

Comparative theoretical study of the UV/Vis absorption spectra of styrylpyridine compounds using TD-DFT calculations

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Abstract This study examined absorption properties of 2-styrylpyridine, *trans*-2-(*m*-cyanostyryl)pyridine, *trans*-2-[3-methyl-(*m*-cyanostyryl)]pyridine, and *trans*-4-(*m*-cyanostyryl)pyridine compounds based on theoretical UV/Vis spectra, with comparisons between time-dependent density functional theory (TD-DFT) using B3LYP, PBE0, and LC- ω PBE functionals. Basis sets 6–31G(d), 6–31G(d,p), 6–31+G(d,p), and 6–311+G(d,p) were tested to compare molecular orbital energy values, gap energies, and maxima absorption wavelengths. UV/Vis spectra were calculated from fully optimized geometry in B3LYP/6–311+G(d,p) in gas phase and using the IEFPCM model. B3LYP/6–311+G(d,p) provided the most stable form, a planar structure with parameters close to 2-styrylpyridine X-ray data. Isomeric structures were evaluated by full geometry optimization using the same theory level. Similar energetic values were found: $\sim 4.5 \text{ kJ mol}^{-1}$ for 2-styrylpyridine and $\sim 1 \text{ kJ mol}^{-1}$ for derivative compound isomers. The 2-styrylpyridine isomeric structure differed at the pyridine group *N*-atom position; structures considered for the other compounds had the

cyano group attached to the phenyl ring *m*-position equivalent. The energy difference was almost negligible between *m*-cyano-substituted molecules, but high energy barriers existed for cyano-substituted phenyl ring torsion. TD-DFT appeared to be robust and accurate approach. The B3LYP functional with the 6–31G(d) basis set produced the most reliable λ_{max} values, with mean errors of 0.5 and 12 nm respect to experimental values, in gas and solution, respectively. The present data describes effects on the λ_{max} changes in the UV/Vis absorption spectra of the electron acceptor cyano substituent on the phenyl ring, the electron donor methyl substituent, and the *N*-atom position on the electron acceptor pyridine ring, causing slight changes respect to the 2-styrylpyridine title compound.

Keywords Absorption maxima · Frontier molecular orbitals · TD-DFT calculations

Introduction

For a long time, polymers, oligomeric organic dyes, and low molecular weight compounds with optical or electrical properties have been widely used in organic materials with electro-optical applications. Such applications have demonstrated the importance of further studying structures showing strong π -electron conjugation, i.e., with electron delocalization. In order to understand the relationship between structure and optical properties, and the influence of the substituent groups on the absorption and emission characteristics of these materials, model compounds of low molecular weight have been investigated both experimentally and theoretically. In particular, low molecular weight structures containing electron donor and acceptor groups have been analyzed.

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Styrylpyridines and stilbazoles are experimentally obtained by a typical condensation reaction of methylpyridines with aromatic aldehydes [1–7] using different catalysts, as well as under catalyst- and solvent-free conditions [8–10]. The latter method resulted in obtaining crystals that were good enough to determine the crystalline structure and characteristics [8–10]. Several styrylpyridines, such as 2-styrylpyridine, 4-styrylpyridine, 2,6-distyrylpyridine, and some derivatives of these molecules, have been synthesized and characterized experimentally [8–11] as well as studied by theoretical calculations [12–14].

To evaluate the effects of substituents on the electronic properties of these compounds, absorption and fluorescence emission spectra have been recorded and compared [10, 15–18]. Percino et al. [10] evaluated the effects of terminal –Cl and –F substituents in the *para*-position of the phenyl ring on the absorption spectra of 2-styrylpyridine; however, no shift of the maximum absorption wavelength occurred with the presence of the halogen with respect to the λ_{\max} of non-substituted 2-styrylpyridine. Lewis and Weigel [15] analyzed the absorption and fluorescence spectra of cyanoaminostilbenes to identify the effects of the cyano; they found important solvatochromic shifts and *meta*-amino effects. Pinto et al. [16] found a more pronounced red shift and higher electroluminescence efficiency in distyrylbenzene copolymers with the cyano group attached to the aromatic ring. Another study examined a series of copolymers of cyano-containing distyrylbenzenes to determine the effect of cyano and dicyanovinyl groups [17]. A longer λ_{\max} was found for the polymer with a more planar structure, and introduction of the dicyanovinyl groups into the polymer main chain resulted in a lower wavelength value for the higher energy absorption peak than those observed for cyano-substituted copolymers. In a series of alkoxy-cyano-substituted diphenylbutadienes [18], the absorption spectra were insensitive to the number and length of the alkoxy substituents; only a cyano group attached in the *para*-position on the phenyl ring affected the absorption spectra.

The time-dependent density functional theory (TD-DFT) [19–23] has been widely used by different authors for calculations of excitation energies and oscillator strengths for organic systems involving interesting optical properties [24–36]. In a series of comparative studies on the use of different functionals with the TD-DFT methodology [32–35], calculated λ_{\max} values closest to experimental values were generally obtained with the functionals PBE0, M05-2X, and M06-2X, and the long-range corrected hybrid functionals CAMB3LYP, LC-PBE, and LC- ω PBE in the analysis of a large set of organic dyes, azobenzenes, anthraquinones, indigoids, coumarins, diarylethenes, and other compounds. Another study of the TD-DFT using several functionals was performed based on comparison with a CASPT2 *ab initio* approach in prototype organic molecules

[36]. Here, the results obtained using B3LYP and PBE0 functionals gave results close to those obtained by CASPT2 for small systems, providing a qualitatively good description of the excitation energies, excited states structures, and their properties. No significant differences in accuracy have been found between the absorption spectra results using B3LYP or PBE0 [36].

When performing calculations to be compared with experimental results such as UV spectra, it is also important to consider the solvation effects. For this, the continuum methods are most commonly used because of the relative simplicity and consistency of their physical foundations [37]. The integral equation formalism polarizable continuum model (PCM) [38], in which the electrostatic interaction between the solute and the solvent is described in terms of a surface charge spread on a cavity of molecular shape, has been shown to be a reliable method for including the solvent effect in this kind of system [30, 39, 40].

The present study is a theoretical comparative investigation of the frontier molecular orbitals energies, gap energies, and the UV/Vis maxima absorption wavelengths (λ_{\max}) of 2-styrylpyridine and three model styrylpyridine-like compounds: *trans*-2-(*m*-cyanostyryl)pyridine, *trans*-2-[3-methyl-(*m*-cyanostyryl)]pyridine, and *trans*-4-(*m*-cyanostyryl)pyridine, using density functional theory calculations. These compounds contain a pyridine ring and a cyano group substituted in the *meta* position of the phenyl ring, with the two rings joined by a double bond (CH=CH) in the *trans* conformation. One of the analyzed compounds has a methyl group in the pyridine ring and was included in order to evaluate its inductive effect in the system (Fig. 1).

