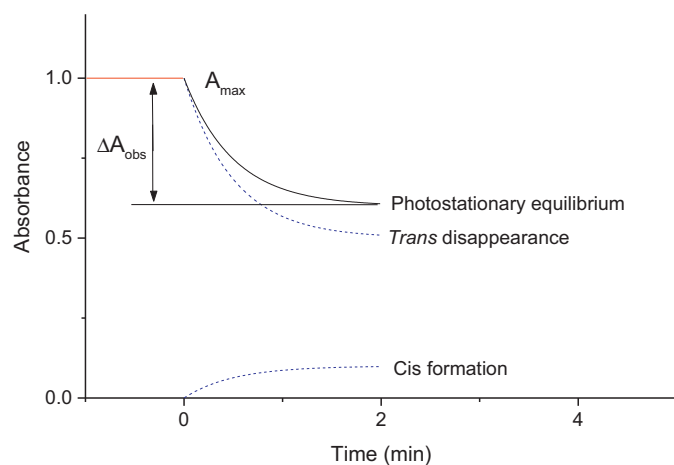
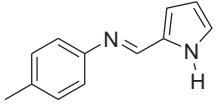
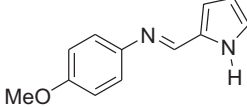
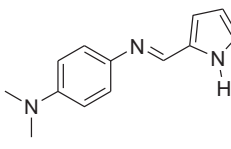
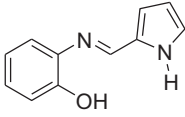
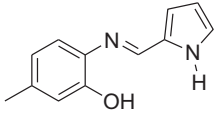
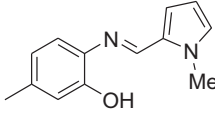
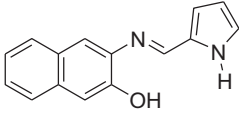
Scheme 3. Photochromic equilibrium for the pyrrolidene imine **5b**.Fig. 4. Contribution of the *trans* and *cis* isomers to the absorbance during the photochemical *trans*–*cis* isomerization.

Table 1
Spectrokinetic properties in acetone under continuous visible irradiation: maximum wavelength of absorption (λ_{\max}), maximum absorbance (A_{\max}), absorbance variation under UV–vis light (ΔA_{obs}), *trans*–*cis* conversion (% *cis*), thermal isomerization rate (k_{Δ}), activation energy (E_a) and half-life time of the *cis*-isomer ($t_{1/2}$) for imines **5**–**7**.

Imine	λ_{\max} (nm)	A_{\max}	Photostationary equilibrium		k_{Δ} (s^{-1})	E_a (kJ/mol)	$t_{1/2}$ (s)
			ΔA_{obs}	% <i>cis</i>			
	332	1.54	0.1	>6	0.051	68	14
	336	1.45	0.35	>24	0.019	82	36
	366	0.69	0.28	>40	0.015	69	48
	356	1.22	0.1	>8	0.093	66	7.5
	359	1.33	0.16	>12	0.070	62	10
	355	0.99	0.05	>5	0.20	73	3.5
	373	0.49	0.014	>3	0.22	64	3.1

was found to accurately fit the data for all compounds and the results are presented in Table 1.

The ratio $\Delta A_{\text{obs}}/A_{\max}$ indicates the loss of absorbance upon UV–vis irradiation due to the photochemical *trans*–*cis* isomerization and is a good estimation of the *trans*–*cis* conversion percentage, nevertheless, due to the superposition of the absorption spectra, the amount of the *cis*-isomer present at the photostationary state is always superior (Fig. 4). Nonetheless, this parameter is not very important since it depends directly on the power of the irradiating beam: as the light power increases more molecules will perform isomerization and the observed ΔA_{obs} will be higher. The kinetic rate constant of the thermal isomerization is more useful for the characterization of this system as it only depends on the imine structure and temperature.

The UV–vis irradiation/dark procedure could be repeated several times and the behaviour was fully reproducible indicating that under these experimental conditions no significant degradation was observed. For compound **6b** the photostationary equilibrium is constituted by more than 12% of the *cis*-isomer and the rate of the *cis*–*trans* thermal re-isomerization is 0.70 s^{-1} , which gives a lifetime ($t_{1/2}$) of 10 s for the *cis*-isomer. For this compound the complete *trans*–*cis*–*trans* cycle can be performed in 2 min (Fig. 3).

