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Excited state intramolecular proton transfer of 2-hydroxy-1-naphthaldehyde semicarbazone: A combined fluorometric and quantum chemical study

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ABSTRACT

Excited state intramolecular proton transfer (ESIPT) of 2-hydroxy-1-naphthaldehyde semicarbazone (2HNS) has been studied in n-heptane and methanol solvents exploiting absorption, steady state and time-resolved fluorometric techniques. Experimental results reveal that although the intramolecular proton transfer (IPT) reaction does not take place in the ground state (S_0), the process is feasible in the lowest excited singlet state (S_1). *Ab initio* quantum chemical calculations have been carried out to judge the feasibility of the IPT process in the different electronic states. Density functional theory (DFT) has been used for the ground state calculations while those relevant to the lowest excited singlet state have been performed exploiting the time dependent density functional theory (TDDFT) using the B3LYP functional at 6-31G** level. The distances of the transferable hydrogen from the oxygen atom (wherefrom it is dislocated during the IPT reaction) as well as the nitrogen atom (to which it gets attached) have been taken as the independent reaction coordinates. The calculations reveal that either of these two parameters may be used to monitor the progress of the prototropic process since both lead to the same prototropic species passing through the same transition state. Simulation of the potential energy curves (PECs) and potential energy surfaces (PESs) leads to visualize the advancement of the reaction. Calculations imply that formation of the tautomer in the S_0 state leads to endothermicity, while the process is exothermic in the S_1 state. The calculated activation energy (E_{act}) of the process also decreases in the excited state. Thus, although the reaction is not feasible in the ground state, both the thermodynamic (ΔH) and the kinetic (E_{act}) factors favor the prototropic process to occur in the S_1 state. This article reveals that any of the suitably and logically chosen structural parameters giving the same value of the reaction parameters and resulting in the same transition state may serve as the reaction co-ordinate.

1. Introduction

Photoinduced electron transfer and proton transfer are the fundamental processes in the realm of photochemistry. Extensive interest has been shown by the photoscientists in studying excited state inter and intramolecular proton transfer (ESPT and ESIPT respectively) reactions owing to, in particular, their simplicity and diverse applications [1–4]. The pioneering works of Weber, Förster and Weller opened a new vista in this arena [5–7]. When either the acidic or basic part of the same molecule becomes stronger acid or base in the excited state, proton transfer takes place in the excited state to form a phototautomer. An intramolecular hydrogen bond formation between the two moieties facilitates the intramolecular proton transfer process [8]. In general, ESIPT is extremely fast occurring within picoseconds, and upon excitation the molecule passes to the potential well of the tautomeric species almost instantaneously and then relaxes vibrationally [9,10]. Such molecules often show dual emission, one corresponding to the normal emission from the locally excited species and the other from the tautomer, largely Stokes'-shifted for different ESIPT compounds [8,11]. The ESIPT process depends very much on the solvent polarity, proticity and pH of the medium [3,4,10–13].

The application of ESIPT reactions is manifold and it includes developments of ultraviolet stabilizers [14], laser dyes [15,16], LEDs [15], radiation hard scintillation counters [17], molecular energy storage [18], molecular switches [19], sensors [20], etc. ESIPT compounds are also used as fluorescent probes to study the homogeneous and biomimicking microenvironments [21,22].

Till date ample works have been carried out both experimentally and theoretically with a variety of molecular systems and the results have been compared and correlated [8,23–31]. The phenomenon of proton transfer in the excited states has often been established from the studies made on the thermochromic and photochromic properties of naphthalenic or other chromophoric moieties [27–31]. For example, esters of o-hydroxynaphthoic acids [28], 1-hydroxy-2-naphthaldehyde [26], benzothiazoles

