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Excited state proton transfer in 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol

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ABSTRACT

A theoretical and experimental study on the absorption and fluorescence properties of a newly synthesized compound 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol in ethanol is reported. Evidence suggesting intramolecular proton transfer in the excited singlet state is presented. All possible tautomeric forms are studied by means of TDDFT B3LYP/6-31G(d,p) in both the ground and the first excited singlet state. On the basis of the results obtained excited state double proton transfer in the title compound is proposed.

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1. Introduction

Proton transfer reactions are among the fundamental processes in chemistry and are involved in many biochemical transformations. Excited state intramolecular proton transfer (ESIPT) reactions have been the subject of intensive investigations in recent years. Such reactions are not only of scientific interest but have also practical importance because many of the organic substances can be used as photostabilizers [1], laser dyes [2,3], metal ion sensors [4], molecular probes [5], luminescent materials [6,7] and molecular logic gates [8].

ESIPT represents a phototautomerization process which proceeds exceptionally fast at a subpicosecond time scale [9]. In most cases where ESIPT is observed, the proton donor is a hydroxyl group (enol structure) and the acceptor is a nitrogen atom or a carbonyl group (keto structure) [10–13]. Eventually, the excited keto structure decays to the ground state either by radiative (fluorescence) or nonradiative (internal conversion) processes, which can be followed by a reverse proton transfer, returning to the original ground state enol structure.

The excited keto tautomer produced by ESIPT usually shows significant differences in geometric structure and electronic configuration in comparison to the original enol species. This fact leads to a large Stokes shifts of the order of 8000–10000 cm^{−1}. This property has always attracted strong interest in ESIPT systems and has led to important applications as already mentioned above.

Multireference methods such as complete active space self-consistent field (CASSCF) and complete active space second order perturbation theory (CASPT2) [14,15], multireference configuration interaction with singles and doubles (MR-CISD) and multireference

averaged quadratic coupled cluster (MRAQCC) [16,17] have been used in the theoretical studies of excited states. These methods, however, are computationally too demanding for most interesting molecules showing ESIPT. In recent years, with the development of the variational formulation [18] of time-dependent density functional theory (TDDFT) substantial progress has been achieved in the calculation of analytic energy gradients of excited states. TDDFT has been successfully used to study ESIPT systems in recent years [19–22].

We consider tautomerism in ground and excited state of a newly synthesized compound 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol, an internally hydrogen-bonded derivative of catechol. The compound is related to bis-3,6-(2-benzoxazolyl)-pyrocatechol [23] and presents a possibility for two-step tautomerisation. Such compounds are a rare example of intramolecular double proton transfer which can occur in the excited state [19,24,25].

2. Experimental and calculation

2.1. Synthesis

2.1.1. Synthesis of benzyl protected bis-aldehyde

To a stirred solution of deprotected 2,3-dihydroxyterephthalaldehyde (0.46 g, 0.0028 mol) in 18 ml CH₃CN were added K₂CO₃ (1.55 g, 0.011 mol, 4 equiv.) and BnBr (0.83 ml, 0.007 mol, 2.5 equiv.). The mixture was stirred for 25 h and then purified by column chromatography (hexane:EtOAc – 4.5:0.5) to give 0.76 g (80%) of **2**.

2.1.2. Synthesis of **3**

To a stirred solution of **2** (0.38 g, 0.0011 mol) in dry DCE, under Ar atmosphere were added 2-aminoethanol (0.53 ml, 0.0044 mol,

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4 equiv.) and MS 4 Å (5 g) and the mixture was refluxed for 20 h. Then it was cooled to room temperature and NBS (0.89 g, 0.005 mol, 4.5 equiv.) was added in portions for 20 min. The resulting mixture was stirred additionally for 2 h. The reaction mixture was then filtered and the solvent was removed by evaporation in vacuum. The crude product was purified by flash-chromatography eluting with hexane:EtOAc (01:1–1:4) to give the compound **3**. Yield: 0.14 g, 30%. ^1H NMR (600.13 MHz, CDCl_3): 3.99 (t, 2H, $\text{CH}_2\text{-N}$, $J = 9.6$ Hz), 4.31 (t, 2H, $\text{CH}_2\text{-O}$, $J = 9.6$ Hz), 5.05 (s, 4H, $\text{CH}_2\text{-Ph}$), 7.25–7.28 (m, 6H, Ph-CH_2), 7.34–7.36 (m, 4H, Ph-CH_2), 7.49 (s, 2H, Ar); ^{13}C NMR (150.9 MHz, CDCl_3): 55.13 (2C), 67.47 (2C), 76.40 (2C), 125.74 (2C), 126.45 (2C), 128.21 (2C), 128.33 (4C), 129.15 (4C), 136.29 (2C), 152.26 (2C), 162.59 (2C). Analysis: calculated for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_4$: C, 72.88; H, 5.65; N, 6.54; O, 14.94; found: C, 72.62; H, 5.40; N, 6.46.