Decreasing the temperature led to a decline in the isomerization rate constant that is accompanied by a more significant

change in the absorbance at λ_{\max} . For compound **6b**, for example, lowering the temperature from 20 to 15 °C, lead to a 60% decrease in the rate constant (from 0.070 to 0.041 s^{-1}) and to a more pronounced ΔA_{obs} (0.23) indicating that at this temperature the photostationary state is constituted by more than 17% of the *cis*-isomer. Under continuous visible irradiation conditions, the decrease in the absorbance at λ_{\max} is inversely related to the kinetic rate of the thermal isomerization process consequently, higher absorbance variations are observed at lower temperatures. Measuring the thermal rate constants in the temperature range 14–28 °C allowed us the determination of the activation energy for the thermal *cis*–*trans* switching of this set of heteroaromatic imines. The values vary between 62 and 82 kJ/mol depending on the imine structure, which are in accordance with previous results [27] (Table 1).

The kinetic rate of the thermal *cis*–*trans* re-isomerization of heteroaryl imines **5**–**7** is considerable slower than that reported for N-benzylidene-aniline imines [25] but show little dependence with the substituents present in the aromatic rings being, nevertheless, considerable slower for imines **5b** and **c** that present strong electron-donating substituents (CH_3O or Me_2N) in the *para*-position [33]. For imine **5c** the photostationary equilibrium is attained after 1 min of UV–vis irradiation and the system returns thermally to the initial *trans* state after ca. 4 min (Fig. 5).

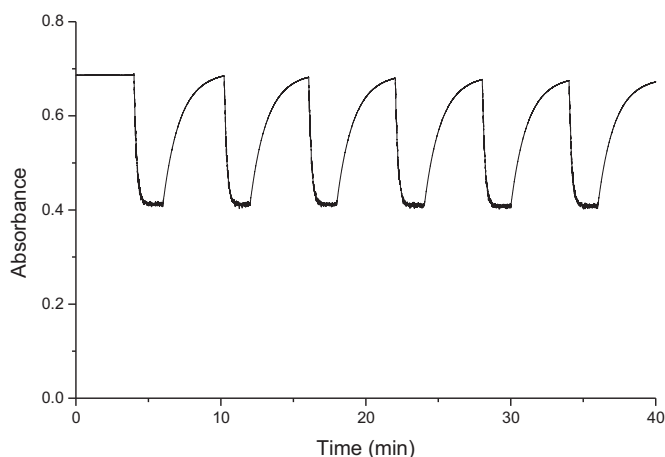


Fig. 5. UV-vis irradiation/dark cycles for imine **5c**.

Table 2

Maximum wavelength of absorption (λ_{\max}), thermal *cis*–*trans* isomerization rate (k) and activation energy (E_a), measured between 14–28 °C, for imines **5b** and **6b** in five solvents of increasing polarity.

Solvent		Et ₂ O	CH ₂ Cl ₂	CH ₃ COCH ₃	CH ₃ CN	CH ₃ OH
Polarity		0.117	0.309	0.355	0.460	0.762
5b	λ_{\max}	335	336	337	334	336
	k	0.034	0.032	0.019	0.012	0.023
	E_a	65	50	82	77	70
6b	λ_{\max}	361	359	359	356	356
	k	0.094	0.35	0.070	0.096	1.0
	E_a	59	^a	62	58	^a

^a The thermal reaction is too fast to make an accurate measurement.

Since the kinetics of the back thermal *cis*–*trans* switching is substantially slower, there is a very noteworthy decrease in the absorbance upon UV irradiation indicating that more than 40% of the initial *trans*-isomer was converted into the *cis*. The lifetime of the *cis*-isomer varies between 3 and 48 s at room temperature.