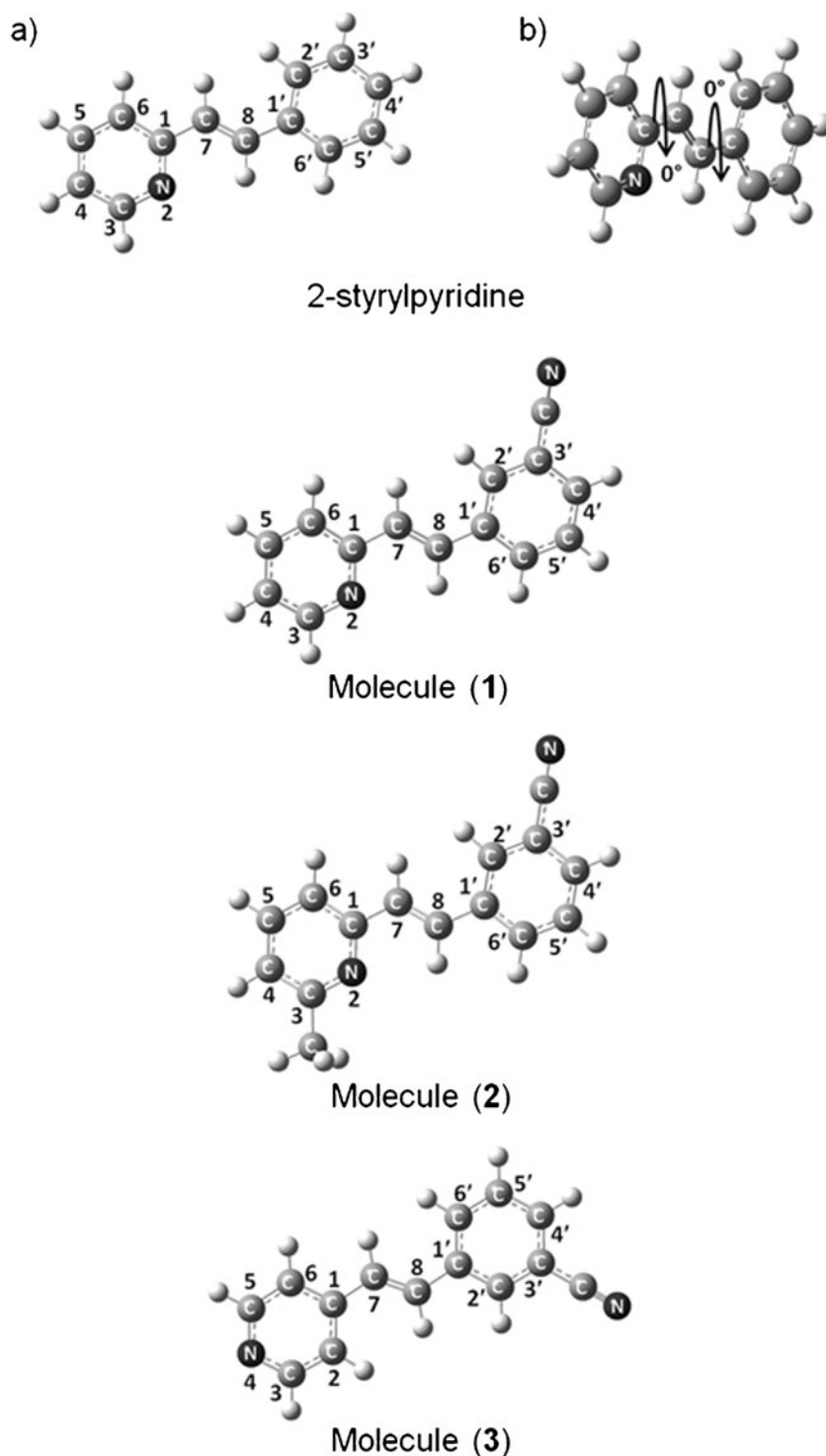
These recently synthesized compounds in our lab might come in useful as model compounds for the complete characterization of their electronic properties known in stilbene-like and styrylpyridine-like compounds as possible potential organic materials to be used in opto-electronic devices [41].

The theoretical results using TD-DFT methods with the B3LYP [42], PBE0 [43], and LC- ω PBE [44] functionals were compared, as well as the results using different basis sets, including polarization and diffuse functions. The theoretical calculations were used to investigate the influence of the strong electron-withdrawing cyano group (–C \equiv N) as a substituent on the phenyl ring of the styrylpyridine-like compounds, as well as the position of the *N* atom and of the electron donor (–CH₃) in the pyridine ring.

Methods

Figure 1 presents the chemical structures and numerical conventions used for the molecules *trans*-2-(*m*-cyanostyryl)pyridine (**1**), *trans*-2-[3-methyl-(*m*-cyanostyryl)]pyridine (**2**) and *trans*-4-(*m*'-cyanostyryl)pyridine (**3**). Calculations were

Fig. 1 Optimized molecular structures and numerical conventions of *trans*-2-(*m*-cyanostyryl)pyridine (**1**), *trans*-2-[3-methyl-(*m*-cyanostyryl)]pyridine (**2**), and *trans*-4-(*m*-cyanostyryl)pyridine (**3**)



carried out for four structures—molecules (**1–3**) and 2-styrylpyridine for the sake of comparison. The calculations were performed in two steps:

(i) The geometries of the ground-state were optimized using DFT calculations with the B3LYP functional [42] and three different basis sets: 6–31G(d) [45], 6–

31+G(d,p) [46], and 6–311+G(d,p) [47] in gas-phase and in solution, including the solvent CHCl_3 effect using the PCM model [38].

(ii) The frontier molecular orbital energies, gap energies, and vertical electronic excitation energies were determined using TD-DFT [48] in both phases from B3LYP/6–311+G(d,p) optimized geometries.

Several different functionals involving exchange and correlation terms (XC) have recently been proposed. These include a group of gradient-corrected functionals for general gradient approximation (GGA), as well as a group corresponding to the hybrid functionals, including a fraction of exact exchange, i.e., Hartree-Fock (HF) exchange. In the B3LYP functional used in this study, the exchange was a combination of 20 % HF exchange, Slater functional, and Becke's GGA correction; the correlation part combined Vosko, Wilk, Nusair, and LYP functionals. The PBE1PBE (named PBE0) reflects the mix of 25 % HF and 75 % of DFT exchange represented by the PBE functional [43], whereas PBE represents 100 % of the correlation part [49]. In addition, a functional including long-range corrections was used as the long-range corrected version of ω PBE. The LC scheme explicitly incorporates the long-range orbital-orbital interaction part in the exchange functional by combining with the HF exchange integral. The long-range corrected hybrid LC- ω PBE involves a single empirical parameter $\mu=0.4$ bohr⁻¹ in the HF exchange integral. The advantage of LC- ω PBE over other global hybrid functionals is the exact asymptote of the exchange potential; however, this scheme worsens the accuracy of the excitation energies [44].