2.1.3. Synthesis of **4**

To a solution of **3** (0.138 g, 0.00032 mol) in dry freshly distilled MeOH was added 5% of Pd/C. The air in the system was evacuated and replaced with hydrogen three times. The mixture was stirred at room temperature for two days. After the first day a second 5 wt% portion of Pd/C was added and the stirring was continued. The mixture was filtrated through Celite pad and the Celite layer was washed with copious CH_2Cl_2 to retrieve the title product. The filtrates were evaporated, the solid residue redissolved in CH_2Cl_2 and the solution filtered through microporous Teflon filter (0.45 μm) and the volatiles removed in vacuo. Yield: 0.071 g, 87%. ^1H NMR (600.13 MHz, CDCl_3): 4.14 (t, 2H, $\text{CH}_2\text{-N}$, $J = 9.5$ Hz), 4.44 (t, 2H, $\text{CH}_2\text{-O}$, $J = 9.6$ Hz), 7.16 (s, 2H, Ar), 12.40 (br.s, 2H, OH); ^{13}C NMR (150.9 MHz, CDCl_3): 53.49 (2C), 66.93 (2C), 112.85 (2C), 116.66 (2C), 149.21 (2C), 166.11 (2C). Analysis: calculated for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_4$: C, 58.06; H, 4.87; N, 11.29; O, 25.78; found: C, 58.50; H, 4.80; N, 11.22.

2.2. Theoretical details

Density Functional Theory (DFT) and Time Dependent DFT (TDDFT) [26,27] optimizations were performed for the ground (S_0) and first ($\pi\pi^*$) singlet excited (S_1) electronic states, respectively. The three parameter hybrid functional of Becke with the correlation functional of Lee, Yang and Parr (B3LYP) [28,29] and 6-31G(d,p) basis set [30,31] were chosen. All the minima and transition states in the ground and excited states were confirmed by normal mode analysis at the same computational level as used for the geometry optimization. The GAMESS program [32], which implements analytical gradients at the TDDFT level, was used to perform the TDDFT calculations. TDDFT is a single excitation theory. The TDDFT codes in GAMESS excite all electrons; there is no frozen core concept.

The values of Gibbs free energies (ΔG) and activation barriers (ΔG^\ddagger) were calculated for a temperature of 298.15 K by the formulae $\Delta G = \Delta H - T\Delta S$ and $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, respectively. The classical rate constants at 298.15 K were obtained using the Eyring equation, $k = (k_B T/h) \cdot e^{-\Delta G^\ddagger/RT}$, where k_B and h are the Boltzmann and Planck constants, respectively. The values of the tautomer and rotamer populations (p_i) were calculated by the standard formula

$$p_i = e^{-\Delta G_i/RT} / \sum_j e^{-\Delta G_j/RT}.$$

The vertical excitation energies were obtained using TDDFT (B3LYP/6-31G(d,p)) calculations at the optimized ground state geometries. Spectra were simulated by associating to each transition a 50/50 GAUSSIAN/LORENTZIAN line shape having a height proportional to the oscillator strength and a full width at half-maximum (fwhm) of 0.2 eV.

2.3. Experimental details

IR spectrum of solid crystalline 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol was recorded on Bruker Tensor 27 FTIR spectrometer in the 4000–515 cm^{-1} spectral region by the use of PIKE MIRacle-ZnSe ATR accessory.

The NMR spectra in CDCl_3 solution were carried out at ambient temperature (300 K) on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ^1H and ^{13}C , respectively, using the standard Bruker software. The chemical shifts were referenced to tetramethylsilane.

The absorption spectra were scanned on a Perkin Elmer Lambda 25 UV-Vis Spectrophotometer and the corrected fluorescence spectra – on a Perkin Elmer LS 55 Spectrofluorimeter. The solvent used was fluorescent grade.