The nature of the solvent has a limited influence on the photochromic behaviour of these imines. The maximum wavelength of absorption, rate constants and activation energy for imines **5b** and **6b** in 5 solvents are showed in Table 2. Although only marginal changes were observed in the λ_{\max} , the thermal *cis*–*trans* rate constant exhibit some changes. For imine **6b** the thermal re-isomerization was faster in CH₂Cl₂ and methanol even though no net correlation between these data and the solvent polarity could be established. The activation energy of the thermal *cis*–*trans* isomerization of imine **5b** is very sensible to the solvent nature being considerable higher in high polarity solvents like acetone or acetonitrile.

3. Conclusion

New photochromic heterocyclic imines derived from pyrrole-2-carbaldehyde were synthesized, in moderate to good yields, using commercially available reagents and simple experimental procedures. UV–vis irradiation of these Schiff bases, at room temperature, leads to the isomerization of the C=N bond with formation of a variable amount of the *cis*-isomer that spontaneously return to the initial *trans* form in the dark in few seconds/minutes. This phenomenon is accompanied by a noteworthy decrease of the absorbance of the system in the UV region. The kinetic rate of the thermal *cis*–*trans* isomerization can be controlled through proper substitution at the aniline ring of the molecule. While for common aromatic imines the *trans*–*cis* photoisomerization is very fast and can only be detected at low temperature, with these easily

synthesized molecular switches, the change between the two isomeric forms can be performed in few seconds/minutes at room temperature.

4. Experimental

4.1. Materials

1H-Pyrrole-2-carbaldehyde, 1-methyl-1H-pyrrole-2-carbaldehyde, 4-methylaniline, 4-methoxyaniline, 4-*N,N*-dimethylaniline, 2-aminophenol, 2-amino-5-methylphenol and 1-amino-naphthalen-2-ol were purchased from Aldrich, Acros or Fluka and used as received. TLC analyses were carried out on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel 60 F254) and spots were visualized under UV light.

4.2. Instruments

NMR spectra were obtained on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz (¹H NMR) and 75.4 MHz (¹³C NMR) or a Bruker Avance III 400 at an operating frequency of 400 MHz (¹H NMR) and 100.6 MHz (¹³C NMR) using the solvent peak as internal reference at 25 °C. All chemical shifts are given in ppm using δ_{H} Me₄Si=0 ppm as reference and J values are given in Hz. Assignments were made by comparison of chemical shifts, 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 using nujol. Mass spectrometry analyses were performed at the “C.A.C.T.I. - Unidad de Espectrometría de Masas” at the University of Vigo, Spain. All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected.

4.3. Synthesis

General procedure for the synthesis of imines **5–7**: a solution of the aldehyde **1a–b** (2 mmol), anilines **2–3** or amino-naphthalene **4** (2 mmol), acetic acid (2 drops) in ethanol (15 mL) was heated at reflux for 4–24 h. After cooling and solvent evaporation, the crude product was recrystallized from light petroleum/dichloromethane or ethanol to afford the pure imines **5–7**.

N-((1H-pyrrol-2-yl)methylene)-4-methylbenzenamine (5a) (reaction time 10 h). Dark brown solid (21%). Mp 299–301 °C. ¹H NMR (DMSO-*d*₆) δ 3.33 (s, 3H, CH₃), 6.18 (t, 1H, J =3.2 Hz, 4'-H), 6.66 (dd, 1H, J =4.4 and J =2.0 Hz, 3'-H), 6.99–7.01 (m, 1H, 5'-H), 7.07 (d, 2H, J =8.2 Hz, 3-H and 5-H), 7.16 (d, 2H, J =8.2 Hz, 2-H and 6-H), 8.28 (s, 1H, CH=N), 11.69 (br s, 1H, NH). ¹³C NMR (DMSO-*d*₆) δ 20.5, 109.6, 116.0, 120.6, 123.6, 129.7, 130.6, 134.1, 149.6, 149.8. IR (Nujol): ν 3463, 2728, 2672, 1891, 1697, 1626, 1599, 1548, 1504, 1305, 1246, 1200, 1170, 1133, 1109, 1033 cm⁻¹. MS (EI) m/z (%) = 184 ([M]⁺, 44), 183 (100). HMRS: m/z (EI) for C₁₄H₁₁NS; calcd 184.1000; found: 184.1007.