UV/Vis spectra of styrylpyridine compounds are determined in solution and can be affected by the solvation effects. Therefore, the PCM model can be used, where the problem is divided into a solute component (2-styrylpyridine and molecules (1–3)) lying inside a cavity and a solvent component (chloroform, in our case) represented as a structure-less material, characterized by its dielectric constant and other parameters. The PCM model is now often used for many electronic properties, including excited states, due to its low computational cost compared to gas phase calculations.

Once the UV/Vis spectra were successively evaluated using TD-DFT scheme with the B3LYP, PBE0, and LC- ω PBE functionals, the results were compared between them using different basis sets—including polarization, 6-31G(d) and 6-31G(d,p), and diffuse functions, 6-31+G(d,p) and 6-311+G(d,p). The Gaussian 09 package [50] was used for calculating the geometry optimizations and the UV/Vis spectra in gas-phase and in solution.

Results and discussion

Molecular structures

We obtained optimized geometries for 2-styrylpyridine and the three derivatives (model compounds (1–3) shown in Fig. 1) using the B3LYP method with the 6-31G(d), 6-31+G(d,p), and 6-311+G(d,p) basis sets. To validate the

theory level used, we calculated selected optimized parameters in gas phase and those including the solvent CHCl₃ effect for 2-styrylpyridine, and compared these with X-ray data [8]. The molecular structure of the title compound has the phenyl ring located *trans* to the pyridine ring in relation to the double bond (Fig. 1a) and shows a planar structure as is shown in the side view (Fig. 1b) with torsional angles of 0° for both substituent rings. X-ray data showed values of the bonds C(1)–C(7), C(8)–C(1'), and C(7)–C(8) to be 1.486, 1.462, and 1.321 Å, respectively; these typical double-bond values did not indicate delocalization of the π electrons of the two six-membered rings through the C(7)–C(8) bond, but a localization of the π electrons over determined bonds across the rings [8].

Table 1 summarizes selected parameters of 2-styrylpyridine, as well as the root-mean-square errors of the calculated geometric parameters with respect to X-ray data for internuclear distances, valence angles, and dihedral angles in gas and solution phases. The root-mean-square error, $\sigma_{\text{parameters}}$, is defined as $(\sum \Delta(\text{value}_{\text{teo}} - \text{value}_{\text{X-ray}})^2/n)^{1/2}$, where n is the number of considered parameters.

We found very similar values of σ_{bond} with the three different basis sets in both gas and solution phases, while the σ_{valence} values indicated an improvement when using the 6-311+G(d,p) basis set in gas phase. With respect to σ_{dihedral} , the best value in the gas phase was obtained with the 6-311+G(d,p) basis set, while in solution phase, the σ_{dihedral} value in the same theory level was slightly larger than that obtained using 6-31G(d). Since the B3LYP/6-311+G(d,p) theory level provided the lowest σ_{valence} and σ_{dihedral} in gas phase, the optimized geometries calculated in this theory level were used for calculating the frontier molecular orbital energies, gap energies, and UV/Vis spectra.

Table 2 summarizes selected parameters obtained at the B3LYP/6-311+G(d,p) theory level for molecules (1–3). We did not observe important changes in the internuclear distances between the three molecules. The central double bond C(7)–C(8), and the single bonds C(7)–C(1) and C(8)–C(1') remained constant between the three structures. The C–N distances in C(3)–N(2) showed similar values in the pyridine ring in molecules with the *N*-atom in position 2 (molecules 1 and 2), which were also similar to the C–N distance in N(4)–C(3) when the *N*-atom is in position 4 (molecule 3) (Fig. 1). The valence angles between atoms C(2)–C(1)–C(7) for molecules (1) and (2) were slightly smaller than for molecule (3), suggesting a stabilizing effect between the H atom and the electron pair of the *N*-atom of the pyridine ring in molecules (1) and (2). In addition, the valence angle for C(1)–C(7)–C(8) was $\sim 2^\circ$ larger for molecule (3) than for molecules (1) and (2). All three molecules showed a planar structure between the pyridine ring and the cyano-substituted phenyl, as was clearly indicated by the

Table 1 Experimental and theoretical B3LYP selected structural parameters of the equilibrium structure of 2-styrylpyridine. The numbering convention is shown in Fig. 1. Internuclear distances in (Å), and valence and dihedral angles in (°)

Parameter	X-ray data ^a	6-31G(d)		6-31+G(d,p)		6-311+G(d,p)	
		Gas	PCM	Gas	PCM	Gas	PCM
7-8	1.321	1.348	1.349	1.349	1.350	1.345	1.345
7-1	1.486	1.466	1.467	1.467	1.468	1.466	1.466
8-1'	1.462	1.464	1.464	1.466	1.466	1.464	1.465
4-3	1.397	1.398	1.398	1.400	1.399	1.396	1.396
3-2	1.335	1.332	1.334	1.334	1.336	1.330	1.332
2-1	1.373	1.351	1.352	1.351	1.353	1.348	1.349
1-7-8	125.7	124.0	124.3	124.2	124.6	124.2	124.5
2-1-7	120.5	118.4	118.5	118.7	118.9	118.7	118.8
7-8-1'	125.2	127.5	127.4	127.4	127.3	127.4	127.3
2-1-7-8	2.1	0.1	0.0	0.0	0.0	0.0	0.0
1-7-8-1'	-177.0	-180.0	-180.0	-180.0	-180.0	-180.0	-180.0
7-8-1'-2'	-4.9	0.0	0.0	-0.1	0.0	-0.3	-0.1
σ_{bond}		0.031	0.032	0.032	0.032	0.030	0.031
σ_{valence}		2.577	2.548	2.514	2.492	2.362	2.505
σ_{dihedral}		3.423	3.434	3.429	3.435	3.409	3.429

^aReference [8]

values of the dihedral angles between C(2)–C(1)–C(7)–C(8) and C(7)–C(8)–C(1')–C(2') (Table 2). No important differences were found between gas phase values and those with solvent effects for the three molecules.

Tests of geometry optimization for isomeric structures revealed interesting facts about the four molecules. The isomer of 2-styrylpyridine included the N atom in position 6 instead of position 2 (Fig. 1), and was obtained by using a

torsion angle formed between atoms C(2)–C(1)–C(7)–C(8). For model compounds (1–3), the structures considered were those with the -CN group attached to the phenyl ring in the *m'*-position, or at C(5') instead of C(3') (Fig. 1), using the torsion motion through the C(7)–C(8)–C(1')–C(2') dihedral angle. The calculations for the isomers were performed using the same theory levels used for 2-styrylpyridine and molecules (1–3): the B3LYP method with the 6-31G(d), 6-

Table 2 Theoretical selected structural parameters calculated using B3LYP/6-311G(d,p) of the equilibrium structure of the styrylpyridine-like compounds (1–3). The numbering convention is shown in Fig. 1. Internuclear distances in (Å), and valence and dihedral angles in (°)