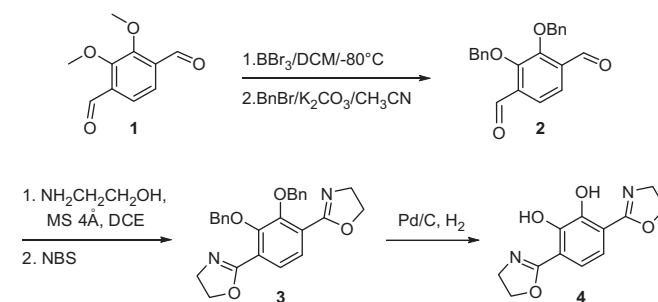
3. Results and discussion

3,6-Bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol was obtained by Scheme 1. The starting aldehyde **1** was obtained by literature procedure [33]. The synthesis required changing two protective groups, since the oxazoline moiety is incompatible with BBr_3 , while on the other hand, benzyl groups change the lithiation step regioselectivity. After oxazoline-rings formation, the protecting groups were removed by catalytic hydrogenation, to afford the desired compound **4**. The product **4** was obtained in 17% overall yield, starting from catechol.

The newly synthesized compound **4** was characterized in solid state by IR spectroscopy (Figure 1). The lack of characteristic stretching bands of C=O group in carbonyl region 1700–1680 cm^{-1} as well as the presence of C=N stretching band at 1638 cm^{-1} in the IR spectrum of 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol clearly show that the dihydroxy form is observed in solid state. The band at 2855 cm^{-1} can be identified as C–H stretching vibration of methylene groups of oxazoline fragment while C–H stretching modes of benzene ring appear in the high frequency region 3020–3000 cm^{-1} .

The very broad band at 2900 cm^{-1} can be assigned to the intramolecular hydrogen bond between the hydrogen atom from the hydroxyl group of the catechol fragment and the nitrogen atom of the oxazoline ring. It cannot be easily identified in the interval 3500–3200 cm^{-1} since there may exist hydrogen bonding with other molecules in solid state.

The UV-Vis absorption and fluorescence spectra of 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol in ethanol are presented in Figure 2. The longest wavelength absorption transition of the studied compound has a maximum at 343.5 nm. It is accompanied by an intense absorption band at around 275 nm with well-defined vibrational structure, which is assigned to the absorption of the aromatic moiety and to a broad band of very low intensity in the region 380–440 nm (see inset on Figure 2).



Scheme 1.

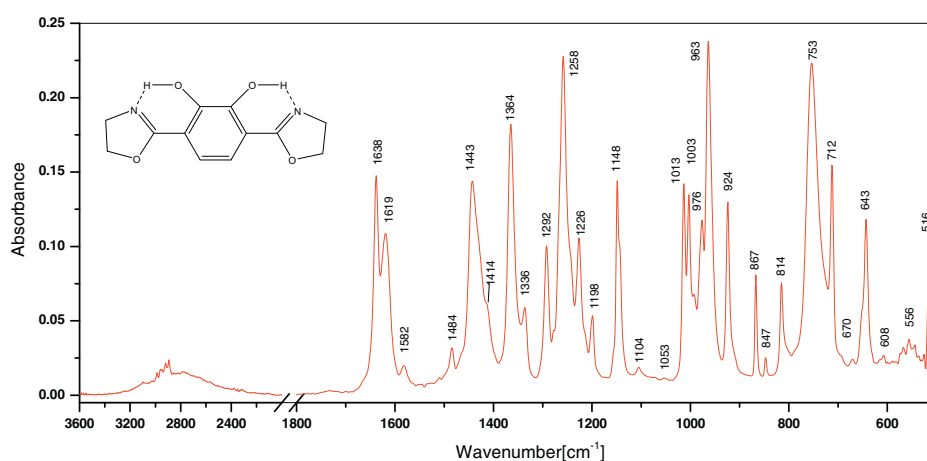


Figure 1. IR spectra of 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol in crystalline powder.