N-((1H-pyrrol-2-yl)methylene)-4-methoxybenzenamine (5b) (reaction time 15 h). Brown solid (72%). Mp 95–96 °C. ¹H NMR (DMSO-*d*₆) δ 3.75 (s, 3H, OCH₃), 6.17 (t, 1H, J =2.8 Hz, 4'-H), 6.64–6.65 (m, 1H, 3'-H), 6.92 (d, 2H, J =8.8 Hz, 3-H and 5-H), 6.97–7.02 (m, 1H, 5'-H), 7.16 (d, 2H, J =8.8 Hz, 2-H and 6-H), 8.29 (s, 1H, CH=N), 11.63 (br s, 1H, NH). ¹³C NMR (DMSO-*d*₆) δ 55.2, 109.5, 114.4, 115.6, 121.8, 123.3, 130.7, 145.0, 148.8, 157.1. IR (Nujol): ν 3460, 2729, 2680, 2052, 1878, 1866, 1691, 1619, 1578, 1551, 1503, 1241, 1203, 1179, 1133 cm⁻¹. MS (EI) m/z (%) = 200 ([M]⁺, 100), 199 (94), 185 (52), 184 (15), 157 (10), 156 (28), 134 (10). HMRS: m/z (EI) for C₁₂H₁₂N₂O; calcd 200.0950; found: 200.0945.

N-((1H-pyrrol-2-yl)methylene)-4-*N,N*-dimethylbenzenamine (5c) (reaction time 20 h). Brown solid (61%).

Mp 123–125 °C. ^1H NMR (DMSO- d_6) δ 2.89 (s, 6H, $2\times\text{CH}_3$), 6.15 (t, 1H, $J=2.8$ Hz, 4'-H), 6.58 (dd, 1H, $J=4.8$ and $J=1.2$ Hz, 3'-H), 6.72 (d, 2H, $J=9.0$ Hz, 3-H and 5-H), 6.93–6.95 (m, 1H, 5'-H), 7.12 (d, 2H, $J=9.0$ Hz, 2-H and 6-H), 8.30 (s, 1H, $\text{CH}=\text{N}$), 11.56 (br s, 1H, NH). ^{13}C NMR (DMSO- d_6) δ 40.4, 109.4, 112.9, 114.8, 121.6, 122.8, 131.0, 141.0, 146.6, 148.6. IR (Nujol): ν 3462, 2726, 2669, 1619, 1558, 1515, 1223, 1164, 1125, 1083, 1093, 1060, 1033 cm^{-1} . MS (EI) m/z (%) = 213 ($[\text{M}]^+$, 100), 212 (77), 199 (11), 198 (24), 197 (19), 196 (41), 169 (14), 168 (11), 164 (11), 146 (11), 135 (13), 120 (16), 119 (11). HMRS: m/z (EI) for $\text{C}_{13}\text{H}_{15}\text{N}_3$; calcd 213.1266; found: 213.1273.

2-((1H-pyrrol-2-yl)methyleneamino)phenol (6a) (reaction time 5 h). Brown solid (78%). Mp 133–136 °C. ^1H NMR (CDCl_3) δ 6.35–6.37 (m, 1H, 4'-H), 6.83 (dd, 1H, $J=3.6$ and $J=1.2$ Hz, 3'-H), 6.90 (dt, 1H, $J=7.2$ and $J=1.2$ Hz, 4-H), 7.01 (dd, 1H, $J=7.8$ and $J=1.4$ Hz, 3-H), 7.12–7.17 (m, 2H, 5'- and 5-H), 7.25 (dd, 1H, $J=7.8$ and $J=1.4$ Hz, 6-H), 8.44 (s, 1H, $\text{CH}=\text{N}$), 9.53 (s, 1H, OH), 10.13 (br s, 1H, NH). ^{13}C NMR (CDCl_3) δ 111.7, 115.6, 116.6, 119.6, 120.4, 125.7, 128.1, 129.6, 146.9, 151.2, 179.3. IR (Nujol): ν 3337, 3274, 3116, 1928, 1692, 1623, 1596, 1586, 1533, 1300, 1282, 1247, 1215, 1173, 1247, 1173, 1118, 1090, 1028 cm^{-1} . MS (EI) m/z (%) = 186 ($[\text{M}]^+$, 38), 185 (34), 184 (100), 170 (21), 169 (72), 157 (14), 156 (13), 155 (15), 144 (39), 92 (12), 91 (15), 64 (17), 63 (23). HMRS: m/z (EI) for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$; calcd 186.0793; found: 186.0797.