Parameter	Molecule (1)		Molecule (2)		Molecule (3)	
	Gas	PCM	Gas	PCM	Gas	PCM
7-8	1.344	1.344	1.344	1.344	1.344	1.345
7-1	1.467	1.467	1.468	1.468	1.465	1.465
8-1'	1.465	1.465	1.464	1.465	1.466	1.466
4-3	1.397	1.397	1.339	1.402	1.335	1.338
3-2	1.330	1.332	1.335	1.337	1.392	1.391
2-1	1.347	1.349	1.346	1.346	1.402	1.403
3'-C	1.433	1.432	1.432	1.432	1.432	1.431
C≡N	1.156	1.156	1.155	1.156	1.155	1.156
1-7-8	124.1	124.5	124.1	124.5	126.5	126.1
2-1-7	118.5	118.7	118.4	118.7	119.3	119.3
7-8-1'	127.1	127.0	127.2	127.0	126.9	126.7
2'-3'-C	119.6	119.5	119.6	119.5	119.7	119.6
3'-C≡N	180.0	179.9	179.9	179.9	179.9	179.9
2-1-7-8	-0.1	0.0	-0.4	-0.1	-0.6	-3.1
1-7-8-1'	-180.0	180.0	180.0	-180.0	-180.0	180.0
7-8-1'-2'	0.4	0.3	0.7	-0.2	179.2	176.6
1'-2'-3'-C	-180.0	-180.0	-180.0	-180.0	180.0	179.9
C-3-2-1	-	-	-179.9	-180.0	-	-

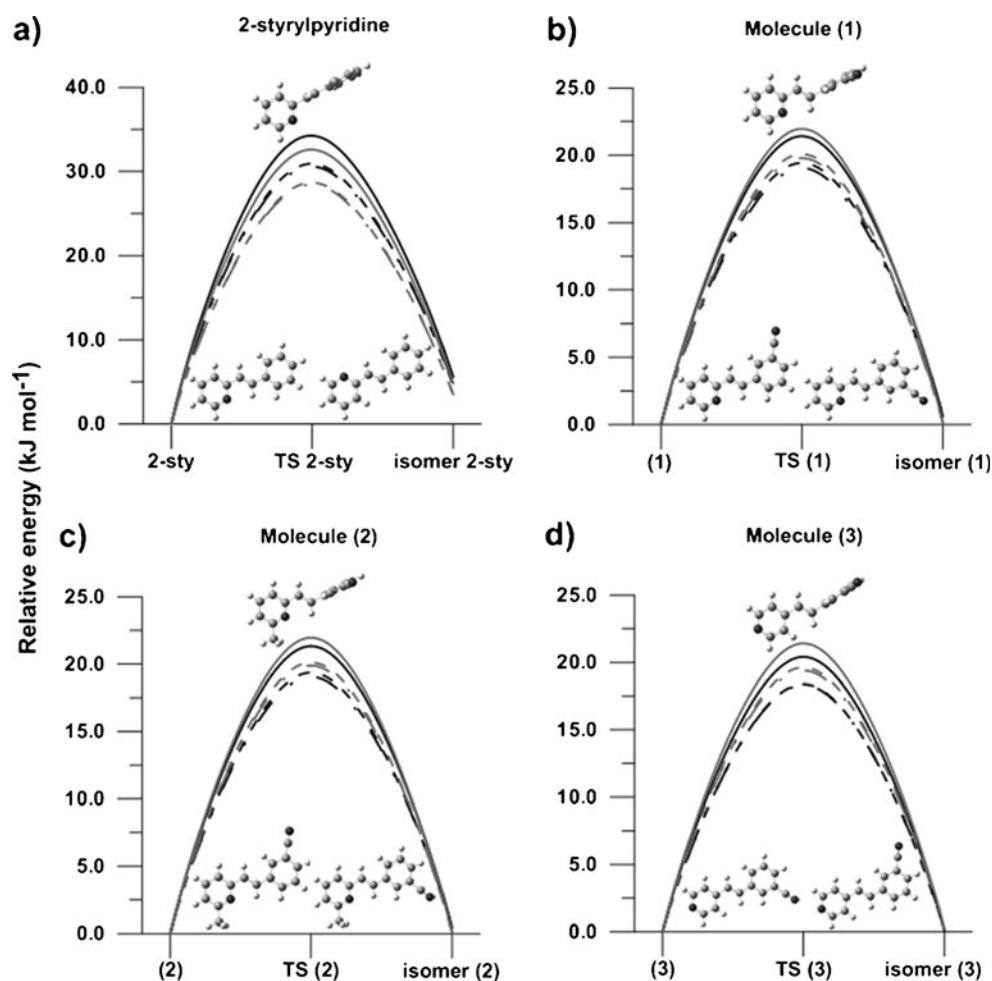
31+G(d,p), and 6–311+G(d,p) basis sets in gas and solution phases. For 2-styrylpyridine (2-sty in Fig. 2a), its isomer (isomer 2-sty) had an energy in the range of 4.536–5.561 kJ mol⁻¹, with a relatively more stable conformer in the three theory levels. The isomers of molecules (1–3) showed energy values close to each other (differing by less than 1 kJ mol⁻¹) in the three theory levels. For the molecules (1) and (2), the structures with the -CN group attached in *m*- or C(3') position of the phenyl ring (Fig. 1) were more stable than their respective isomers (isomer (1) and isomer (2) in Fig. 2b and c). However, for molecule (3), the *m'*-position phenyl substituted compound was energetically more stable than its respective isomer (isomer (3) in Fig. 2d).

The difference in energy was almost negligible between *m*- and *m'*-cyano-substituted molecules (1–3). However, high energy barriers were found for the torsion through the dihedral angle C(7)–C(8)–C(1')–C(2') between the two isomers for (1), (2), and (3), respectively, within the ranges of 0.574–0.596, 0.313–0.463, and 0.042–0.197 kJ mol⁻¹ in gas phase, and 0.083–0.096, 0.036–0.113, and 0.203–0.222 kJ mol⁻¹ in solution phase. Figure 2 shows the relative energies and energy barriers for the torsion through the dihedral C

(2)–C(1)–C(7)–C(8) for 2-styrylpyridine and C(7)–C(8)–C(1')–C(2') for molecules (1–3) and their respective isomers. In general, for the four molecules, the energy barriers decreased when the basis size was increased; the smallest energy barrier values were found by using the B3LYP/6–311G+(d,p) level as gas phase and including PCM contribution. For 2-styrylpyridine, the energy barriers decreased when the solvent effect was taken into account, while for molecules (1–3), the barriers calculated in gas phase were smaller.