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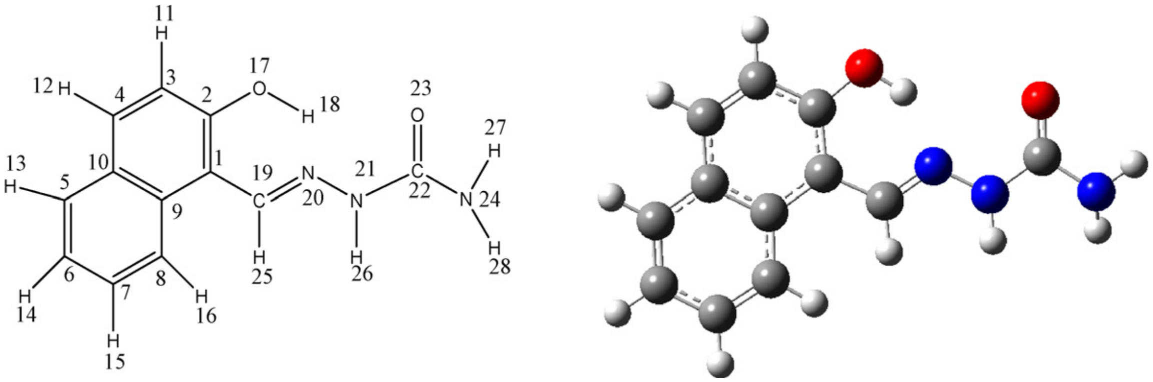


Scheme 1. Schematic and optimized structures of 2-hydxoxy-1-naphthaldehyde semicarbazone (2HNS).

[29], 2-hydroxy-1-naphthaldehyde [30], 1-hydroxy-2-naphthyl-s-triazines [31], etc. show ESIPT reaction. All these compounds exist in two different forms, normal and the tautomer, differing vastly in structure, charge density distribution, dipole moment and emission properties. The interesting observations of the ESIPT compounds have stimulated us to study the photophysics of 2-hydroxy-1-napthaldehyde semicarbazone (2HNS, Scheme 1), a newly synthesized semicarbazone derivative of the ESIPT probe 2-hydroxy-1-naphthaldehyde.

2HNS is a potentially useful analytical reagent (ligand) because it forms colored complexes with various metal ions. It is found to form chelates with metals like tin, iron, etc. with biological relevance. The semicarbazone derivatives have antimicrobial activity which is ascribed to their power of chelation with traces of metal ions present in the biological systems [32,33].

In the present article we report our precise investigation on ESIPT, based on the spectral and photophysical properties of 2HNS. The study is made in two solvents of widely different polarity and proticity. Steady state absorption and emission as well as time resolved fluorometric techniques are exploited for the purpose. The spectroscopic observations have been correlated with the theoretical results. Density functional theory (DFT) and time dependent density functional theory (TDDFT) are used to simulate the ground state and the excited state potential energy curves (PECs) respectively. The simulated potential energy curves reveal that the intramolecular proton transfer reaction is feasible, both thermodynamically and kinetically, in the S_1 state but not in the ground state. The study further establishes that either of the distances of the transferable hydrogen from the oxygen atom (wherefrom it is dissociated during the IPT reaction) as well as the nitrogen atom (to which it is attached) can be considered as the reaction coordinate to follow the course of the process.

2. Materials and methods

2.1. Experimental

2HNS (Scheme 1) was synthesized using the method mentioned elsewhere [32,33]. It was purified through recrystallization from ethanol. The solvents n-heptane and methanol were of UV spectroscopic grade (Spectrochem, India). Methanol was used as received but n-heptane was dried and made free of moisture by refluxing with sodium [34].

Shimadzu UV-2450 absorption spectrophotometer and Spex fluorolog-2 spectrofluorimeter were used for the absorption and emission studies respectively. Fluorescence lifetimes were determined from the time resolved intensity decays by the method of time-correlated single-photon-counting (TCSPC) using nano-LED excitation source at 370 nm and TBX-04 detector (both IBH, UK). The instrument response time was ~1 ns. The decays were analyzed using IBH DAS-6 decay analysis software. Goodness of fits was judged from the χ^2 criterion and visual inspection of the randomness of the residuals of the fitted function to the data. Throughout the study the sample concentration was kept low at $\sim 10^{-5}$ mol dm^{-3} in order to avoid aggregation and re-absorption effects. All experiments were performed with air equilibrated solutions at ambient temperature (300 K).