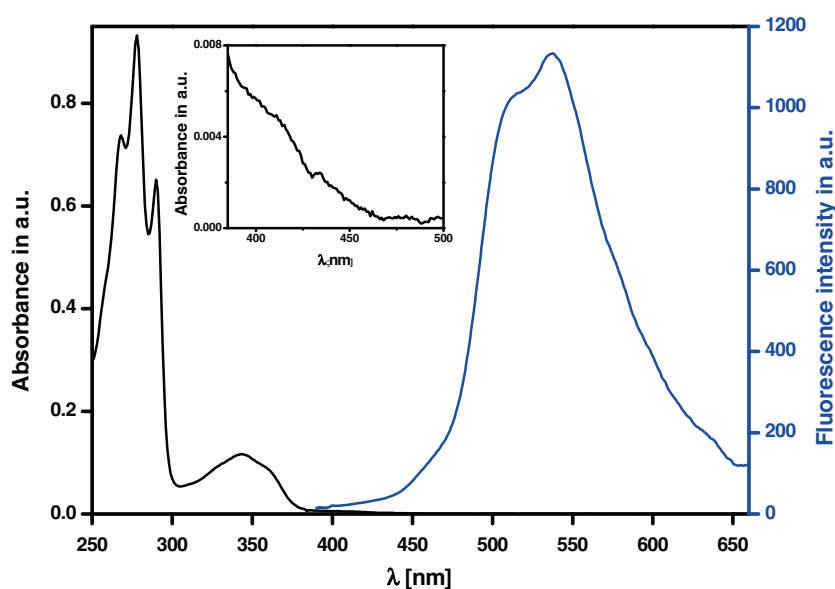


Figure 2. UV-Vis absorption (left) and fluorescence (right) spectra of 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol in ethanol ($c = 1 \times 10^{-5}$ M). Inset: Absorption spectrum of the same solution in the region 380–500 nm.

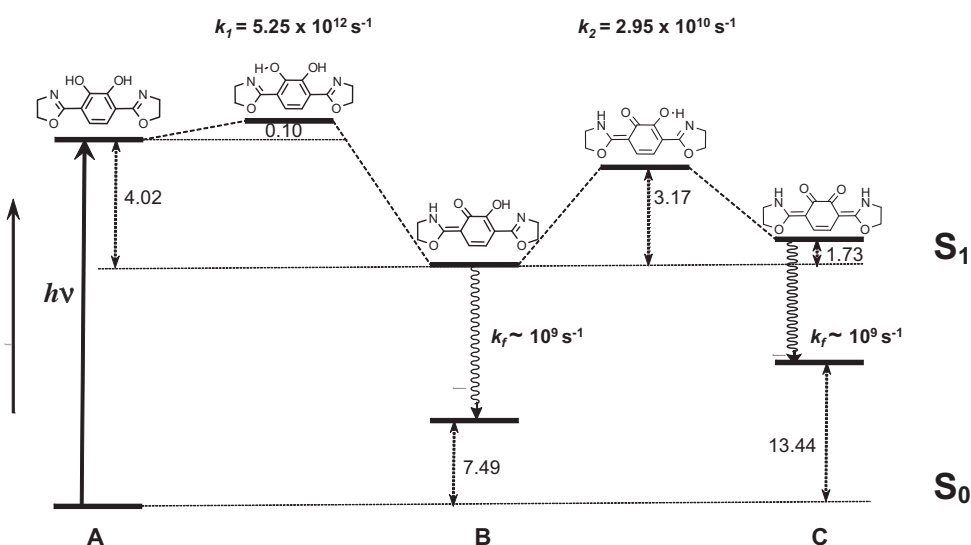


Figure 3. Schematic presentation of the energy differences, ΔG_{298} , and energy barriers, $\Delta G_{298}^{\ddagger}$, (in kcal mol^{-1}) of 3,6-bis(4,5-dihydroxy-oxazo-2-yl)benzene-1,2-diol tautomers in the ground (S_0) and first singlet excited electronic (S_1) states calculated at B3LYP/6-31G(d,p) and TDDFT (B3LYP/6-31G(d,p)) levels, respectively. The rate constants of the tautomeric conversions $A \rightarrow B$ (k_1) and $B \rightarrow C$ (k_2) in S_1 state and fluorescence (k_f) are presented.

3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol has an intense fluorescence band with a maximum at 535 nm (Figure 2). The observed extremely large Stokes shift is about 190 nm. This abnormally large Stokes shift suggests a significant reorganization of the electronically excited molecule before emission takes place, presumably due to proton transfer in the first excited singlet state.

