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# Photophysical properties of a series of 4-aryl substituted 1,4-dihydropyridines

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**In this article, a series of Hantzsch 1,4-dihydropyridines with different substituted aryl groups were synthesized and its spectral data obtained by UV–Vis absorption and fluorescence emission spectroscopies in solution. The dihydropyridines present absorption located around 350 nm and fluorescence emission in the blue–green region. A higher Stokes' shift could be observed for the derivative 3b because of an intramolecular charge transfer in the excited state from the dimethylaniline to the dihydropyridine chromophores, which was corroborated by a linear relation of the fluorescence maxima ($\nu_{max}$) versus the solvent polarity function ($\Delta f$) from the Lippert–Mataga correlation. A comparison between the experimental data and time-dependent density functional theory-polarizable continuum model calculations of the vertical transitions was performed to help on the elucidation of the photophysics of these compounds. For these calculations, the $S_0$ and $S_1$ states were optimized using Becke, three-parameter, Lee–Yang–Parr/6-31 G* and Configuration Interaction Singles/6-31 G*, respectively. The predicted absorption maxima are in good agreement with the experimental; however, the theoretical fluorescence emission maxima do not match the experimental, which means that the excited specie cannot be related to neither a locally excited state nor to an aromatized structure. Copyright © 2012 John Wiley & Sons, Ltd.**
*Supporting information may be found in the online version of this paper.*

**Keywords:** aromatization; charge transfer; fluorescence; Hantzsch; NADH biomimmetics; oxidation photophysics; photophysics; time-dependent density functional theory; UV–Vis absorption; 1,4-dihydropyridines

## INTRODUCTION

The 1,4-dihydropyridines, so called Hantzsch's esters are low molecular weight heterocyclic compounds described more than a century ago.[1] These compounds have been shown a wide-scope of biological activity and present a recognized capacity as calcium channel blockers, thus acting as vital drugs against heart diseases.[2,3] The dihydropyridine moiety (1,4-DHP) is common in many commercialized drugs (Scheme 1). Furthermore, the 1,4-dihydropyridines show other properties such as antioxidant, antiatherosclerosis, bronchodilator, antitumor, antidiabetic and neuroprotector properties, and are promising drugs for Alzheimer's disease treatment.[4] The 1,4-dihydropyridines are also known as biomimetic analogues of the reduced form of nicotinamide adenine dinucleotide (NADH) hydrogen donor coenzyme system, bearing an oxidizable dihydropyridine core-based structure (DHP) connected to a π aromatic ($\pi_{Ar}$) system through an $sp^3$ carbon.[5]

The classical Hantzsch synthesis involves multicomponent one-pot condensation of an aldehyde, ethyl acetoacetate and ammonia under reflux in alcoholic solvent, as presented in Scheme 2.[1,6] It is worth to mention that this methodology is associated with some disadvantages, such as long reaction times, harsh conditions and low product yields. However, because of its medicinal importance, the search for novel derivatives, improved reaction conditions and environmentally beneficial methods have been widely developed.[7–12]

The photochemical oxidation and rearrangement mechanisms of the 1,4-dihydropyridines have already been studied.[13] These antihypertensive drugs, for example Nifedipine, are rapidly metabolized by oxidative mechanisms to dehydro-derivatives in human liver.[14] However, these compounds are highly sensitive to photo-oxidation and its photodegraded products may possess none or little biological activity.[15–17] Nifedipine decomposes in UV light to give the aromatized 4-(2-nitrosophenyl)-pyridine homologue and in presence of oxygen, the nitroso group is reoxidized resulting in the 4-(2-nitrophenyl)pyridine homologue (Scheme 3).[18–20] It is worth to mention that the nitroso product can be related to different biological applications.[21,22]

The photochemical characterization of bioactive molecules is extremely relevant considering the light absorption and consequent modified pharmaco-dynamics, which results in unexpected efficiency of these drugs.[13] Although the fluorescence emission from the DHPs derivatives is well known,[23–26] no agreement