2-((1H-pyrrol-2-yl)methyleneamino)-5-methylphenol (6b) (reaction time 4 h). Light brown solid (86%). Mp 165–167 °C. ^1H NMR (CDCl_3) δ 2.32 (s, 3H, CH_3), 6.33–6.35 (m, 1H, 4'-H), 6.71 (ddd, 1H, $J=8.0$ Hz, $J=2.4$ Hz and $J=0.8$ Hz, 4-H), 6.77 (dd, 1H, $J=3.6$ Hz and $J=1.2$ Hz, 3'-H), 6.83 (br d, 1H, $J=1.2$ Hz, 6-H), 7.08–7.10 (m, 1H, 5'-H), 7.14 (d, 1H, $J=8.0$ Hz, 3-H), 8.42 (s, 1H, $\text{CH}=\text{N}$), 9.54 (s, 1H, OH), 10.34 (br s, 1H, NH). ^{13}C NMR (CDCl_3) δ 21.3, 111.3, 115.9, 116.0, 118.5, 121.0, 124.8, 123.0, 138.4, 146.0, 151.1, 179.4. IR (Nujol): ν 3338, 3249, 3106, 1873, 1717, 1704, 1628, 1604, 1580, 1555, 1500, 1288, 1264, 1243, 1200, 1179, 1154, 1119, 1090 cm^{-1} . MS (EI) m/z (%) = 200 ($[\text{M}]^+$, 30), 199 (24), 198 (93), 197 (43), 184 (13), 183 (100), 169 (16), 78 (11). HMRS: m/z (EI) for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}$; calcd 200.0950; found: 200.0947.

2-((1-Methyl-1H-pyrrol-2-yl)methyleneamino)-5-methylphenol (6c) (reaction time 5 h). Brown solid (59%). Mp 123–124 °C. ^1H NMR (DMSO- d_6) δ 2.27 (s, 3H, CH_3), 3.96 (s, 3H, NCH_3), 6.13–6.15 (m, 1H, 4'-H), 6.59–6.63 (m, 1H, 4-H), 6.67 (br d, 1H, $J=1.2$ Hz, 6-H), 6.73 (dd, 1H, $J=4.0$ Hz and $J=1.2$ Hz, 3'-H), 6.98 (d, 1H, $J=8.0$ Hz, 3''-H), 7.02 (t, 1H, $J=2.4$ Hz, 5'-H), 8.44 (s, 1H, $\text{CH}=\text{N}$), 9.51 (s, 1H, OH). ^{13}C NMR (DMSO- d_6) δ 20.7, 36.1, 108.4, 116.1, 117.4, 118.1, 120.1, 129.1, 130.3, 135.6, 136.5, 149.2, 179.5. IR (Nujol): ν 3111, 2727, 1864, 1741, 1694, 1603, 1570, 1528, 1341, 1315, 1296, 1268, 1245, 1194, 1158, 1114, 1093, 1057 1012 cm^{-1} . MS (EI) m/z (%) = 213 ($[\text{M}-\text{H}]^+$, 12), (12), 212 (62), 211 (100). HMRS: m/z (EI) for $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}$; calcd 213.1028; found: 213.1026.

1-((1H-pyrrol-2-yl)methyleneamino)naphthalen-2-ol (7) (reaction time 24 h). Green solid (102 mg, 59%). Mp 230–232 °C. ^1H NMR (DMSO- d_6) 6.56 (t, 1H, $J=2.0$ Hz, 4'-H), 6.96 (br d, 1H, $J=8.8$ Hz, naphthyl-H), 7.06 (br d, 1H, $J=8.8$ Hz, 1H, naphthyl-H), 7.22–7.25 (m, 1H, 3'-H), 7.40 (br t, 1H, $J=7.6$ Hz, naphthyl-H), 7.51–7.60 (m, 2H, 5'-H and naphthyl-H), 7.66 (br s, 1H, naphthyl-H), 7.95 (br d, 1H, $J=8.4$ Hz, naphthyl-H), 8.13 (s, 1H, $\text{CH}=\text{N}$), 13.5 (br s, 2H, NH and OH). IR (Nujol): ν 2726, 1656, 1631, 1513, 1603, 1322, 1285, 1268, 1254, 1211, 1114, 1089, 1077, 1045, 1000 cm^{-1} . MS (EI) m/z (%) = 236 ($[\text{M}]^+$, 16), 235 (16), 234 (100), 219 (22), 206 (16), 205 (28), 194 (30), 178 (12), 114 (18), 113 (11). HMRS: m/z (ESI) for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$; calcd 236.0950; found: 236.0948.