In order to obtain insight into the process that is not easily attainable through experimental measurements, B3LYP/6-31G(d,p) calculations were performed. Theoretically, compound **4** can exist in three tautomeric forms: dihydroxy **A**, hydroxy-oxo **B** and dioxo **C**, shown in Figure 3, with the most stable form in the ground electronic state being the dihydroxy tautomer. Our theoretical results are in agreement with the ^1H and ^{13}C NMR measurements in CDCl_3 solution of compound **4** where signals assigned only to the dihydroxy form are observed – broad singlet at 12.40 ppm for protons in hydroxyl groups and signals at 149.21 ppm for $\text{C}=\text{OH}$. Three rotamers of the dihydroxy form are

possible: **A** ($\text{OH}\cdots\text{N}$; $\text{OH}\cdots\text{N}$), **A1** ($\text{OH}\cdots\text{N}$; $\text{OH}\cdots\text{O}$) and **A2** ($\text{OH}\cdots\text{O}$; $\text{OH}\cdots\text{O}$). Rotamer **A** is the most stable while **A1** and **A2** are 4.91 and 10.25 kcal mol^{-1} higher in energy. According to the calculated relative stabilities the populations of the species **A**, **A1** and **A2** are 99.98%, 0.02% and $3.6 \times 10^{-6}\%$, respectively. Rotamers **A1** and **A2** are distinguishable in the ^{13}C NMR, but their concentrations are too low to be observed experimentally. On the other hand, their UV–Vis spectra are very similar and they cannot be distinguished in practice.

The percent concentrations of the tautomers **B** and **C** were calculated to be $3.2 \times 10^{-4}\%$ and $1.4 \times 10^{-8}\%$, respectively. Tautomer **B** has a very low concentration, but it should be observable in the absorption spectrum. Figure 4 shows the wavelengths of the theoretically predicted absorption maxima for tautomers **A–C** under the Franck–Condon assumption. On the basis of the TDDFT calculations the $S_0 \rightarrow S_1$ transitions were calculated to be 359 nm for **A** and 431 nm for **B**. These results are well-correlated with the absorption band at 344 nm of **A** and with very low intensity band

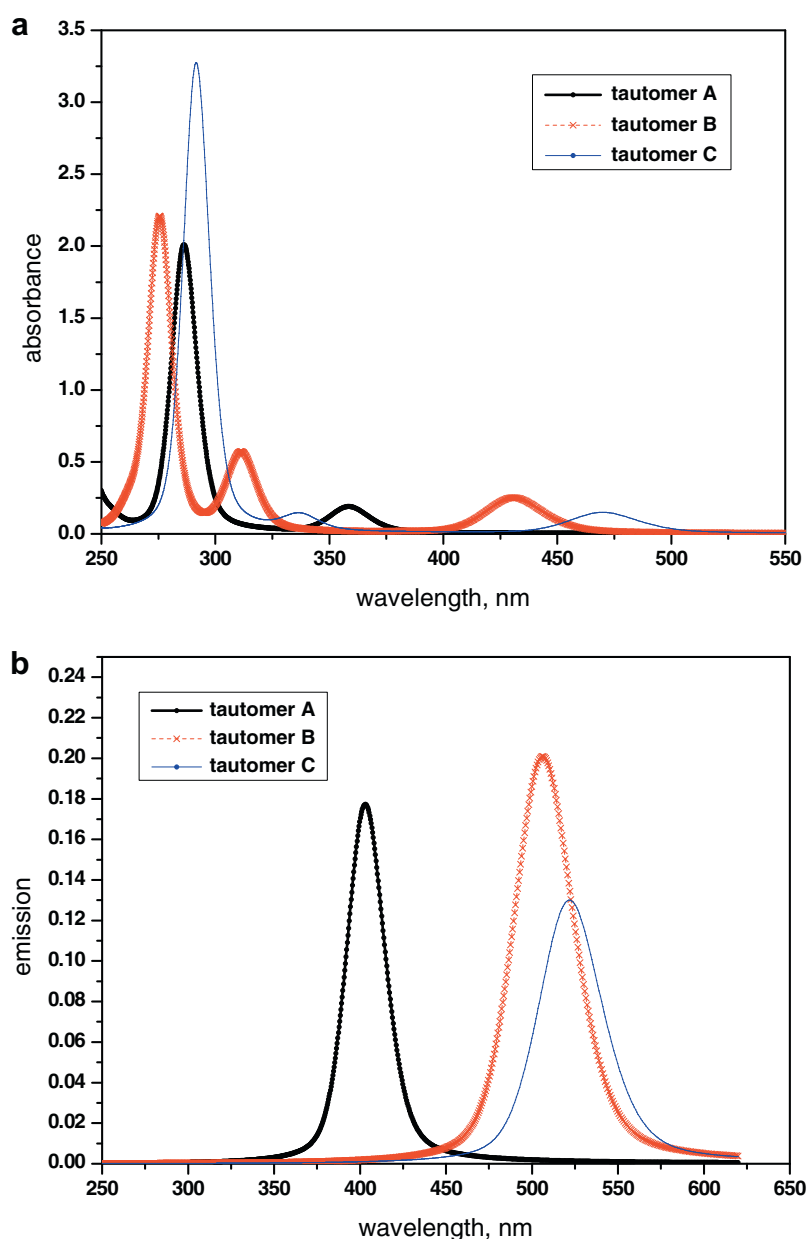
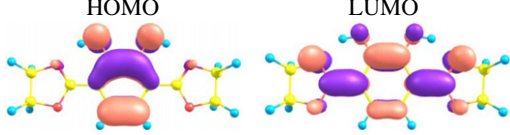
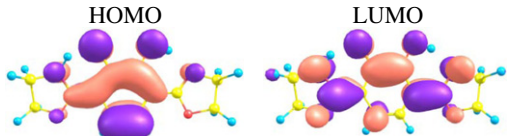
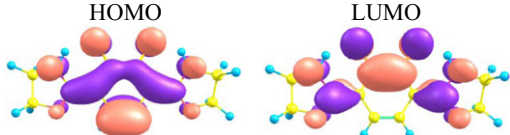