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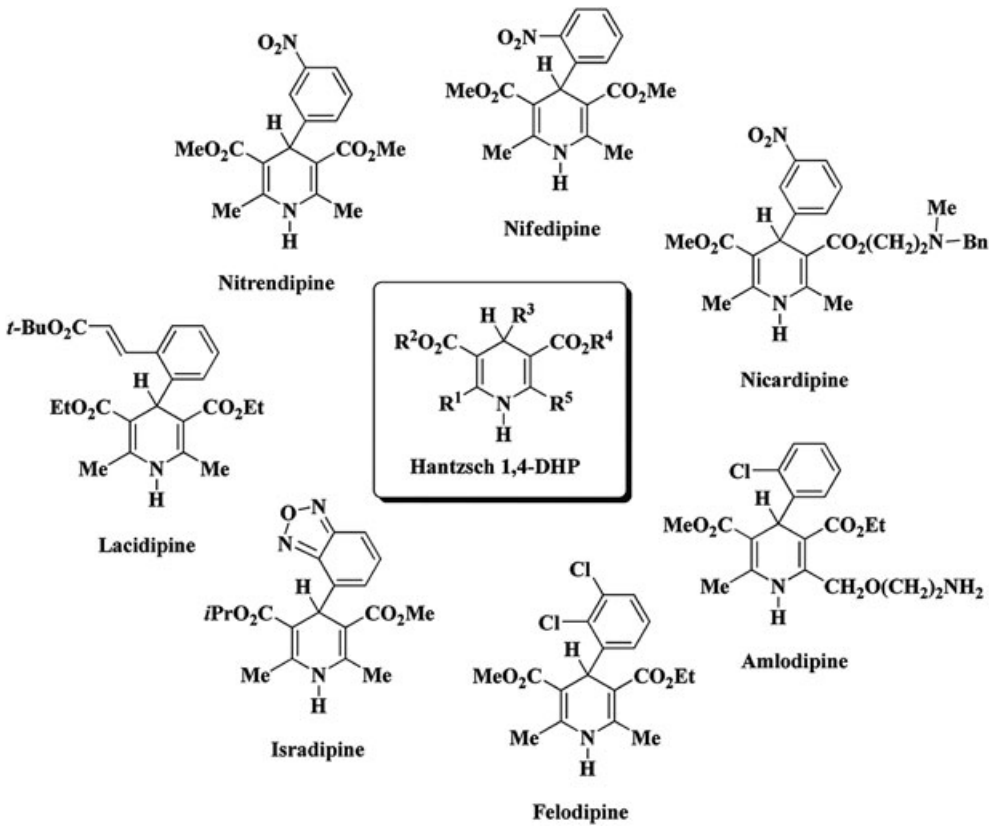
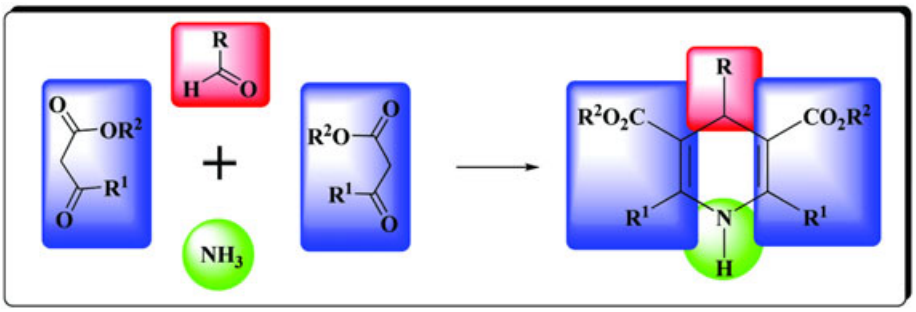
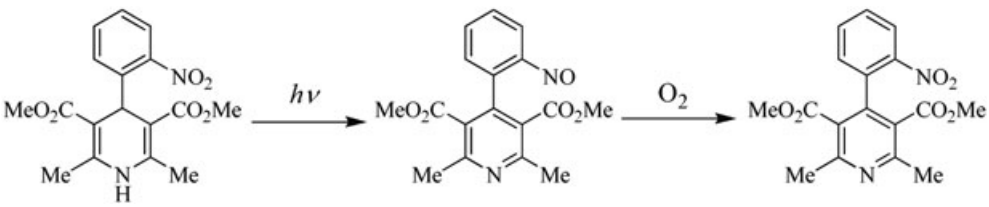



**Scheme 1**. Commercially available Hantzsch 1,4-dihydropyridines



**Scheme 2**. Multicomponent synthesis of 1,4-dihydropyridines




**Scheme 3**. Photochemical oxidation of Nifedipine

can be found about the excited species responsible for their photophysical behaviour. Some authors describe the radiation deactivation from locally excited species, which arise from an irreversible photochemical aromatization of the DHP moiety. On the other hand, several zwitterionic species are described leading to fluorescence emission from a charge transfer mechanism, where the aromatic DHP is not directly involved in the fluorescence emission.[27–30] Recent results indicates that 2-nitrophenyldihydropyridines, such as the well-known Nifedipine and Nisoldipine, present a fast intramolecular electron transfer when UV exposed in a solid matrix, followed by a proton transfer leading to an irreversible zwitterionic intermediate.[27] Therefore, it could be observed that the two chromophores (DHP-$\pi_{Ar}$) of the derivative 3-nitrophenyldihydropyridine presents absorption

end emission independently, where the dihydropyridine decays from a singlet and a triplet state while the 3-nitrophenyl moiety decays by internal conversion.[28] Additionally, Jimenez *et al*.[30] demonstrated by fluorescence and phosphorescence studies that it is possible to excite the DHP-$\pi_{Ar}$ systems independently by choosing an appropriate wavelength as far as these systems interact significantly in the excited state only, where energy and electron transfer are strongly related to the substituent. It could also be observed that the photochemical aromatization of the DHP systems, although inefficient, takes place in the UV exposure of solutions of nitro and chloro-phenyl substituted compounds.[29] Nevertheless, there is no evidence for a reversible aromatization in the system.

In the present work, we dedicate our efforts to synthesize and study alternate substituted dihydropyridines in search for a better understanding of the photophysics of these compounds in the excited state comparing with theoretical studies by computational time-dependent density functional theory-polarizable continuum model (TDDFT-PCM) calculations.

## EXPERIMENTAL

### General information

All chemicals were purchased from commercial sources and used without further purification. The products were purified by column chromatography performed in silica gel (200–400 mesh) with different solvent mixtures (hexane/ethyl acetate) and the reactions were monitored by thin layer chromatography. Nuclear magnetic resonance (NMR) data were recorded with Varian VNMRS (Agilent Technologies, Colorado Springs, Colorado, USA) 300 MHz and 75 MHz spectrometers, for $^{1}$H and $^{13}$C-NMR respectively. Chemical shifts were reported as $\delta$ values (ppm) relative to the internal reference Tetramethylsilane (TMS) peak set at $\delta = 0.0$ ppm ($^{1}$H NMR) and $CDCl_3$ set at $\delta = 77.0$ ppm ($^{13}$C NMR). Coupling constants (*J*) were expressed in Hz. Infrared spectra were obtained as KBR pellets on a Perkin Elmer FTIR Spectrum 1000 (Perkin Elmer, Waltham, Massachusetts/USA), with resolution of 4 $cm^{-1}$ between 400 and 4000 $cm^{-1}$. Melting points were determined with an Olympus BX41 (Olympus Optical do Brasil, Ltda., São Paulo, São Paulo/Brazil) optical microscope and a Mettler Toledo FP-90 F 982 T (Mettler-Toledo Ind. e Com. Ltda., Barueri, São Paulo/Brazil) temperature-controlled furnace. An ultrasound bath Thornton T14 (THORNTON INPEC, Vinhedo, São Paulo/Brazil) of 40 kHz (50 W) was used for the chemical aromatization reaction. Spectroscopic grade solvents dichloromethane, acetonitrile and 1,4-dioxane (Merck) were used in fluorescence emission and UV–Vis absorption spectroscopy measurements. UV–Vis absorption spectra were recorded in a spectrophotometer Shimadzu UV-2450PC (Shimadzu Corporation, Kyoto/Japan). Fluorescence emission and excitation spectra were measured in spectrofluorometer Shimadzu, Model RF-5301PC. Spectrum correction was performed to enable measuring of a true spectrum by eliminating instrumental response such as wavelength characteristics of the monochromator or detector using Rhodamine B as an internal standard (quantum counter). The Lippert–Mataga correlation was performed using DHP solutions of acetonitrile/1,4-dioxane (1:0, 1.0:0.5, 1.0:1.0, 1.0:1.5, 1.0:2.0, 1.0:2.5 v/v).[31,32] All experiments were performed at room temperature in a concentration range of $10^{-6}$ M.