The importance of the evaluation of these isomers, between several possible isomers, is due to the *trans*-styrylpyridines compounds present a high conformational flexibility through single bonds linking the substituent rings to the central double bond (Figs. 1 and 2). Theoretically two more stable isomers with energies very close were found, while two structural isomers substituted in equivalent *meta*-position (C(3') or C(5')) in Fig. 1 are difficult to recognize using experimental spectroscopic characterization. In addition, the population of isomers was obtained as a function of the dihedral torsional angles mentioned above for 2-styrylpyridine and molecules (1–3) and of potential energy

Fig. 2 Energy barriers for the torsion through the dihedral angle C(2)–C(1)–C(7)–C(8) for 2-styrylpyridine, and C(7)–C(8)–C(1')–C(2') for molecules (1–3) and their respective isomers using B3LYP with 6–31G(d) (solid line), 6–31+G(d,p) (dash line), and 6–311G+(d,p) (dash dot line) basis sets in gas phase (black line) and including solvent effect (gray line)



function. This model is based on a semiclassical conformational partition function defined for the overall rotation and the conformational motions [51]. For all cases, the calculated population (in %) at room temperature were larger for the 2-styrylpyridine and molecules (1–3) than their respective isomers in Fig. 2. Values of 17.0 and 2.57 % were obtained for 2-sty and isomer 2-sty, respectively, in gas phase, while in solution values of 14.7 and 3.6 % were found, respectively. For molecules (1–3) the difference between the values of population respect to their isomers (isomer (1), (2) and (3)) are smaller. In gas phase, 6.9, 6.8, and 6.2 % were calculated for (1–3), while 5.5, 5.6 and 5.8 % were obtained for their isomers, respectively. In solution phase, values of 6.6, 6.7 and 6.7 % were calculated for (1–3) and 6.4, 6.4 and 6.0 % for their respective isomers. With these results, another theoretical criterion to evaluate the more stables isomers was taken into consideration for calculating the molecular orbitals, gap energies and maxima absorption wavelength values.

Molecular orbitals

The energies of the main molecular orbitals, HOMO, HOMO-1, LUMO, and LUMO+1, were calculated using TD/DFT methods with the different basis sets, including polarization and diffuse functions, 6–31G(d), 6–31G(d,p), 6–31+G(d,p), and 6–311+G(d,p) in gas and solution phases. Three functionals were tested in the TD/DFT methodology, B3LYP, PBE0, and LC- ω PBE, with the above-mentioned basis sets. The theoretical gap energy was estimated as $\Delta E = \varepsilon_{LUMO} - \varepsilon_{HOMO}$.

All calculations were carried out from the B3LYP/6–311+G(d,p) optimized geometries for the four molecules, as described above in the Molecular structures section. Figure 3 shows the main molecular orbitals (HOMO-1, HOMO, LUMO, LUMO+1) and gap energies for 2-styrylpyridine and molecules (1–3) for each method in gas and including the solvent effect using the PCM model.

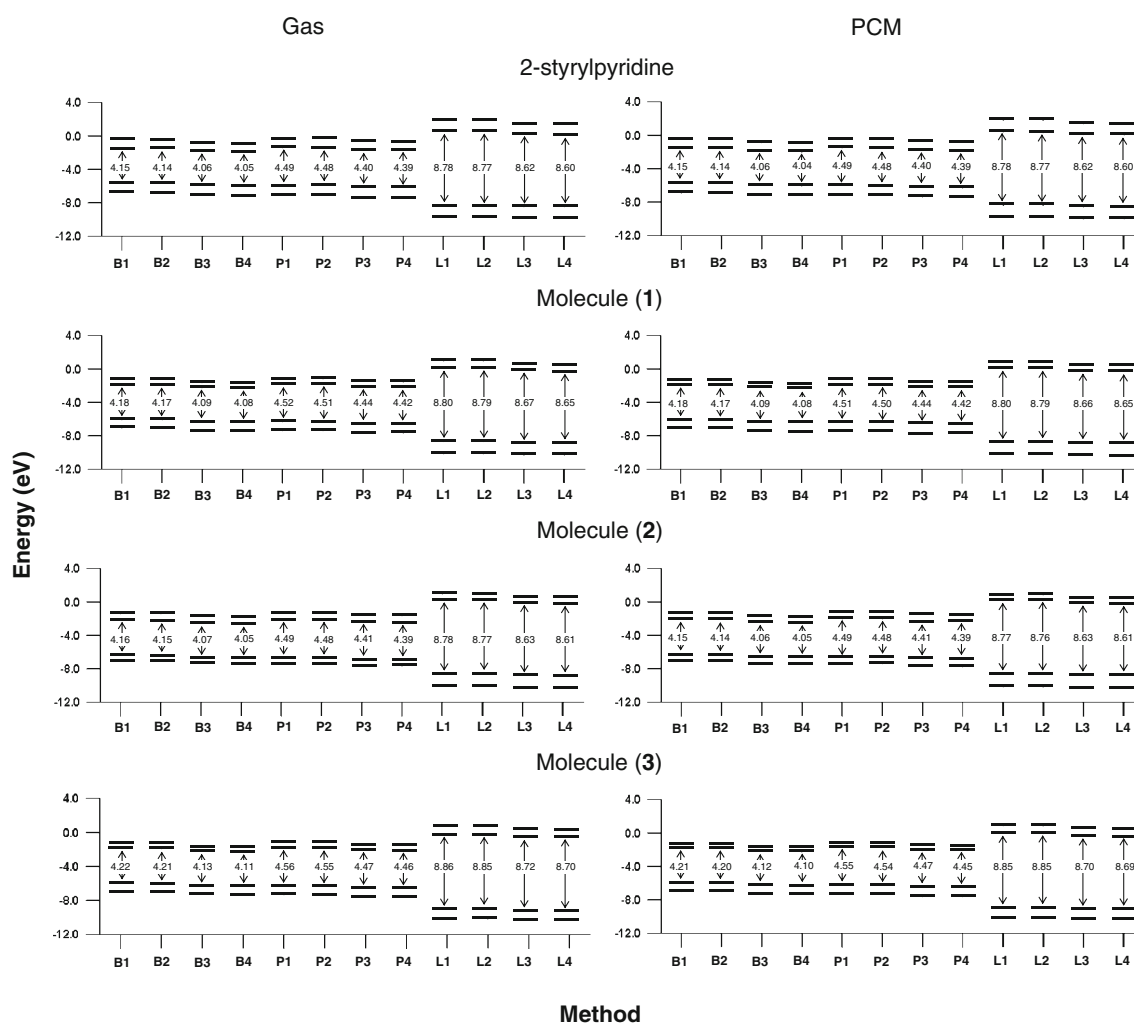


Fig. 3 Molecular orbitals and gap energies for 2-styrylpyridine and molecules (1–3) using TD-B3LYP (B1–B4), TD-PBE0 (P1–P4), and TD-LC- ω PBE methods in gas phase and including the solvent effect.

The numbers correspond to the different basis sets used as follows: 6–31G(d)=1, 6–31G(d,p)=2, 6–31+G(d,p)=3, 6–311+G(d,p)=4

A comparison was made between the calculated values of the molecular orbitals and gap energies obtained using TD-B3LYP, TD-PBE0, and TD-LC- ω PBE methods. The average differences were calculated using each basis set for each molecule. For further discussion of the results, the key letter corresponds to the method used—B3LYP (B), PBE0 (P), and LC- ω PBE (L)—and the key number correspond to the different basis set used as follows: 6-31G(d)=1, 6-31G(d,p)=2, 6-31+G(d,p)=3, and 6-311+G(d,p)=4. The results obtained with TD-B3LYP and TD-PBE0 approaches showed similar behaviors for the four molecules, while TD-LC- ω PBE results were not in good agreement.