Figure 4. B3LYP/6-31G(d,p) calculated UV–Vis (a) and fluorescence (b) spectra of tautomers **A–C** of 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol.

Table 1

B3LYP/6-31G(d,p) calculated transition energies ($\lambda_{\text{calc.}}$), oscillator strengths (f) and frontier orbitals of tautomers **A–C** of 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol.

Transition	Excitation	$\lambda_{\text{calc.}}$ (nm)	f
$S_0 \rightarrow S_1$	Tautomer A HOMO \rightarrow LUMO (99.2 %)	359	0.0448
			
$S_0 \rightarrow S_1$	Tautomer B HOMO \rightarrow LUMO (99.2%)	431	0.0622
			
$S_0 \rightarrow S_1$	Tautomer C HOMO \rightarrow LUMO (99.2%)	470	0.0364
			

in the region 380–440 nm (inset, Figure 2) which could be assigned to tautomer **B**.

The ESIPT reaction is initiated by excitation of tautomer **A** to its first excited state S_1 . The vertical excitation energies for the $S_0 \rightarrow S_1$ transition in tautomers **A**, **B** and **C** are dominated by the monoexcited HOMO–LUMO configurations – 81.9%, 99.2% and 99.8%, respectively (Table 1). The shape of the frontier molecular orbitals involved in the $S_0 \rightarrow S_1$ transition indicates that HOMO and LUMO are π orbitals. According to the TDDFT calculations the S_1 state is of $\pi\pi^*$ character and the $^1\pi\pi^*$ state plays a key role in the determination of the nature of the excited state reaction, since the proton transfer should occur in the $^1\pi\pi^*$ state.

Figure 3 shows schematically the Gibbs energies of the different tautomers in their ground (S_0) and first singlet excited electronic (S_1) states. In the ground electronic state tautomer **A** is the most stable and the tautomers **B** and **C** are higher in energy by 7.49 and 13.44 kcal mol $^{-1}$, respectively. The situation is different in the S_1 excited state where the hydroxy-oxo tautomer **B** is the most stable one whereas the dihydroxy form **A** is, in fact the most unstable tautomer by 4.02 kcal mol $^{-1}$ and tautomer **C** is 1.73 kcal mol $^{-1}$ higher in energy than **B** (Figure 3). Rotamers **A1** and **A2** are also energetically unfavorable in S_1 excited state – the calculated relative stabilities by TDDFT are 12.12 and 20.57 kcal mol $^{-1}$, respectively. On the other hand the excitation of tautomer **A** from ground state S_0 to excited state S_1 leads to a shortening of both the carbon–carbon bond between the oxazoline ring and catechol moiety, and the OH \cdots N hydrogen bond. Thus, the rotation around the single C–C bond makes rotamer formation difficult.