### Synthesis of the 1,4-DHPs

In a 25 mL round-bottom flask were added 2 mmol of the ethyl acetoacetate and 1.0 mmol of the corresponding aldehyde followed by the addition of 2.0 mmol of $NH_4OAc$. The catalyst $In/SiO_2$ (10 mol%) was added in a single portion and the stirring mixture was heated at 100 °C for 30 min until total consumption of the reagents as indicated by TLC (Thin layer chromatography). The crude product was dissolved in ethyl acetate, washed and the organic layer dried over magnesium sulfate. After the filtration, the solvent was then evaporated affording a crude solid product, which was finally purified by column chromatography (ethyl acetate : hexane mixtures).

### Chemical aromatization

The chemical oxidation of the 1,4-DHP diethyl 1,4-dihydro-2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate was performed in a 10 mL round-bottom flask with a solution 1.0 mmol of the 1,4-DHP in 5 mL of MeCN and 2.0 mmols of $I_2$. The mixture was sonicated for 10 min and then refluxed for 5 h. After cooling the reaction mixture, a saturated solution of sodium thiosulfate was added and extracted with dichloromethane (3×10 mL). The organic phase was dried over sodium sulfate and concentrated affording the crude product. The crude product was purified in column chromatography affording the pure pyridine derivative (86%).[33]

### Computational details

Calculations were performed employing the GAUSSIAN 03 (Gaussian, Inc., Wallingford, Connecticut/USA) package.[34] A conformational analysis was carried out at semi-empirical level (Parametric Method 3 parameterization) for the seven DHP derivatives in the ground and $S_1$ state, and for the aromatized structure. This allowed establishing the most stable orientation of the 4,5 substituents, which was used in all subsequent calculations. For the calculation of the vertical transitions, the ground state was further optimized using DFT at Becke, three-parameter, Lee–Yang–Parr (B3LYP)/6-31 G* level, while the excited $S_1$ state was optimized using CIS/6-31 G*. The conformations were also optimized at higher level (DFT and CIS) to confirm the semi-empirical minimum-energy structures. No symmetry restrictions were applied on these optimizations. Franck–Condon transitions were obtained by TDDFT calculations (singlet states only) on the previously minimized structures. Thus, absorption is considered as the TDDFT electronic excitation from the B3LYP/6-31 G* optimized ground state, while fluorescence is taken as the electronic excitation from the ground state, taking the CIS/6-31 G* excited-state optimized geometry. For these calculations, the PBE0 exchange-correlation functional was chosen. PBE0 is a parameter-free, 25% exact exchange-correlation functional, built on Perdew–Burke–Erzenhof pure functional,[35,36] and is known for giving results in good agreement with experimental absorption and fluorescence measurements for a wide variety of chromophores.[37–44] All calculations were performed at 6-31-G + d level. Solvent effects were evaluated by the PCM self-consistent reaction field model. Two nonprotic solvents (dichloromethane and acetonitrile) were chosen, for which experimental spectra are available for comparison.

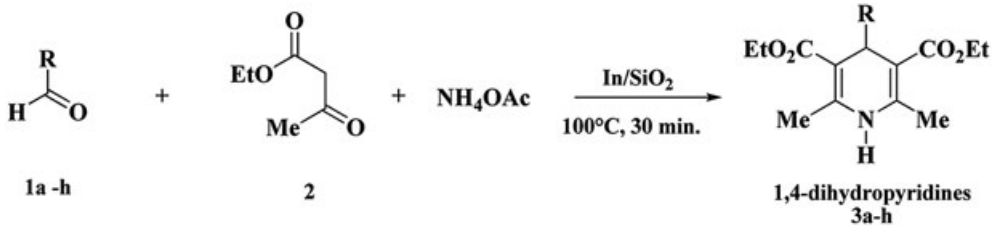
## RESULTS AND DISCUSSION

### Synthesis

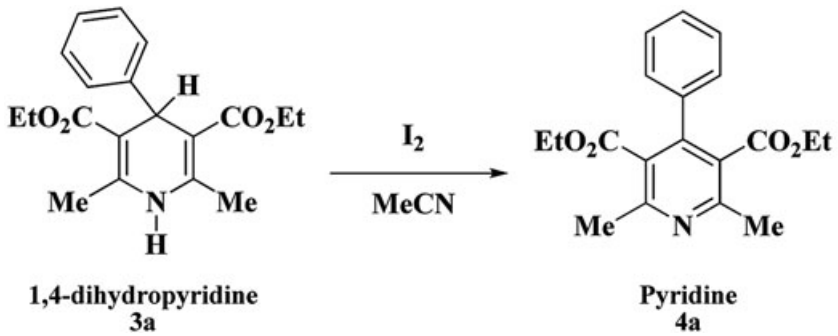
The 1,4-dihydropyridines and the catalyst were synthesized according to the method described in the literature (Scheme 4).[45] The 1,4-dihydropyridines synthesis started with the condensation of an aldehyde (**1a–h**), ethyl acetoacetate (**2a**) and ammonium acetate with $In/SiO_2$ composite as catalyst heated with no solvent at 100 °C affording the desired dihydropyridine (**3a–h**) within 30 min of reaction. We also performed a chemical oxidation of the 1,4-DHP derivative **3a** to afford the aromatized derivative **4a** (Scheme 5).

*Diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3, 5-dicarboxylate **(3a)***

Yield: 75%. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.22 (t, *J* = 17.1, 6H); 2.33 (s, 6H); 4.04–4.13 (m, 4H); 4.99 (s, 1H); 5.64 (bs, 1H); 7.12–7.30 (m, 5H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 14.2; 19.6; 39.6; 59.7; 104.2; 126.1; 127.8; 128.0; 143.8; 147.7; 167.6. IR (KBr, $\upsilon$ = $cm^{-1}$): 3342, 3060, 2982, 1687, 1652, 1488, 1211, 703. M.p.: 154–160 °C.[46]




**Scheme 4**. Synthesis of 1,4-dihydropyridines (**3a–h**) from different aldehydes (**1a–h**), where (a) R = Ph, (b) R = 4-*N*,*N*-$(Me)_2$-$C_6H_4$, (c) R = 4-$NO_2$–$C_6H_4$, (d) R = 4-MeO–$C_6H_4$, (e) R = 3,4-$(MeO)_2$–$C_6H_3$, (f) R = 1-Naphtyl, (g), R = 4-CN–$C_6H_4$ and (h) R = 2-Thiophenyl




**Scheme 5**. Chemical oxidation of 1,4-dihydropyridine **3a** to pyridine **4a**

*Diethyl 2,6-dimethyl-4-(4-N,N-*dimethylaminophenyl)-1, 4-dihydropyridine-3,5-dicarboxylate **(3b)**

Yield: 50%. $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.23 (t, *J* = 7.2 Hz, 6H); 2.26 (s, 6H); 2.86 (s, 6H); 4.04–4.13 (m, 4H); 4.89 (s, 1H); 6.43 (bs, 1H); 6.60 (d, *J* = 8.7 Hz, 2H); 7.15 (d, *J* = 8.7 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.1; 19.1; 38.2; 40.6; 59.4; 103.8; 112.2; 128.4; 136.6; 142.9; 148.8; 167.9. IR (KBr, υ = $cm^{-1}$): 3354, 3095, 2976, 1693, 1652, 1488, 1212. M.p.: 158–162 °C.[47]

*Diethyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3, 5-dicarboxylate **(3c)***

Yield: 78%. $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.22 (t, *J* = 7.2 Hz, 6H); 2.35 (s, 6H); 4.08–4.10 (m, 4H); 5.09 (s, 1H); 5.90 (bs, 1H); 7.45 (d, *J* = 9.0 Hz, 2H); 8.08 (d, *J* = 9.0 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.2; 19.5; 40.1; 59.9; 103.0; 123.2; 128.9; 144.8; 146.2; 155.1; 167.1. IR (KBr, υ = $cm^{-1}$): 3319, 3102, 2978, 1704, 1651, 1519, 1488, 1348, 1212. M.p.: 118–127 °C.[48]

*Diethyl 2,6-dimethyl-4-(4-methoxyphenyl)-1,4-dihydropyridine-3, 5-dicarboxylate **(3d)***

Yield: 62%. $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.23 (t, *J* = 7.2 Hz, 6H); 2.31 (s, 6H); 3.75 (s, 3H); 4.07–4.10 (m, 4H); 4.92 (s, 1H); 5.73 (bs, 1H); 6.74 (d, *J* = 7.5 Hz, 2H); 7.19 (d, *J* = 7.8 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.2; 19.6; 38.7; 55.1; 59.7; 104.3; 113.1; 128.9; 140.3; 143.5; 157.8; 167.7. IR (KBr, υ = $cm^{-1}$): 3342, 3096, 2984, 1690, 1651, 1490, 1211. M.p.: 148–153 °C.[49]

*Diethyl 2,6-dimethyl-4-(3,4-dimethoxyphenyl)-1,4-dihydropyridine-3, 5-dicarboxylate **(3e)***

Yield: 69%. $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.1 Hz, 6H); 2.33 (s, 6H); 3.82 (s, 3H); 3.84 (s, 3H); 4.09–4.122 (m. 4H); 4.94 (s, 1H); 5.81 (bs, 1H); 6.74–6.99 (m, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.4; 19.5; 38.9; 55.7; 59.7; 104.1; 110.7; 111.6; 119.7; 140.7; 143.7; 147.2; 148.0; 167.7. IR (KBr, υ = $cm^{-1}$): 3343, 3096, 2982, 1686, 1651, 1483, 1208. M.p.: 137–145 °C.[50]

*Diethyl 2,6-dimethyl-4-(1-naphthyl)-1,4-dihydropyridine-3, 5-dicarboxylate **(3f)***

Yield: 84%. $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.2 Hz, 6H); 2.33 (s, 6H); 4.09–4.22 (m, 4H); 5.34 (s, 1H); 5.98 (bs, 1H); 6.78–6.85 (m, 2H) 7.05 (d, *J* = 2.4 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.3; 19.4; 34.3; 59.9; 103.4; 123.0; 123.1; 126.3; 144.5; 151.5; 167.3. IR (KBr, υ = $cm^{-1}$): 3373, 3098, 2985, 1679, 1630, 1483, 1200, 793. M. p.: 197–200 °C.[3]

*Diethyl 4-(4-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3, 5-dicarboxylate **(3g)***

Yield: 71%. $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, *J* = 7.2 Hz, 6H); 2.35 (s, 6H); 4.05–4.13 (m, 4H); 5.03 (s, 1H); 6.00 (bs, 1H); 7.39 (d, *J* = 8.4 Hz, 2H) 7.51 (d, *J* = 8.1 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.2; 19.5; 40.4; 59.9; 103.1; 109.6; 119.3; 128.8; 131.8; 144.6; 153.1; 167.1. IR (KBr, υ = $cm^{-1}$): 3344, 3091, 2981, 2228, 1682, 1489, 1214. M.p.: 196–199 °C.[51]