2.2. Computational procedure

The ground and excited state electronic calculations on 2HNS have been performed using Gaussian 03 suite of quantum chemical program [35]. We have used a combination of different quantum chemical methods and basis sets and found that the DFT-based calculations give the best output in terms of feasibility for carrying out the elaborate electronic structural calculations within a limited computational resource [26–28,36–39]. The ground state geometry of 2HNS has been obtained by full optimization of the structural parameters using DFT employing 6-31G** basis set. The geometry optimizations has been carried out using Becke's three-parameter hybrid functional B3 [40], with nonlocal correlation of Lee–Yang–Parr, LYP abbreviated as B3LYP [41]. The potential energy curve (PEC) for the ground state intramolecular proton transfer (GSIPT) process is constructed using the energies (E_g) at the B3LYP/6-31G** fully optimized geometries at different pre-fixed O–H distances over a wide range (0.85–2.3 Å) [26,36–39,42].

Though TDDFT method of calculation fails to optimize the geometries in the excited states, the excitation energies are obtained by vertical excitation of the optimized ground states (obtained at pre-fixed O–H distances) at the TDDFT/B3LYP/6-31G** level. The calculations yield the transition energies ($\Delta E_{i\to j}$) to the first excited singlet state. $\Delta E_{i\to j}$ corresponds to the excitation of an electron from the orbital ϕ_i (occupied in the ground state) to the orbital ϕ_j (unoccupied in the ground state). The energy of the excited state (E_j) is then calculated as $E_j = E_g + \Delta E_{i\to j}$. Several scholastic articles employing this theoretical approach have already been reported [22,23,25,26,30,36–39]. Making a rational compromise with the available computational resources, till now the time dependent density functional theory is accepted to be the most realistic and reliable method for calculating PE curves along the proton transfer coordinate. The intramolecular proton transfer reaction has been studied with reference to the interaction site model using the self-consistent field method [43].

The solvent stabilization of the various prototropic species in the different electronic states has been calculated from the solvation energy based on Onsager's continuum model [44,45]. Assuming that the solute molecule with a dipole moment μ_i in the ith electronic state is fully solvated, the solvation energy is given by

$$\Delta E_{solv.} = \frac{2\mu_i^2(\varepsilon_r - 1)}{a^3(2\varepsilon_r + 1)} \quad (1)$$

where ε_r is the bulk relative permittivity of the solvent and a, the cavity radius. We have taken the maximum molecular length of the optimized geometry (11.65 Å) as the cavity diameter for the present molecular system. It is pertinent to mention here that specific solvent interactions like hydrogen bonding, etc. have not been considered. The dipole moments of ground states are calculated at the DFT-B3LYP/6-31G** level while the excited state dipole moments are calculated using the configuration interaction singles (CIS) at the same level.

3. Results and discussion

3.1. Absorption and steady state emission studies

The absorption and fluorescence spectra of 2HNS in aprotic and non-polar solvent n-heptane and protic polar solvent methanol are presented in Fig. 1. In both the solvents, 2HNS exhibits structured absorption spectra. Broadly, there are two structured bands, one covering the range 300–330 nm and the other in the range 330–390 nm. There is not much difference in the absorption spectrum of 2HNS in the two solvents apart from a slight blue shift in methanol. This indicates that the ground state is more stabilized in the protic solvent and is ascribed to the intermolecular hydrogen bonding with the solvent molecules [30]. The similarity in the absorption spectra in the two solvents rules out the occurrence of the ground state intermolecular proton transfer (IPT) in either solvent since that should lead to the development of new band/s. The very low value of the ground state acid dissociation constant of the skeletal molecular system, 2-naphthol (pK_a = 9.51), with a similar –OH group makes the non-occurrence of the ground state IPT process reasonable in the solvents studied here [46].