The comparison of the structure of the tautomer **A** in S_0 and S_1 states shows changes in the whole molecule upon excitation (Figure 5). The all double carbon–carbon bonds (C6–C11, C7–C8 and C9–C10) in the catechol fragment are elongated by 0.04 Å while the single C–C and C–O bonds are shortened. There is an observable elongation by 0.02 Å only in the double carbon–nitrogen bonds (C12–N16 and C5–N1) in the oxazoline ring.

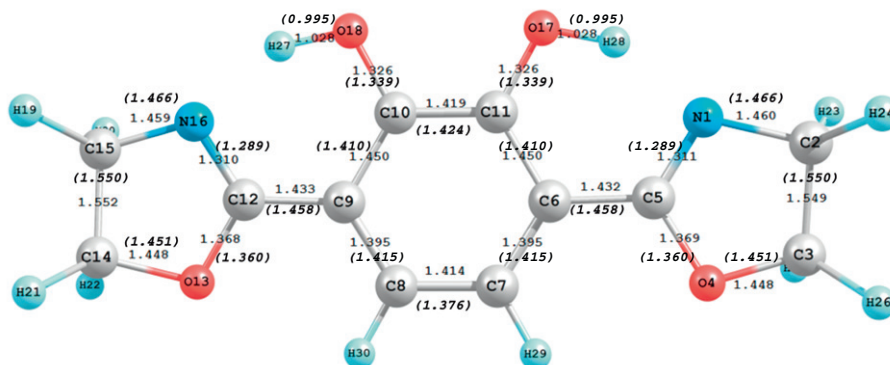
The optimized geometries of tautomers **A–C** and respective transition state structures (**TS1** and **TS2**) for the first excited state

S_1 are shown on Figure 5. For transition state **TS1** substantial changes are observed in the moiety in which proton transfer occurs. The C6–C11 and C5–N1 bonds lengthen while the C11–O17 and C5–C6 bond lengths shorten. The N1 \cdots O17 distance is shortened from 2.564 Å in tautomer **A** to 2.432 Å in **TS1**. The migrated proton is located at 1.301 Å from N1 and 1.201 Å from O17. Similar changes are observed in reaction **B** \rightarrow **C**. Formation of **TS2** is attended by elongation of C9–C10 and C12–N16, and shortening of C9–C12 and C10–O18 in tautomer **B**. The transferred proton is situated approximately in the middle between N16 and O18 atoms and the N16 \cdots O18 distance is shortened from 2.607 Å in **B** to 2.418 Å in **TS2**.

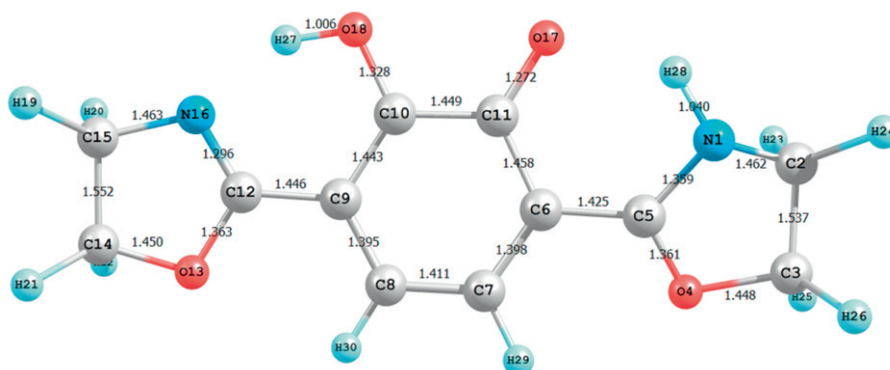
Upon photoexcitation, tautomer **A** undergoes very fast ESIPT yielding tautomer **B**. The free energy barrier of the reaction is only 0.10 kcal mol $^{-1}$. The rate constant of this very fast tautomeric conversion is calculated to be $k_1 = 5.25 \times 10^{12}$ s $^{-1}$. In light of the above result, we conclude that the **A** \rightarrow **B** proton transfer in S_1 is faster than fluorescence ($k_f \sim 10^7$ – 10^9 s $^{-1}$) [34] and probably for that reason there is no observed fluorescence band of tautomer **A** which is calculated to be at 403 nm (Figure 4b). The second tautomeric conversion in S_1 , **B** \rightarrow **C** is characterized by a rate constant of $k_2 = 2.95 \times 10^{10}$ s $^{-1}$ corresponding to the low energy barrier (3.17 kcal mol $^{-1}$). Since the ESIPT is much faster than the fluorescence process, the second proton transfer **B** \rightarrow **C** in excited state should be favored.