*Diethyl 2,6-dimethyl-4-(2-thiophenyl)-1,4-dihydropyridine-3,5-dicarboxylate **(3h)***

Yield: 77%. $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, *J* = 7.2 Hz, 6H); 2.35 (s, 6H); 4.05–4.13 (m, 4H); 5.03 (s, 1H); 6.00 (broad s, 1H); 6.80–6.79 (m, 1H); 6.84 (dd, *J* = 4.2 Hz and *J* = 3.3 Hz, 1H); 7.05 (dd, *J* = 5.1 Hz and *J* = 1.2 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.3; 19.4; 34.3; 59.9; 103.4; 123.0; 123.1; 126.3; 144.5; 151.5; 167.3. IR (KBr, υ = $cm^{-1}$): 3345, 3098, 2979, 1692, 1658, 1486, 1211, 722. M.p.: 164–168 °C.[46]

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### Photophysical characterization

The photophysical study was performed in dichloromethane and acetonitrile only in the photoactive DHP derivatives and in dichloromethane for the aromatized **3a**. Considering that the DHP bearing an electron-withdrawer nitro group at the *para* position of the aromatic ring (**3c**) showed no visible fluorescence in solid state when irradiated at 365 nm, as its synthesized analogues, it has been excluded from the photophysical study. In the Fig. 1 are presented the normalized UV–Vis absorption spectra of these dyes. The relevant UV–Vis data are summarized in Table 1.

An absorption band maxima ($\lambda_{abs}$) located around 326–352 nm and 331–356 nm, with molar extinction coefficient values ($\varepsilon_{max}$) in agreement with $\pi$–$\pi^*$ transitions, could be observed with the dyes in dichloromethane and acetonitrile, respectively. The difference of the absorption band location in the same solvent can be associated with the different auxochrome groups presented in the DHP moiety. It could also be observed that the absorption maxima in the more polar solvent acetonitrile are red shifted in relation to the spectra in dichloromethane, as expected.

Figure 2 presents the normalized fluorescence emission spectra of these dyes. The curves were obtained using the absorption maxima as the excitation wavelengths. The relevant data are also summarized in Table 1. A fluorescence emission maxima can be observed located at 420 nm in both solvents, with a Stokes shift at around 70 nm. The same red shift can be observed for the DHPs in acetonitrile when compared with the less polar solvent dichloromethane. Because the emission maxima location is not shifted by the substituents (Ph, 4-MeO–$C_6H_4$, 3,4-$(MeO)_2$–$C_6H_3$, 4-CN-$C_6H_4$, 1-Naphthyl and 2-Thiophenyl), which are electronically different, the emission can be attributed to the dihydropyridine chromophore. Furthermore, the observed Stokes shift is plausible to an energy loss in the excited state, which is usually related to internal electron transfer and/or energy transfer character of the corresponding excited state.[29,30]

It is worth mentioning that the DHP **3b** presents a particular photophysical behaviour indicating a higher energy loss in the excited state, which leads to a Stokes shift from 151 to 185 nm, in dichloromethane and acetonitrile, respectively (9710.4 $cm^{-1}$ and 10831.7 $cm^{-1}$, respectively), which concerning the data reported in the literature cannot be related to electron or energy transfer character.[29,30] However, as already observed in similar structures, the photophysical behaviour can be ascribed as a charge transfer from the dimethylaniline to the dihydropyridine moiety.[52] To support the affirmation that intramolecular charge transfer (ICT) state takes place in the excited state of the DHP **3b**, we studied the linear relation of the solvatochromic shifts from the fluorescence and absorption maxima ($\nu_{max}$) versus the solvent polarity function ($\Delta f$) from the well-known Lippert–Mataga correlation.[53,54] In this approach, it is supposed that a point dipole is situated at the center of the spherical cavity and

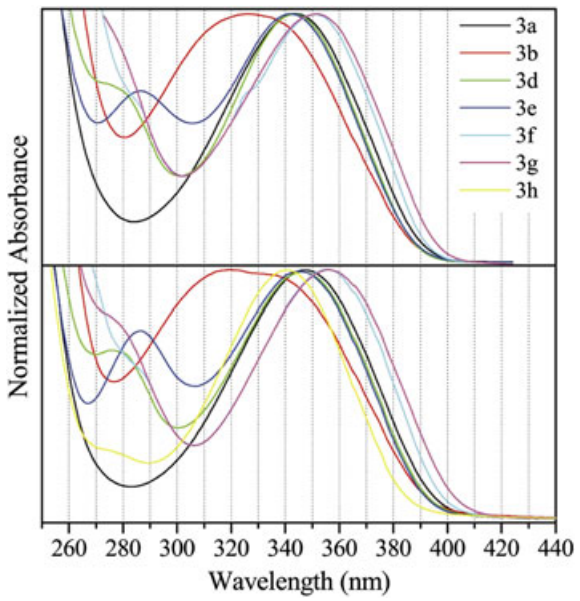


**Figure 1**. Normalized absorption spectra of the photoactive DHPs in dichloromethane (top) and acetonitrile (bottom)

**Table 1.** UV–Vis and fluorescence emission data of the photoactive DHPs

| Solvent | DHP | $\lambda_{abs}$ (nm) | $\varepsilon_{max} \times 10^4$ ($l \cdot mol^{-1} \cdot cm^{-1}$) | $\lambda_{em}$ (nm) | $\Delta\lambda_{ST}$ (nm/$cm^{-1}$) |
|---|---|---|---|---|---|
| $CH_2Cl_2$ | 3a | 344 | 0.50 | 417 | 73/5089.0 |
| | 3b | 326 | 1.44 | 477 | 151/9710.4 |
| | 3d | 343 | 1.15 | 415 | 72/5058.1 |
| | 3e | 342 | 1.10 | 416 | 74/5201.3 |
| | 3f | 351 | 0.94 | 418 | 67/4566.6 |
| | 3g | 352 | 0.50 | 413 | 61/4196.0 |
| | 3h | 338 | 1.38 | 402 | 64/4710.2 |
| $CH_3CN$ | 3a | 347 | 0.97 | 420 | 73/5008.9 |
| | 3b | 331 | 1.11 | 516 | 185/10831.7 |
| | 3d | 347 | 0.90 | 419 | 72/4952.1 |
| | 3e | 344 | 0.97 | 422 | 78/5373.1 |
| | 3f | 356 | 0.88 | 421 | 65/4336.9 |
| | 3g | 356 | 0.94 | 429 | 73/4779.9 |
| | 3h | 340 | 0.75 | 410 | 70/5021.6 |