4.4. Photochromic measurements

UV irradiation experiments were made using a UV-vis Cary 50 Varian spectrometer coupled to a 150W ozone free Xenon

lamp. The light from the UV lamp was filtered using a water filter and then carried to the spectrophotometer holder perpendicularly to the monitoring beam using an optical fibre system. The light flux power, 40 W/m^2 , was measured with a Photometer with UV-A probe. A temperature controlled (20 °C) 10 mm quartz cell (3.5 mL) equipped with magnetic stirring was used. The maximum absorption wavelength of the stable *trans*-isomer of the imines was determined and then the absorbance was measured at λ_{max} while performing UV-vis light irradiation/dark cycles.

Acknowledgments

Thanks are due to the *Fundação para a Ciência e Tecnologia* (Portugal) and FEDER-COMPETE for financial support through the research units Centro de Química - Universidade do Minho and Centro de Química-Vila Real, Projects PTDC/QUI/66251/2006 (FCOMP-01-0124-FEDER-007429), PEst-C/QUI/UI0686/2011 (FCOMP-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 within the framework of the National program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jphotochem.2013.03.004>.

References

- J.S. Yang, K.L. Liao, C.Y. Hwang, C.M. Wang, Photoinduced single versus double-bond torsion in donor-acceptor-substituted *trans*-stilbenes, *Journal of Physical Chemistry A* 110 (2006) 8003.
- T. Fuhrmann, M. Kunze, I. Lieker, A. Stracke, J.H. Wendorff, Light-induced isomerization and photo-orientation in azo and stilbene polymers, in: *Nonlinear optical properties of organic materials IX*, Proceedings of the SPIE 2852 (1996) 42–52.
- M. Uda, T. Mizutani, J. Hayakawa, A. Momotake, M. Ikegami, R. Nagahata, T. Arai, Photoisomerization of stilbene dendrimers: the need for a volume-conserving isomerization mechanism, *Photochemistry and Photobiology* 76 (2002) 596–605.
- J.N. Moorthy, P. Venkatakrishnan, G. Savitha, R.G. Weiss, *Cis* \rightarrow *trans* and *trans* \rightarrow *cis* isomerizations of styrylcoumarins in the solid state. Importance of the location of free volume in crystal lattices, *Photochemical and Photobiological Sciences* 5 (2006) 903–913.
- S.L. Sin, L.H. Gan, X. Hu, K.C. Tam, Y.Y. Gan, Photochemical and thermal isomerizations of azobenzene-containing amphiphilic diblock copolymers in aqueous micellar aggregates and in film, *Macromolecules* 38 (2005) 3943–3948.
- S. Ludwig, H. Bayley, Photoisomerization of an individual azobenzene molecule in water: an on-off switch triggered by light at a fixed wavelength, *Journal of the American Chemical Society* 128 (2006) 12404–12405.
- D. Statman, I. Janossy, Study of photoisomerization of azo dyes in liquid crystals, *Journal of Chemical Physics* 118 (2003) 3222–3232.
- S.S. Sun, A.J. Lees, Synthesis, photophysical properties, and photoinduced luminescence switching of trinuclear diimine rhenium(I) tricarbonyl complexes linked by an isomerizable stilbene-like ligand, *Organometallics* 21 (2002) 39–49.
- D.L. Ross, J. Blanc, Photochromism by *cis*–*trans* isomerization, in: G.H. Brown (Ed.), *Photochromism*, Wiley-Interscience, New York, 1971, pp. 471–556.
- R.H. Lambeth, J.S. Moore, Light-induced shape changes in azobenzene functionalized polymers prepared by ring-opening metathesis polymerization, *Macromolecules* 40 (2007) 1838–1842.
- R.H. El Halabieh, O. Mermut, C.J. Barrett, Using light to control physical properties of polymers and surfaces with azobenzene chromophores, *Pure and Applied Chemistry* 76 (2004) 1445–1465.
- F. Ercole, T.P. Davis, R.A. Evans, Photo-responsive systems and biomaterials: photochromic polymers, light-triggered self-assembly, surface modification, fluorescence modulation and beyond, *Polymer Chemistry* 1 (2010) 37–54.
- H.K. Kim, X.S. Wang, Y. Fujita, A. Sudo, H. Nishida, M. Fujii, T. Endo, A rapid photochemical switching polymer blend system composed of azobenzene-carrying poly(vinylether) and poly(carbonate), *Polymer* 46 (2005) 5879–5883.
- W. Wang, X.Z. Wang, F.T. Cheng, Y.L. Yu, Y.T. Zhu, Light-driven soft actuators based on photoresponsive polymer materials, *Progress in Chemistry* 23 (2011) 1165–1173.