As Fig. 1 reveals, in methanol 2HNS yields vibrationally structured emission with a maximum at ~440 nm and a hump at ~425 nm. This is assigned to the fluorescence from the normal form of 2HNS. In n-heptane, however, in addition to the said normal band, a much prominent and largely Stokes' shifted band is observed with a maximum at ~496 nm with a hump at ~525 nm. This low energy emission band shows a dramatic dependence on the protic character of the solvent and, consistent with the literature, is assigned to originate from the tautomeric species of 2HNS formed in the photoexcited state [26–31,36–39,47,48]. The forthcoming theoretical calculations indicate the possibility of a single tautomeric species for the present molecular system in which H_{18} is detached from O_{17} and is bonded to N_{20} (Scheme 1). Insignificant intensity of the tautomer fluorescence in methanol implies that stabilization of the normal form through intermolecular hydrogen bond formation with the probe in the protic solvents inhibits the formation of the tautomer. The noticeable red shift in the fluorescence band of the normal band in methanol relative to that in n-heptane is ascribed to an increased solvent stabilization due to the enhanced polarity of the species in the excited state. It is verified that the relative intensities of the normal to the tautomer emissions remain invariant with a change in the concentration of 2HNS in the concentration range of ~10^{-5} mol dm^{-3}. This supports the occurrence of the intramolecular proton transfer for the system.

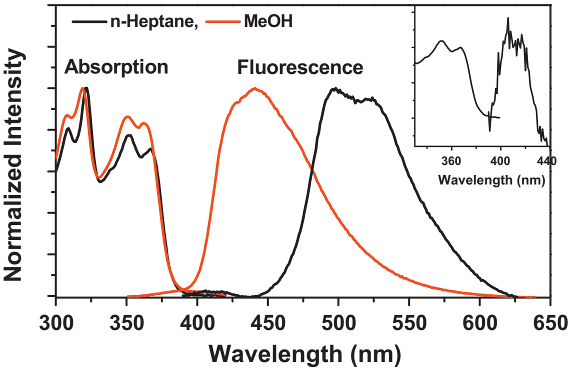


Fig. 1. Normalized absorption and emission spectral overlay of 2HNS in n-heptane (black) and methanol (red) to show the 0–0 transitions. Inset shows the amplified overlay in n-heptane. Fluorescence intensity of 2HNS in n-heptane is nearly double the intensity in methanol (φ_fs are determined to be 0.0074 and 0.0038 in the two solvents respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

From the intersections of the normalized absorption and emission spectra the zero–zero transitions are obtained at 392 nm and 388 nm in heptane and methanol solvents respectively. The small increase in the zero–zero transition energy in methanol compared to that in n-heptane is ascribed to a greater solvent stabilization of the ground state of the probe as described before.

Thus, the experimental results suggest the existence of ground state intermolecularly hydrogen bonded solvated species in methanol and intramolecularly hydrogen bonded species in n-heptane. The excited state scenario is, however, different. Presence of the two emission bands in the non-polar, aprotic solvent, like n-heptane, establishes the presence of both normal enolic species as well as the keto tautomeric species in the excited state. Observation of the much stronger low energy Stokes' shifted emission in heptane compared to the relatively weak high energy band suggests that formation of the tautomer is very much favored in the photoexcited state. Observation of the tautomeric fluorescence in n-heptane only (and not in methanol) suggests that the intramolecular hydrogen bonding of the closed conformer of 2HNS, prior to the formation of the tautomer, has an important role in the intramolecular proton transfer (IPT) process.

3.2. Fluorescence lifetime studies

Fluorescence lifetime measurement serves as an excellent tool to pinpoint the existence of different emitting species in the excited state of 2HNS. The fluorescence decays of 2HNS have been monitored in both the solvents at room temperature. In n-heptane both the normal (monitored at 420 nm) and the tautomeric (monitored at 540 nm) emission bands exhibit biexponential decays. Bi-exponential decays in both the emission positions in n-heptane suggest that there is a prototropic equilibrium between the normal and the tautomeric forms of 2HNS. Interestingly, in methanol the normal emission (monitored at 440 nm) exhibits a single exponential decay. The fluorescence decays of 2HNS in the two solvents are shown in Fig. 2. The deconvoluted fluorescence lifetime data of 2HNS are presented in Table 1. We could not see any growth for the tautomer emission indicating that the ESIPT process is very fast for the present system and is beyond the detection limit of our set-up (~1 ns). This is consistent with many ESIPT systems where the transferable proton is structurally in a favored position through intramolecular hydrogen bonding prior to the proton transfer [8].