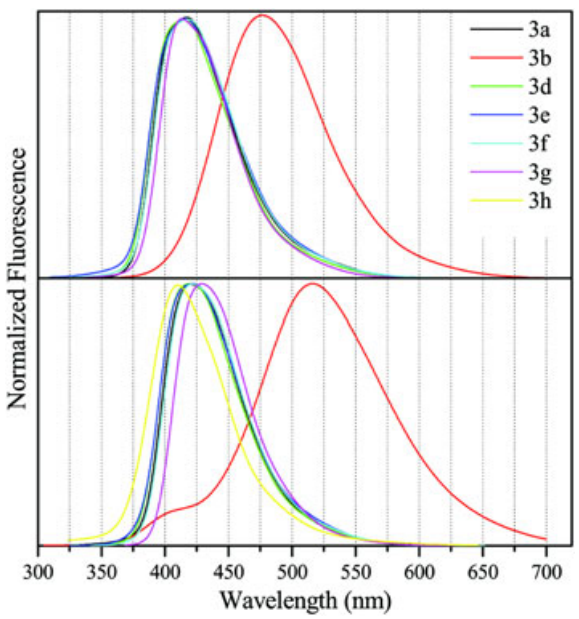


**Figure 2**. Normalized fluorescence emission spectra of the photoactive DHPs in dichloromethane (top) and acetonitrile (bottom)

neglecting the mean solute polarizability (α) in the states involved in the transition (α = $\alpha_e$ = $\alpha_g$ = 0, where e and g stand for excited and ground states, respectively) one obtains[55,56]:

$$hc\nu_{max} = hc\nu_{max}(0) - \left[2\boldsymbol{\mu}_e\left(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g\right)/a^3\right] * \Delta f, \quad (1)$$

$$\Delta f = f(\boldsymbol{\varepsilon}) - (1/2)f(n), \quad (2)$$

$$f(\boldsymbol{\varepsilon}) = (\boldsymbol{\varepsilon} - 1)/(2\boldsymbol{\varepsilon} + 1); \boldsymbol{f}(n) = \left(n^2 - 1\right)\left(2n^2 + 1\right), \quad (3)$$

where $\mu_g$ is the dipole moment of the solute in the ground state, $\nu_{max}$ is the solvent-equilibrated fluorescence maxima and $\nu_{max}$ (0) is the value of spectral position of the fluorescence maxima extrapolated to the gas phase, *a* is the radius of the cavity in which the molecule resides. Because charge transfer states can be more stabilized increasing the solvent polarity, a linear relation of the fluorescence maxima ($\nu_{max}$) versus the solvent polarity function (Δ*f*) indicates the occurrence of the internal charge transfer state. For mixed solvents, as used in this work, the dielectric constant ($\varepsilon_{mix}$) and the refractive index ($n_{mix}$) were calculated as already presented in the literature, where $f_A$ and $f_B$ are the volumetric fractions of the two solvents[31,57]

$$\boldsymbol{\varepsilon}_{mix} = f_A\boldsymbol{\varepsilon}_A + f_B\boldsymbol{\varepsilon}_B \quad (4)$$

$$n^2\text{mix} = f_A n^2{}_A + f_B n^2{}_B \quad (5)$$

Figure 3 shows the solvatochromic shifts from the absorption and fluorescence emission curves versus the solvent polarity function. It is worth mentioning that no linear correlation could be observed for all studied DHPs when the solvatochromic shift is calculated taking into account the absorption maxima ($r^2$ = 0.531, 0.164, 0.645 and 0.296 to **3a**, **3b**, **3d** and **4a** respectively), which indicates that no ICT takes place in the ground state. The same could be observed in the excited state for the DHPs **3a** and **3d**, and even the aromatized **4a**, because the fluorescence emission maxima versus the solvent polarity function could not be fitted by a linear plot ($r^2$ = 0.352, 0.181, 0.674 to **3a**, **3d** and **4a**, respectively). However, the DHP **3b** fits a linear plot ($r^2$ = 0.996), which corroborates to an intramolecular charge transfer mechanism in the excited state, as already described.[55–58] The additional DHPs, and even the aromatized **4a**, could not be fitted by a linear plot ($r^2$ = 0.352, 0.181, 0.674 to **3a**, **3d** and **4a**, respectively).