This assumption is further confirmed by analyzing the position of the fluorescence band (Figure 2). The calculated fluorescence maxima for **B** is at 506 nm and for **C** it is 522 nm (Figure 4b), i.e. there is a difference of about 16 nm. The experimentally determined fluorescence peak is at 535 nm with a shoulder at 516 nm (Figure 2), i.e. there is a difference of 19 nm. The close agreement between the predicted band positions and the calculated ones gives us ground to consider that the observed fluorescence band is in fact a superposition of the bands of tautomers **B** and **C**. This indicates that in 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol, a double proton transfer in two sequential reactions in the first excited singlet state occurs.

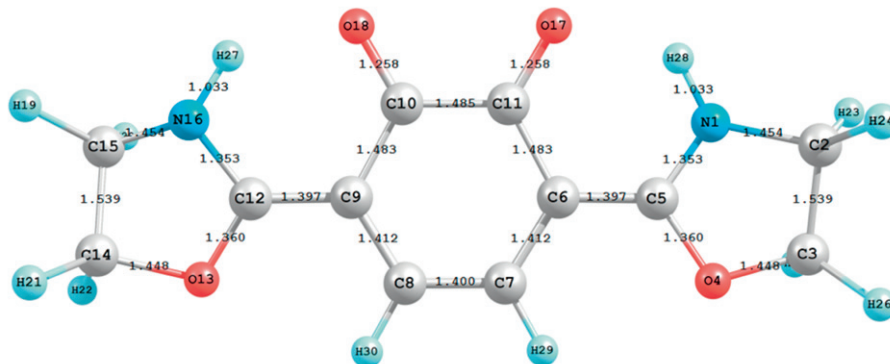
A



B



C



TS (A→B)

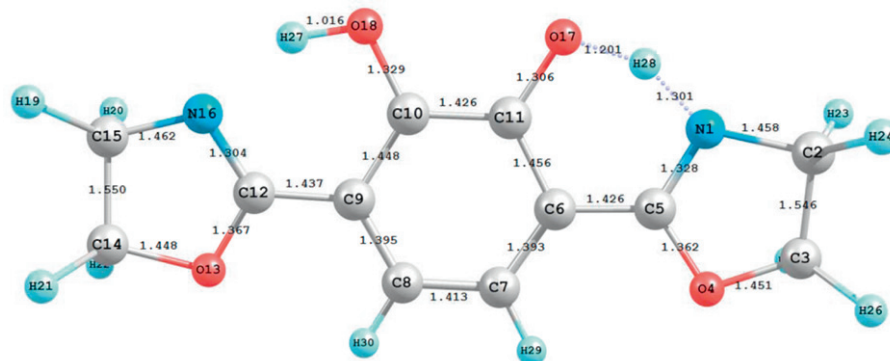


Figure 5. B3LYP/6-31G(d,p) optimized geometries of tautomers **A–C** of 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol and respective transition state structures for first excited state S_1 . All distances are in Å. The values in brackets for tautomer **A** refer to ground state S_0 .

TS (B → C)

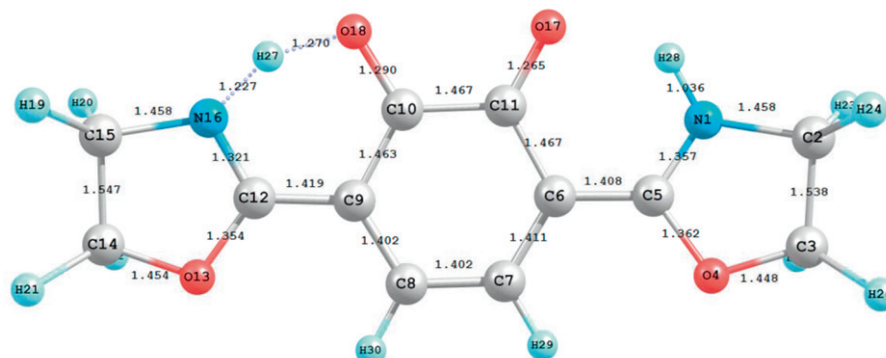


Fig. 5. (continued)

Acknowledgements

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