Table 1
Fluorescence lifetimes of 2HNS in n-heptane and methanol media.

Solvent	λ_{em} (nm)	a_1	τ_1 (ns)	a_2	τ_2 (ns)	χ^2
n-Heptane	540	0.96	0.31	0.04	2.53	1.07
	420	0.99	0.1	0.01	2.39	1.09
Methanol	440	1	0.08	–	–	1.18

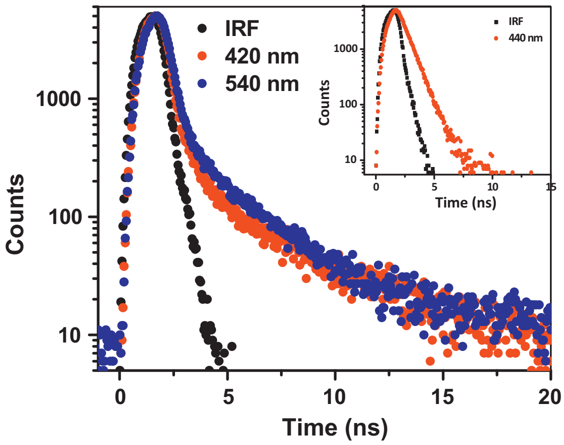


Fig. 2. Decay profiles of 2HNS in n-heptane monitored at 420 nm (red) and 540 nm (blue) and in methanol (inset) monitored at 440 nm (λ_{exc} = 370 nm). The sharp profiles in the left show the instrument response function (IRF). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 2
Comparison of the calculated ground state optimized geometric parameters of 2NIH with the crystallographic data [49].

Molecular parameters	Calculated (Å)	Crystal data (Å)
$C_2–O_{17}$	1.337	1.358
$C_2–C_1$	1.411	1.380
$C_1–C_{19}$	1.448	1.451
$C_{19}–N_{20}$	1.293	1.279
$N_{20}–N_{21}$	1.361	1.388
$N_{21}–C_{22}$	1.383	1.359
$C_{22}–O_{23}$	1.219	1.205

4. Quantum chemical calculations

As already mentioned, the ground state geometry optimization of 2HNS has been done using density functional theory (DFT) at the B3LYP/6-31G** level. Since, the crystallographic data of 2HNS is not available in literature hence to verify the reliability of our calculations we have extended the similar method of quantum chemical calculation to optimize the geometry for another analogous molecular system, namely, 2-hydroxy-1-naphthaldehyde methyl isonicotinoyl hydrazone (2NIH) (Scheme 2) for which the crystal structure is available in the literature [49].

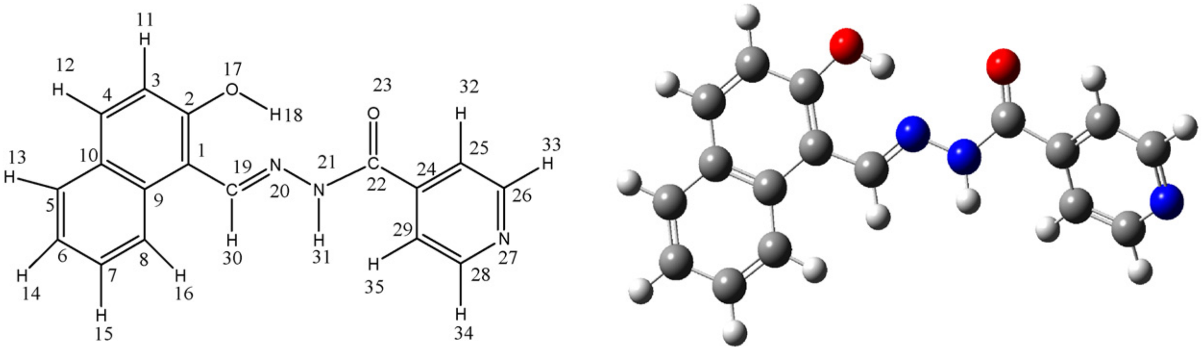
Table 2 compares the calculated ground state optimized geometric parameters of 2NIH with the literature crystallographic data. A good correspondence between the calculated parameters and the crystallographic data establishes the suitability and reliability of the method of our calculations. Table 3 presents the calculated optimized geometric parameters for 2HNS in the ground state.