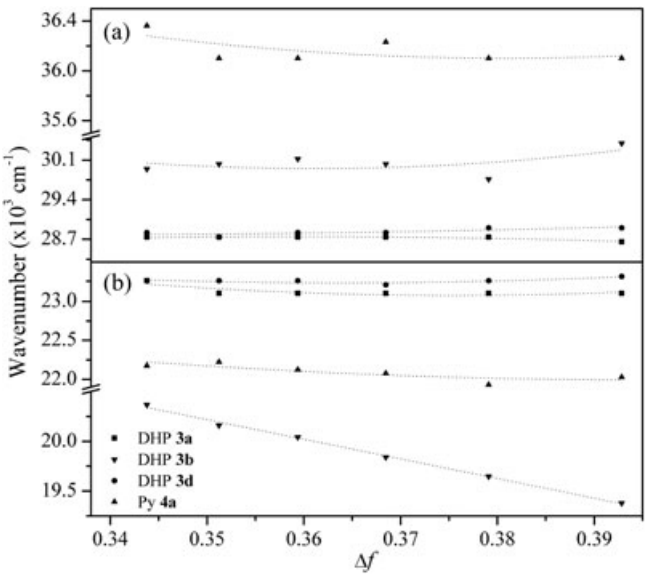


**Figure 3**. Solvent effect on the spectral position of the (a) absorption and (b) fluorescence emission maxima, for the 1,4-dihydropyridines **3a**, **3b**, **3d** and the aromatic **4a**. The Lippert–Mataga solvent polarity function Δ*f* is given in Eqn (2)

To investigate the electronic structure of the excited specie responsible for the fluorescence emission in the DHPs, we also performed a photophysical study in dichloromethane of the DHP **3a** and its synthesized aromatized analogue **4a** (Fig. 4). At this time, this comparison is relevant because several publications indicate irreversible photochemical aromatization of 1,4-dihydropyridines; however, no spectral comparison is found between the reduced and oxidized forms.[27,59,60]

It could be observed that the DHP **3a** absorbs at higher wavelengths (~340 nm) with extinction coefficient ascribed to π–π* transitions. On the other hand, the aromatized **4a** presents an intense absorption band at 270 nm. These absorption spectra are similar to the spectra of NADH/$NAD^+$ system,[61] which indicates that **3a**/**4a** simulate very well the photophysical behaviour of this coenzyme pair. Additionally, the emission spectra can also be useful to discuss the electronic changes between the nonaromatized and aromatized structures, where the **3a** presents an emission located at 420 nm, as expected for a nonaromatized dihydropyridine ring in the NADH. Moreover, it is well known that the oxidized form $NAD^+$ does not present fluorescence emission.[62] The dye **4a** shows fluorescence emission located at 372 nm, which can be probably related to an energy or electron transfer[29,30] between the two aromatic systems, because the pyridine moiety presents a fluorescence emission at 290 nm.[63]

## Theoretical results

To provide a better understanding of the excited state of the studied dihydropyridines, the calculations were performed assuming normal and aromatized forms of the structures, as

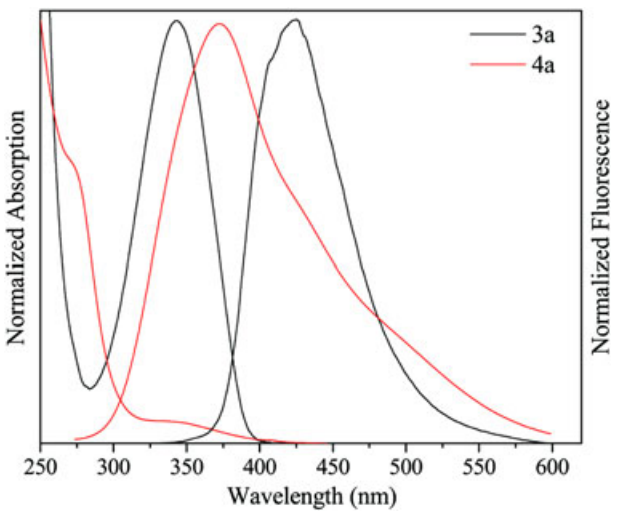


**Figure 4**. Normalized absorption and emission spectra of **3a** and **4a** in dichloromethane

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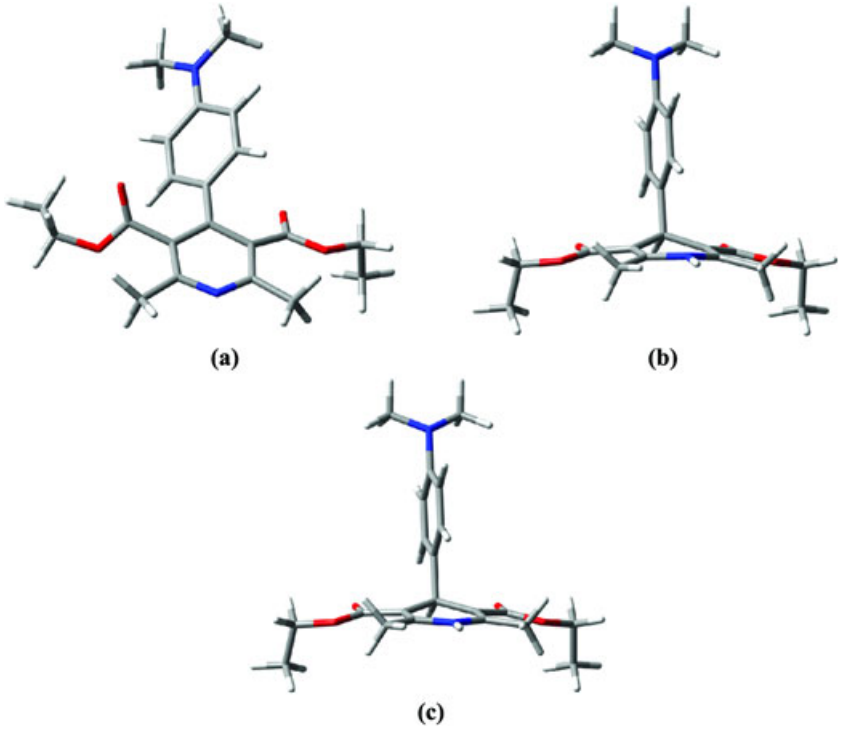


**Figure 5**. DHP derivative **3b** optimized in the excited state $S_1$ for the (a) aromatized and (b) non-aromatized structure at CIS/6-31G* level and (c) in the ground state $S_0$ at B3LYP/6-31G* level.

already discussed. The most stable calculated conformations for the ground and excited state (both normal and aromatized forms) are represented in Fig. 5, for the representative structure **3b**. No significant structural changes were observed for the rest of the series. The most important alteration with the electronic transition is the partial planarization of the pyridine moiety in the excited state. In the aromatized form, the structural changes are more drastic – both rings are forced in a nearly coplanar geometry (full coplanarity is not reached possibly because of the steric hindrance from the carboxyl oxygen). Geometry optimization of aromatized structure DHP **3h** failed to reach a stable minimum, leading to ring opening during calculations.