In general, the HOMO-1 and HOMO energy values obtained using B1–B4 were slightly smaller than those values obtained using P1–P4 methods; the LUMO and LUMO+1 values were slightly higher in both phases. The average differences for HOMO-1, HOMO, LUMO, and LUMO+1, respectively, were 0.3, 0.2, 0.1, and 0.1 eV between B1–B4 and P1–P4 in gas, and 0.3, 0.2, 0.1, and 0.1 eV between B1–B4 and P1–P4 in solution. Slightly higher gap energies were found when using P1–P4 than with B1–B4, with an average of 0.3 eV in both phases. On the other hand, the energy values of the HOMO-1 and HOMO orbitals obtained by the L1–L4 methods were lower than those obtained using the B1–B4 and P1–P4 methods, while the LUMO and LUMO+1 values were higher in both gas and solution phases. The average differences for L1–L4 for HOMO-1, HOMO, LUMO, and LUMO+1, respectively, were 2.9, 2.5, 2.0, and 2.2 eV respect to B1–B4, and 2.7, 2.3, 1.9, and 2.0 eV respect P1–P4 in gas. Higher gap energies were found using L1–L4 than B1–B4 and P1–P4 methods with averages of 4.6 and 4.2 eV, respectively, in both phases.

The energy values of the molecular orbitals including the PCM solvent effect were slightly smaller than those calculated in gas phase. The gap energy values were practically the same in both phases using the same method (Fig. 3).

With respect to the basis set, it was observed that using basis including diffuse functions (B3, B4, P3, P4, L3 and L4) resulted in smaller values of the HOMO-1, HOMO, LUMO, and LUMO+1 compared to the values obtained using only polarized functions (B1, B2, P1, P2, L1, and L2). The smallest molecular orbitals energies values were obtained with the 6-311+G(d,p) basis set (B4 and P4), whereas the smallest gap energy was obtained by using only B4 theory level for all molecules.

UV/Vis spectra properties

TD-DFT (with B3LYP, PBE0, and LC- ω PBE) using different basis sets (6-31G(d), 6-31G(d,p), 6-31+G(d,p), and 6-311+G(d,p))—were used to calculate the UV/Vis spectra for

the 2-styrylpyridine and molecules (1–3) in gas and solution phases. As previously mentioned only the lowest energy conformers of the four compounds were studied. The comparison between theoretical and experimental UV/Vis spectra was performed with respect to the fully optimized structure obtained by B3LYP/6-311+G(d,p) calculations.

Table 3 presents the collected maxima absorption wavelength values (λ_{\max}) together with the values calculated in chloroform solution. The three first low-lying excited states were computed. For the four molecules, the electronic excitation presented a typical $\pi \rightarrow \pi^*$ character that is often associated with a large oscillator force. The theoretical λ_{\max} bands were always related to the electronic transition between $S_0 \rightarrow S_1$ states (denoted as the transition between molecular orbitals HOMO \rightarrow LUMO); the corresponding oscillator strengths are also shown in Table 3. The results were compared with the available experimental data for 2-styrylpyridine and molecules (1) and (2) [52]. We compared the λ_{\max} values calculated using TD-B3LYP, TD-PBE0 and TD-LC- ω PBE; these data are described using the same nomenclature as in the Molecular orbitals section.

In gas phase, for 2-styrylpyridine and molecules (1) and (2), the calculated λ_{\max} showed an error of approximately 2.3, 1.9, and 2.2 %, respectively, with the B1–B4 methods. With P1–P4, the error was 1.8 % for 2-styrylpyridine, and 1.6 % for molecules (1) and (2); however, the error increased to 10.2 % for 2-styrylpyridine and 10.5 % for (1) and (2) when L1–L4 were used.

By using TD-DFT schemes, we identified an important difference between the errors obtained with polarized functions and diffuse functions. In the case of 2-styrylpyridine, B1 and B2 provided a mean error of 0.3 %, while B3 and B4 increased the mean error to 4.3 %; however P1 and P2 methods gave a mean error of 1.8 % the same as P3 and P4 methods. Contrary to the behavior of B3LYP functional, L1 and L2 gave a mean error of 11.7 % larger than 8.8 % with L3 and L4 methods.

For molecules (1) and (2), errors of 0.1 and 0.3 %, were obtained using B1 and B2 levels, while including diffuse functions (B3 and B4) increased the errors to 3.7 and 4.1, respectively. For P1 and P2, error values of \sim 2.0 % were found for 2-styrylpyridine and molecules (1) and (2), while slightly smaller values (range: 1.2–1.8) were obtained by using P3 and P4 methods. For L1 and L2, mean errors of 10.5 % were obtained, while by using L3 and L4 the error values decreased to 9.2 % for both molecules.

Wilberg et al. [53] recommend that the 6-311++G(d, p) basis set or a larger basis set generally be used for excited state calculations [54]. However, in our study, using the B3LYP method with the double- ζ basis set and only polarization functions, B1 and B2, we found that the error in the calculated λ_{\max} was <1 % for 2-styrylpyridine and for molecules (1) and (2) in gas phase. This suggests that although

Table 3 Maxima absorption wavelengths (λ_{max}) and oscillator strengths (f) of the 2-styrylpyridine and molecules (1–3) calculated using TD-DFT methods. Geometries are optimized at the B3LYP/6–311+G(d,p) level

Method	2-styrylpyridine						Molecule (1)						Molecule (2)						Molecule (3)					
	λ_{max} (nm)			f			λ_{max} (nm)			f			λ_{max} (nm)			f			λ_{max} (nm)			f		
	Gas	PCM	Gas	PCM	Gas	PCM	Gas	PCM	Gas	PCM	Gas	PCM	Gas	PCM	Gas	PCM	Gas	PCM	Gas	PCM	Gas	PCM	Gas	PCM
B1	311.6	323.3	0.8922	1.0597	309.3	320.9	0.9656	1.1193	312.7	324.1	0.9432	1.0916	307.2	318.3	0.7615	0.9422								
B2	312.0	323.8	0.8903	1.0580	309.8	321.3	0.9620	1.1169	313.2	324.6	0.9405	1.0895	307.7	318.8	0.7615	0.9402								
B3	323.6	335.8	0.8391	1.0094	320.2	331.9	0.8883	1.0655	323.8	335.3	0.8781	1.0443	318.2	329.6	0.7239	0.9074								
B4	325.2	337.4	0.8268	1.0015	321.9	333.6	0.8732	1.0568	325.6	337.2	0.8671	1.0384	319.9	331.3	0.7100	0.8978								
P1	305.1	316.5	0.9266	1.0901	303.0	314.1	0.9894	1.1426	306.2	317.1	0.9679	1.1169	300.3	311.1	0.8249	0.9958								
P2	305.5	316.9	0.9244	1.0881	303.5	314.6	0.9858	1.1398	306.7	317.7	0.9649	1.1144	300.8	311.6	0.8222	0.9925								
P3	315.7	327.5	0.8756	1.0416	312.6	323.9	0.9229	1.0907	316.1	327.2	0.9092	1.0689	310.0	321.0	0.7803	0.9593								
P4	317.3	329.1	0.8657	1.0354	314.3	325.7	0.9112	1.0840	317.8	329.0	0.9007	1.0644	311.6	322.6	0.7679	0.9507								
L1	274.4	283.1	0.9581	1.1019	272.6	280.8	0.9735	1.1153	274.5	282.51	0.9569	1.0969	268.2	276.6	0.9166	1.0613								
L2	274.8	283.5	0.9553	1.0995	273.0	281.2	0.9700	1.1123	274.9	282.9	0.9541	1.0944	268.7	276.5	0.9110	1.0613								
L3	282.8	291.8	0.9109	1.0540	280.2	288.7	0.9198	1.0626	282.4	290.6	0.9051	1.0445	275.8	284.3	0.8707	1.0285								
L4	284.6	293.8	0.9043	1.0508	282.2	290.8	0.9130	1.0597	284.4	292.8	0.9002	1.0429	277.7	286.3	0.8617	1.0229								
Experimental	311.0				309.6				312.0				–											