- [15] R. Pardo, M. Zayat, D. Levy, Photochromic organic-inorganic hybrid materials, *Chemical Society Reviews* 40 (2011) 672–687.
- [16] E. Merino, M. Ribagorda, Control over molecular motion using the *cis-trans* photoisomerization of the azo group, *Beilstein Journal of Organic Chemistry* 8 (2012) 1071–1090.
- [17] C.J. Barrett, J.I. Mamiya, K.G. Yager, T. Ikeda, Photo-mechanical effects in azobenzene-containing soft materials, *Soft Matter* 3 (2007) 1249–1261.
- [18] Y.Y. Lin, Y. Qiao, P.F. Tang, Z.B. Li, J.B. Huang, Controllable self-assembled laminated nanoribbons from dipeptide-amphiphile bearing azobenzene moiety, *Soft Matter* 7 (2011) 2762–2769.
- [19] A. Shimamura, A. Priimagi, J. Mamiya, T. Ikeda, Y.L. Yu, C.J. Barrett, A. Shishido, Simultaneous analysis of optical and mechanical properties of cross-linked azobenzene-containing liquid-crystalline polymer films, *ACS Applied Materials and Interfaces* 3 (2011) 4190–4196.
- [20] M. Ziolk, G. Burdzinski, K. Filipczak, J. Karolczak, A. Maciejewski, Spectroscopic and photophysical studies of the hydroquinone family of photochromic Schiff bases analyzed over a 17-orders-of-magnitude time scale, *Physical Chemistry Chemical Physics* 10 (2008) 1304–1318.
- [21] L.Y. Zhao, Q.F. Hou, D. Sui, Y. Wang, S.M. Jiang, Spectroscopic Multi-state/multifunctional switches based on photochromic Schiff base, *Acta Part A-Molecular and Biomolecular Spectroscopy* 67 (2007) 1120–1125.
- [22] M. Ziolk, K. Filipczak, A. Maciejewski, Spectroscopic and photophysical properties of salicylaldehyde azine (SAA) as a photochromic Schiff base suitable for heterogeneous studies, *Chemical Physics Letters* 464 (2008) 181–186.
- [23] Q.H. Wang, L.Z. Cai, F. Gao, Q.R. Zhou, F.P. Zhan, Q.X. Wang, Photochromism of Schiff base compounds derived from N,N-bis(2-aminophenyl)isophthalamide: structure and photosensitivity, *Journal of Molecular Structure* 977 (2010) 274–278.
- [24] H. Fukuda, K. Amimoto, H. Koyama, T. Kawato, Crystalline photochromism of N-salicylidene-2,6-dialkylanilines: advantage of 2,6-dialkyl substituents of aniline for preparation of photochromic Schiff base crystals, *Organic and Biomolecular Chemistry* 1 (2003) 1578–1583.
- [25] E. Fischer, Y. Frei, Photoisomerization equilibria involving the CN double bond, *Journal of Chemical Physics* 27 (1957) 808.
- [26] G. Wettermark, J. Weinstein, J. Sousa, L. Dogliotti, kinetics of *cis-trans* isomerization of para-substituted n-benzylideneanilines, *Journal of Physical Chemistry* 69 (1965) 1584.
- [27] Y. Luo, M. Utecht, J. Dokic, S. Korchak, H.M. Vieth, R. Haag, P. Saalfrank, *Cis-trans* isomerisation of substituted aromatic imines: a comparative experimental and theoretical study, *ChemPhysChem* 12 (2011) 2311–2321.
- [28] G. Wettermark, E. Wallstrom, *Cis-trans* isomerization of Schiff bases, *Acta Chemica Scandinavica* 22 (1968) 675.