Table 3
Optimized geometric parameters of 2HNS in the ground state (for structure of 2HNS *vide* Scheme 1).

Molecular parameters	Calculated data	
	(Å)	(°)
$C_2–O_{17}$	1.339	
$C_2–C_1$	1.409	
$C_1–C_{19}$	1.452	
$C_{19}–N_{20}$	1.291	
$N_{20}–N_{21}$	1.361	
$N_{21}–C_{22}$	1.398	
$C_{22}–O_{23}$	1.215	
$H_{18}–O_{17}–C_2$		109.24
$O_{17}–C_2–C_1$		123.67
$C_1–C_{19}–N_{20}$		121.31
$C_{19}–N_{20}–N_{21}$		119.13
$N_{20}–N_{21}–C_{22}$		118.09
$N_{21}–C_{22}–N_{24}$		112.02
$N_{21}–C_{22}–O_{23}$		123.81
$O_{23}–C_{22}–N_{24}$		124.15

Since, experiments provide sound support in favor of the excited state intramolecular proton transfer of 2HNS, construction of the potential energy curves (PECs) in the ground and the lowest excited singlet states has been undertaken. The distances of the transferable hydrogen (H_{18}) from the oxygen atom (O_{17}, wherefrom it is dissociated during the IPT reaction) as well as the nitrogen atom (N_{20}, to which it gets attached) have been considered as the independent reaction coordinates following the "distinguished coordinate" approach as proposed by Sobolewski and Domcke [36,38,50]. Fig. 3 depicts such PECs in S_0 and S_1 states where $O_{17}–H_{18}$ distance is taken as the reaction coordinate. In the figure panel (A) gives the potential energies of the system in vacuum and panel (B) gives the same along with those in n-heptane and methanol media. The solvation energies are calculated adopting Onsager's continuum model [23,44,45]. Inclusion of the stabilization energy due to the solvation in the medium, however, does not seem to change the picture qualitatively.

The simulation generates double well potentials in both the electronic states; one corresponding to the normal (enolic) and the other to the tautomer. However, there are obvious differences in the PECs of the two electronic states that can legibly describe the experimental observations in terms of the IPT process. The PECs reveal that in the ground state the global minimum rests on the normal form of 2HNS while the same corresponds to the tautomer form in the S_1 state. This suggests that in the ground state the most stable species is the normal form whereas in the photoexcited state it is the tautomer. In quantitative terms, in the ground state the nor-



Scheme 2. Schematic and optimized structures of 2-hydroxy-1-naphthaldehyde isonicotinoyl hydrazone (2NIH).