diffuse functions are essential to describe Rydberg states [55], the presence of diffuse functions is not crucial for calculating the low-lying excited state (first excited state with non-zero oscillator strength).

We used PCM calculations to include the chloroform solvent effect on calculated λ_{\max} . Calculated λ_{\max} was increased by $\sim 4\%$ for 2-styrylpyridine and for molecules (1) and (2) when solvent effect was included compared to gas phase using B1–B4. When using P1–P4 in solution, an $\sim 2\%$ increment of the error with respect to gas was found for 2-styrylpyridine and molecules (1) and (2). L1–L4 methods gave smaller errors in solution than in gas of $\sim 3\%$.

This analysis led us to choose the B3LYP method including polarized functions, B1 and B2 in gas phase, as the method to study the absorption spectra; the values obtained with this method corresponded well with the experimental ones. On the other hand, the PBE0 method was the most appropriate for calculating the absorption spectrum in solution in these molecular systems. TD-LC- ω PBE showed large errors with respect to the experimental maxima absorption wavelengths, which is in according with the previous results obtained for other conjugated organic compounds [33–35]. In these studies, the authors obtained larger mean absolute errors using TD-LC- ω PBE than using TD-PBE0 [33] and TD-B3LYP [34, 35].

As an example, the B1 in gas calculated for the three lowest excited states of 2-styrylpyridine were as follows: 311.6 nm [HOMO \rightarrow LUMO (99 %), $f=0.8922$], 291.2 nm [HOMO-2 \rightarrow LUMO (97 %), $f=0.0012$], and 271 nm [HOMO-1 \rightarrow LUMO (72 %) + HOMO \rightarrow LUMO+2 (25 %), $f=0.0030$]. It is known that the observed intensity is proportional to the square of the oscillator strength; therefore, the calculated λ_{\max} was 311.6 nm.

As shown in Table 3, the λ_{\max} values calculated using B1 method in gas were the closest to the experimental λ_{\max} values of 2-styrylpyridine (311 nm) and molecules (1) (309.6 nm) and (2) (312 nm). However, both methods B3LYP and PBE0 overestimated the calculated values with respect to the experimental λ_{\max} for the three molecules in solution.

In the similar compounds halogen-substituted styrylpyridines, a strong absorption signal in the 311–318 nm range was observed for the band of the π - π^* transition that is typically assigned to the double bond; furthermore, no significant shifts were observed in the absorption λ_{\max} values due to the F- and Cl-substitutions [10]. In our study, similar behavior was observed for the 2-styrylpyridine cyano-substituted molecules (1) and (2). The calculated λ_{\max} values were closer to the values for 2-styrylpyridine, indicating that all compounds were located in the *trans* conformation and there was not an important effect of the electroattractor –CN group on the value of λ_{\max} .

In accordance with the calculated results, the best value of λ_{\max} for molecule (3) was predicted to be 307.2 nm using

the TD-B3LYP method with the 6–31G(d) basis set in gas phase. A similar value of 309 nm was found for the Cl-substituted 4-styrylpyridine, which also was close to the λ_{\max} for 4-styrylpyridine at 304 nm [10], as it was predicted in the present study for the cyano-substituted molecule (3). The difference of ~ 4 nm between λ_{\max} of molecule (3) and the molecule (1) isomer could be attributed to the possible change caused by the π -delocalization length regulated by the *N*-position in the pyridine ring. Finally, according to the results obtained, molecule (3) was the most stable molecular structure when the –CN group was located in the *m'*-position, indicating the possibility that another stable molecular structure exists. It would be interesting to perform further calculations taking into account the conformational flexibility of the molecule in order to evaluate the effect on its absorption properties.

Conclusions

The present work is a comparative theoretical study of the absorption properties of cyano-substituted styrylpyridine compounds using time-dependent density functional theory (TD-DFT) methods.

The B3LYP/6–311+G(d,p) level provided the most stable form for the four studied molecules as planar structures in gas as well as in solution phases. No important differences were found between the optimized parameters obtained in the gas phase and those with chloroform solvent effect for the four molecules.

The most stable isomeric structures of 2-styrylpyridine and of the three model styrylpyridine-like compounds were fully optimized using the same theory level. High energy barriers were found through the torsion of the cyano-substituted phenyl ring between the two isomers in molecules (1–3). For molecules (1) and (2), the structures with the –CN group attached in the *meta* position of the phenyl ring were more stable than their respective isomers with the –CN group attached in the equivalent *meta'* position. However, for molecule (3), the *m'*-position of the substituted phenyl was energetically more stable than its respective isomer. For 2-styrylpyridine, the energy barriers decreased when the solvent effect was taken into account, while for molecules (1–3), the barriers calculated in gas phase were smaller. Furthermore, the calculations allowed us to propose different isomers that may be present in solution or solid state, e.g., 2-styrylpyridine might adopt two isomeric forms where the *N*-atom can be located at position C(2) or C(6).

The main molecular orbitals and theoretical UV/Vis spectra calculated indicate the possibility of finding a relationship between the structure and absorption properties of the conjugated compounds substituted with different electron-withdrawing and electron donor groups.

In choosing the basis set, when diffuse functions were included in double- ζ and triple- ζ basis sets, the values of HOMO-1, HOMO, LUMO, and LUMO+1 were smaller than the values obtained using only polarized functions in both B3LYP and PBE0 functionals. The smallest molecular orbitals and gap energies were obtained with the triple- ζ basis set with diffuse and polarized functions at the TD-B3LYP/6-311+G(d,p) theory level in all cases.

For both phases, the TD-LC- ω PBE method overestimated the theoretical λ_{\max} values with regard to experimental λ_{\max} of 2-styrylpyridine and molecules (1) and (2). The TD-B3LYP/6-31G(d) values were the closest to the experimental values in the gas phase. However, both methods B3LYP and PBE0 overestimated the calculated values with respect to experimental λ_{\max} for the three molecules in solution.