- [29] L.M.N. Saleem, *Trans-cis* isomerization of schiff-bases (n-benzylideneanilines) on addition of lanthanide shift-reagents, *Organic Magnetic Resonance* 19 (1982) 176.
- [30] L.R. Knopke, A. Spannenberg, A. Bruckner, U. Bentrup, The influence of substituent effects on spectroscopic properties examined on benzylidene aniline-type imines Spectrosc, *Acta Part A-Molecular and Biomolecular Spectroscopy* 95 (2012) 18–24.
- [31] H.H. Jaffe, S.J. Yeh, R.W. Gardner, The electronic spectra of azobenzene derivatives and their conjugate acids, *Journal of Molecular Spectroscopy* 2 (1958) 120–136.
- [32] K. Maeda, K.A. Muszkat, S. Sharafiozeri, The conformations of *cis*-isomers and *trans*-isomers of benzylideneanilines – H-1 nuclear magnetic-resonance and optical spectroscopic studies, *Journal of the Chemical Society-Perkin Transactions 2* (1980) 1282–1287.
- [33] N.R. King, E.A. Whale, F.J. Davis, A. Gilbert, G.R. Mitchell, Effect of media polarity on the photoisomerisation of substituted stilbene, azobenzene and imine chromophores, *Journal of Materials Chemistry* 7 (1997) 625–630.
- [34] P.J. Coelho, M.C.R. Castro, A.M.C. Fonseca, M.M.M. Raposo, Photoswitching in azo dyes bearing thienylpyrrole and benzothiazole heterocyclic systems, *Dyes Pigments* 92 (2012) 745–748.
- [35] M.M.M. Raposo, A.M.C. Fonseca, M.C.R. Castro, M. Belsley, M.F.S. Cardoso, L.M. Carvalho, P.J. Coelho, Synthesis and characterization of novel diazenes bearing pyrrole, thiophene and thiazole heterocycles as efficient photochromic and nonlinear optical (NLO) materials, *Dyes Pigments* 91 (2011) 62–73.
- [36] P.J. Coelho, M.C.R. Castro, S.S.M. Fernandes, A.M.C. Fonseca, M.M.M. Raposo, Enhancement of the photochromic switching speed of bithiophene azo dyes, *Tetrahedron Letters* 53 (2012) 4502–4506.
- [37] P.J. Coelho, L.M. Carvalho, A.M.C. Fonseca, M.M.M. Raposo, Photochromic properties of thienylpyrrole azo dyes in solution, *Tetrahedron Letters* 47 (2006) 3711–3714.
- [38] P. Coelho, L. Carvalho, J.C.V.P. Moura, M.M.M. Raposo, Novel photochromic 2,2'-bithiophene azo dyes, *Dyes Pigments* 82 (2009) 130–133.
- [39] P.J. Coelho, C.M. Sousa, M.C.R. Castro, A.M.C. Fonseca, M.M.M. Raposo, Fast thermal *cis-trans* isomerization of heteroaromatic azo dyes in PMMA polymers, *Optical Materials* 35 (2013) 1167–1172.
- [40] J. Garcia-Amoros, D. Velasco, Recent advances towards azobenzene-based light-driven real-time information-transmitting materials, *Beilstein Journal of Organic Chemistry* 8 (2012) 1003–1017.
- [41] M. Amati, C. Bonini, M. D'Auria, M. Funicello, F. Lejl, R. Racioppi, Synthesis of heteroaryl imines: theoretical and experimental approach to the determination of the configuration of C=N double bond, *Journal of Organic Chemistry* 71 (2006) 7165.