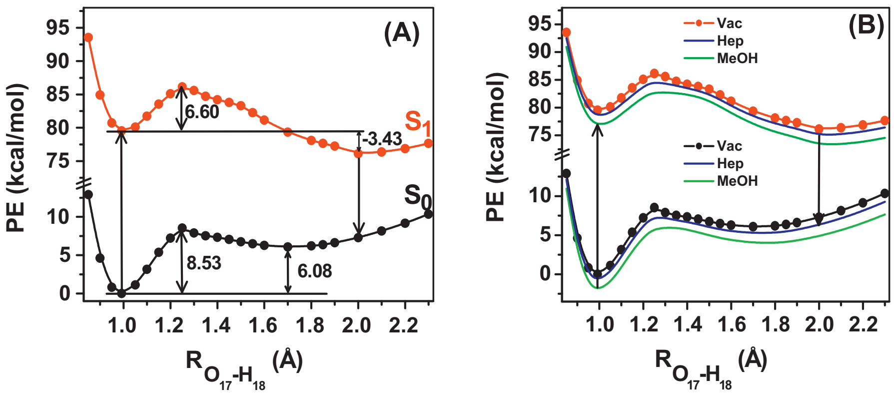


Fig. 3. Simulated PECs for the IPT process of 2HNS in S_0 and S_1 states in vacuum (A) and in vacuum as well as in the solvents n-heptane and methanol (B) using 6-31G** basis set at B3LYP level. In (B), legends show the respective media. The solvation energies are calculated following the method described in the computational procedure section.

mal form is more stable than the tautomer by 6.08 kcal/mol while in the S_1 state it is less stable than its counterpart by 3.43 kcal/mol. Thus, the intramolecular proton transfer reaction of 2HNS appears thermodynamically unfavorable in the ground state as the process leads to endothermicity. In the photoexcited state however, the process leads to exothermicity and seems plausible. The PECs also enlighten on the feasibility of the IPT reaction from the kinetic point of view. Fig. 3 reveals that in vacuum the activation energy for the IPT process in the ground state is 8.53 kcal/mol. The same is reduced appreciably in the S_1 state going in favor of the occurrence of the ESIPT in the excited state. Consideration of both the thermodynamic and the kinetic factors in the two electronic states, thus, implies that the IPT process does not occur in the ground state but it is feasible in the S_1 state; corroborating with the experimental observation.

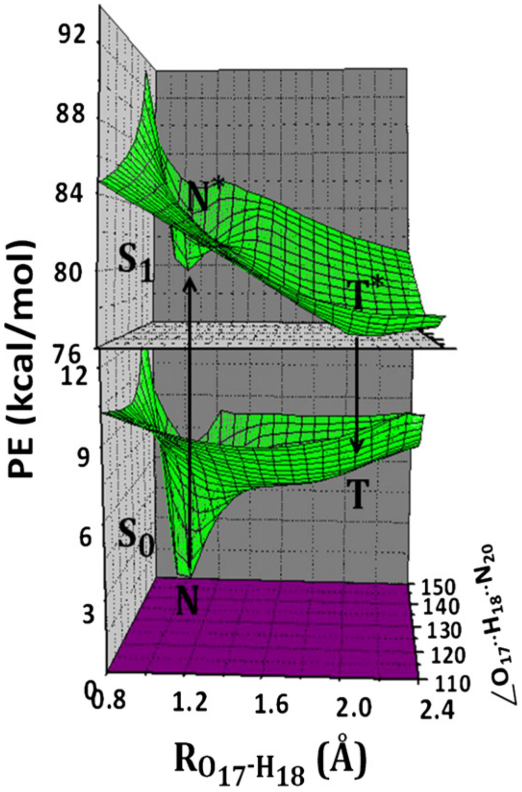


Fig. 4. Simulated potential energy surfaces for the IPT process of 2HNS in vacuum in its S_0 and S_1 states taking simultaneously O_{17}–H_{18} distance and $O_{17}\cdots H_{18}\cdots N_{20}$ angle as the reaction coordinates.

Potential energy surfaces for both the GSIPT and the ESIPT reactions have been generated in vacuum taking, simultaneously, the O_{17}–H_{18} distance ($R_{O_{17}-H_{18}}$ in Å) and the O_{17}–H_{18}–N_{20} angle as the reaction coordinates and are depicted in Fig. 4.

The thermodynamic and the kinetic parameters, namely, the heats of reaction (ΔH) and the activation energies (E_{act}) in the two electronic states in vacuum and in the two solvents studied, as calculated from the simulated PECs (Fig. 3), are presented in Table 4.