Our results suggest that is not necessary to use diffuse functions for calculating the low-lying excited state in these kinds of compounds when using TD-B3LYP and TD-PBE0 schemes.

Using PCM calculations to include the effect of chloroform increased the errors in the λ_{\max} values for 2-styrylpyridine and molecules (1) and (2) with all methods. According to the calculated results, the best possible value predicted for the λ_{\max} of molecule (3) was 307.2 nm. Based on the absorption properties determined in the present work, we suggest that future studies include an exhaustive conformational analysis of molecule (3), as well as the substitution of other electron acceptor and electron donor groups on its structure.

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References

- Langer G (1905) *Ber* 38:3704–3709
- Shaw BD, Wagstaff EA (1933) *J Chem Soc* 77–79
- Phillips AP (1947) *J Org Chem* 12:333–341
- Horwitz L (1955) *J Am Chem Soc* 77:1687–1690
- Trippett S (1960) *Advances in organic chemistry*. In: Raphael RA, Taylor EC, Wynberg H (eds) *Methods and resolutions*, vol I. Interscience, New York, p 83
- Williams JLR, Adel RE, Carlson JM, Reynolds GA, Borden DG, Ford JA Jr (1963) *J Org Chem* 28:387–390
- Clavreul R, Bloch B, Brigodiot M, Maréchal E (1987) *Makromol Chem* 188:47–65
- Percino MJ, Chapela VM, Salmón M, Espinosa-Pérez G, Herrera AM, Flores A (1997) *J Chem Crystallogr* 27(9):549–552
- Percino MJ, Chapela VM, Sánchez A, Maldonado-Rivera JL (2006) *Chem Indian J CAIJ* 3(9–10):262–267
- Percino MJ, Chapela VM, Montiel L-F, Pérez-Gutiérrez E, Maldonado JL (2010) *Chem Pap* 64(3):360–367
- Chapela VM, Percino MJ, Rodríguez-Barbarin C (2003) *J Chem Crystal* 33(2):77–83
- Atalay Y, Basoglu A, Avci D (2008) *Spectrochim Acta A* 69:460–466
- Daku LML, Linares J, Boillot M-L (2007) *ChemPhysChem* 8:1402–1416
- Melendez FJ, Urzúa O, Percino MJ, Chapela VM (2010) *Int J Quantum Chem* 110:838–849
- Lewis FD, Weigel WJ (2000) *Phys Chem A* 104:8146–8153
- Pinto MR, Hu B, Karasz FE, Akcelrud L (2000) *Polymer* 41:2603–2611
- Liu SL, Jiang X, Liu S, Herguth P, Jen AKY (2002) *Macromolecules* 35:3532–3538
- Davis R, Kumar NSS, Abraham S, Suresh CH, Rath NP, Tamaoki N, Das S (2008) *J Phys Chem C* 112:2137–2146
- Runge E, Gross EKV (1984) *Phys Rev Lett* 52:997–1000
- Gross EKV, Kohn W (1985) *Phys Rev Lett* 55:2850–2852
- Gross EKV, Kohn W (1990) *Adv Quantum Chem* 21:255–291
- Wacker OJ, Kümmel R, Gross EKV (1994) *Phys Rev Lett* 73:2915–2918
- Marques MAL, Gross EKV (2004) *Annu Rev Phys Chem* 55:427–455
- Chen PC, Chieh YC (2003) *J Mol Struct (THEOCHEM)* 624:191–200
- Stratmann RE, Scuseria GE, Frisch MJ (1998) *J Chem Phys* 109(19):8218–8224
- Guillaumont D, Nakamura S (2000) *Dyes Pigment* 46:85–92
- Improta R, Santoro F (2005) *J Phys Chem A* 109:10058–10067
- Belletete M, Morin J-F, Leclerc M, Durocher G (2005) *J Phys Chem A* 109:6953–6959
- Badaeva EA, Timofeeva TV, Masunov A, Tretiak S (2005) *J Phys Chem A* 109:7276–7284
- Hommen de Mello P, Mennucci B, Tomasi J, da Silva ABF (2005) *Theor Chem Accounts* 113:274–280
- Hartley CS (2011) *J Org Chem* 76:9188–9191
- Jacquemin D, Assfeld X, Preat J, Perpète EA (2007) *Mol Phys* 105:325–331
- Jacquemin D, Perpète EA, Scuseria GE, Ciofini I, Adamo C (2008) *J Chem Theor Comput* 4:123–135
- Jacquemin D, Wathélet V, Perpète EA, Adamo C (2009) *J Chem Theor Comput* 5:2420–2435
- Jacquemin D, Perpète EA, Ciofini I, Adamo C (2010) *J Chem Theor Comput* 6:1532–1537
- Guido CA, Jacquemin D, Adamo C, Mennucci B (2010) *J Phys Chem A* 114:13402–13410
- Tomasi J, Persico M (1994) *Chem Rev* 94:2027–2094
- Cossi M, Rega N, Scalmani M, Barone V (2001) *J Chem Phys* 114:5691–5701
- Improta R, Barone V (2004) *J Am Chem Soc* 126:14320–14321
- Shukla MK, Leszczynski J (2004) *J Phys Chem A* 108:10367–10375
- André JM, Delhalle J, Brédas JL (1991) *Quantum chemistry aided design of organic polymers—an introduction to the quantum chemistry of polymers and its applications*. World Scientific, London
- Becke AD (1993) *J Chem Phys* 98:5648–5652
- Adamo C, Barone V (1999) *J Chem Phys* 110:6158–6169
- Tawada Y, Tsuneda T, Yanagisawa S, Yanai T, Hirao K (2004) *J Chem Phys* 120:8425–8433
- Hariharan PC, Pople JA (1973) *Theor Chem Accounts* 28:213–222
- Ditchfield R, Hehre WJ, Pople JA (1971) *J Chem Phys* 54:724–728
- McLean AD, Chandler GS (1980) *J Chem Phys* 72:5639–5648
- Casida ME, Jamorski C, Casida KC, Salahub DR (1998) *J Chem Phys* 108:4439–4449

49. Perdew JP, Burke K, Ernzerhof M (1996) *Phys Rev Lett* 77:3865–3868
50. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA Jr, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam NJ, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) *Gaussian 09*, revision A.1. Gaussian Inc, Wallingford
51. Muñoz-Caro C, Niño A, Mora M, Reyes S, Melendez FJ, Castro ME (2005) *J Mol Struct (THEOCHEM)* 726:115–124
52. Castro ME, Percino MJ, Chapela VM, Ceron M, Soriano-Moro G, Lopez-Cruz J, Melendez FJ (2012) *Molecules* (submitted)
53. Wiberg KB, Stratmann RE, Frisch MJ (1998) *Chem Phys Lett* 297:60–64
54. Wiberg KB, De Olivera AE, Trucks G (2002) *J Phys Chem A* 106:4192–4199
55. Jacquemin D, Preat J, Charlot M, Wathelet V, Andre JM, Perpète EA (2004) *J Chem Phys* 121:1736–1743