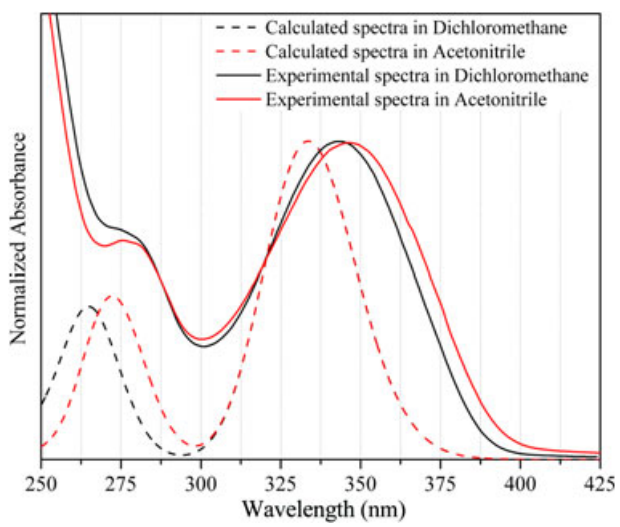


**Figure 6**. Experimental and calculated spectra of DHP **3d**

In accordance with other studies applying the TDDFT/PBE0 approach on chromophores presenting large Stokes shifts[42–44] the absorption wavelengths are remarkably well matched by calculated transitions, where an average absolute deviation of 10.7 nm for the whole series could be obtained. Figure 6 shows a comparison between experimental and calculated absorption spectra of a representative structure, convoluted using SWizard program, revision 5.6.[64,65]

The TDDFT formalism[66–79] has proven to be a useful method for an accurate prediction of electronic absorption energies,[80–87]

**Table 2.** B3LYP/6-31*G(d) and PBE0/6-31*G(d) TDDFT-PCM calculated transition maxima of 1,4-DHPs

| Solvent | DHP | λabs (nm) | | λem (nm) | |
|---|---|---|---|---|---|
| | | Exp. | Calc. | Exp. | Calc. (normal/aromatized) |
| $CH_2Cl_2$ | **3a** | 344 | 334 | 417 | 410/380 |
| | **3b** | 326 | 332 | 477 | 333/438 |
| | **3d** | 343 | 332 | 415 | 333/402 |
| | **3e** | 342 | 333 | 416 | 332/416 |
| | **3f** | 351 | 327 | 418 | 341/355 |
| | **3g** | 352 | 347 | 413 | 344/353 |
| | **3h** | 338 | 331 | 402 | 332/– |
| $CH_3CN$ | **3a** | 347 | 335 | 420 | 410/381 |
| | **3b** | 331 | 334 | 516 | 334/438 |
| | **3d** | 347 | 333 | 419 | 334/410 |
| | **3e** | 344 | 334 | 422 | 333/396 |
| | **3f** | 356 | 328 | 421 | 343/355 |
| | **3g** | 356 | 350 | 429 | 347/352 |
| | **3h** | 340 | 333 | 410 | 334/– |

but not so accurate concerning emission processes.[42–44] In this work, the calculated fluorescence emission maxima from normal or aromatized species do not match with the experimental data (Table 2). It has to be remarked that the geometry optimization of the structures in the ground and excited states were performed with different formalisms (HF and CIS), to which the large differences in average errors between experimental and calculated wavelengths for absorption and emission can be attributed, and have been observed in other similar studies.[43] For this series, the calculated normal fluorescence wavelengths are practically not redshifted with respect to the absorption values (Table 2), excepting the DHP **3a**, indicating that the applied methodology works well to non-substituted 4-aryl-DHPs. The obtained calculated fluorescence spectra indicates that the theoretical model does not fit very well the emission maxima location when energy or electron transfer processes take place in the excited state, ruling out a normal fluorescence relaxation process.[88] The theoretical method also seems to be unable to predict the emission maxima for structures with intramolecular charge transfer in the excited state, as observed to the DHP **3b**.

Although the calculated transitions for most of the aromatized structures fall closer to the experimental values than the normal structure one (Table 2), a comparison between normal and aromatized excited state energy minima shows that the aromatized form is less stable in all the compounds studied (see Table S1). Further investigations are currently being carried out employing TDDFT to optimized the excited state as well, which is known to provide better results for the fluorescence emission.[41,42]

## CONCLUSIONS

A series of 4-aryl substituted dihydropyridines were synthesized and characterized. These dyes present absorption maxima in the UV and fluorescence emission in the blue–green region. The observed emission maxima location was not shifted by the electronically different substituents, indicating that the emission is due to the dihydropyridine chromophore. The Stokes shift is reasonable for an energy loss in the excited state related to the DHP moiety. The *N,N*-dimethylamino substituted dihydropyridine **3b** presented a redshifted emission band ascribed to an ICT state between the DHP-Aryl chromophores. The ICT state in this DHP was confirmed by a linear relation of the fluorescence maxima versus the solvent polarity function from the Lippert–Mataga correlation. It was also observed that aromatization of the 1,4-DHPs does not takes place on measuring irradiation conditions by comparing spectral data from normal (**3a**) and oxidized derivative (**4a**). The electronic transitions were investigated by computational method TDDFT-PCM and show a good agreement with the experimental absorption UV–Vis spectra, although the fluorescence emission theoretical results do not match the experimental, meaning that the excited specie cannot be related to a locally excited state neither to an aromatized structure. Further investigations are under way employing a different methodology for the excited states optimization.

## SUPPORTING INFORMATION

Theorethical Data from $S_1$ state SCF energy from the DHPs and their aromatized analogues, the DHPs Cartesian Geometries and the Data from the calculated spectra of DHPs.

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