The other aspect relevant to the IPT process is the spectroscopic aspect. The energy difference between the ground and excited states of the normal (enolic) form of 2HNS is 79.54 kcal/mol that corresponds to the energy of a radiation of wavelength 359.4 nm. Taking the solvation energy into account, this comes to 360.6 nm and 362.4 nm in n-heptane and methanol solvents respectively. Considering the molecular structural aspect in mind, this should correspond to the zero–zero transition energy for the absorption. The experimental values of the zero–zero transitions of the normal form of the probe (see above) correspond satisfactorily with the calculated values. The slight discrepancy in the experimental and the calculated data is ascribed to the additional stabilization because of the specific effects that has not been taken into account during the calculation. The difference in energies between the excited and ground states of the tautomeric form of 2HNS are calculated to be 68.82 kcal/mol, 68.67 kcal/mol and 68.44 kcal/mol in vacuum, n-heptane and methanol respectively; corresponding to the fluorescence transitions wavelengths of 415.4 nm, 416.4 nm and 417.8 nm respectively in these media. Since the tautomeric form of the probe is non-existent in the ground state, it is not possible to get the zero–zero transition energy experimentally. Although the tautomer fluorescence in n-heptane is obtained at a much lower energy as compared to the fluorescence of the normal form, grossly consistent with that predicted from the PECs, the experimental value of the fluorescence maximum in n-heptane (496 nm) is quite off from the calculated transition energy. This discrepancy might be assigned to the specific interactions like intra- and inter-molecular hydrogen bonding, since the calculations as already discussed.

Table 4
ΔH and E_{act} for the IPT process of 2HNS in S_0 and S_1 states.

Electronic state	Heat of reaction (ΔH) (kcal/mol)	Activation energy (E_{act}) (kcal/mol)
S_0 (vacuum)	+6.08	8.53
(n-heptane)	+6.10	8.33
(methanol)	+6.12	8.03
S_1 (vacuum)	−3.43	6.60
(n-heptane)	−3.46	6.40
(methanol)	−3.50	6.10

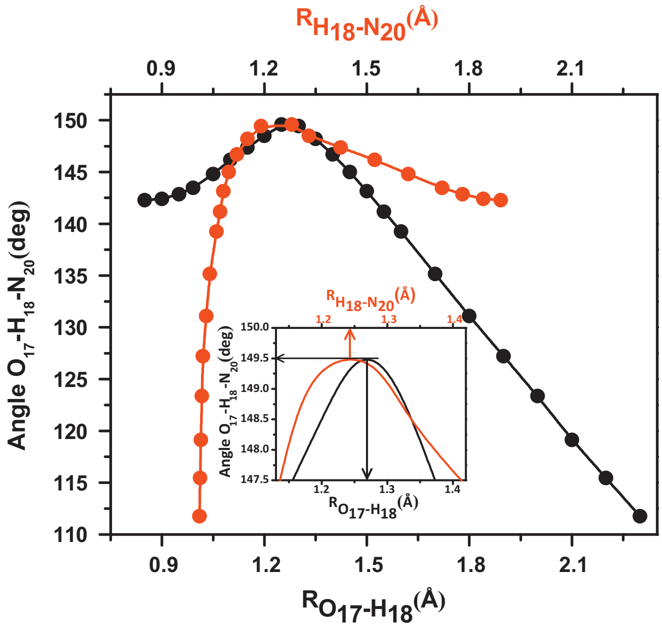


Fig. 5. Variation of $O_{17}\cdots H_{18}\cdots N_{20}$ angle with a change in the reaction coordinates, O_{17}–H_{18} and H_{18}–N_{20} distances. For details see text. Inset shows the magnified image of the same near the cross-over point.

There are options of choosing different structural parameters as the reaction coordinate to monitor the progress of the IPT process theoretically. We have given emphasis on establishing that any of the suitably and logically chosen parameters may depict the process properly and the calculated reaction parameters should be the same. This is the novelty of the present work. For the purpose we have chosen the two obvious and simplest parameters, namely, the distances of the transferable hydrogen from the oxygen atom (O_{17}–H_{18}), wherefrom it is dissociated during the IPT reaction and the nitrogen atom (H_{18}–N_{20}), to which it gets attached. We intended to see if selection of either of them leads to the same intermediate or not. For the purpose, the potential energy curves are computed to follow the progress of the ESIPT process taking the two said parameters independently as the reaction coordinates. The geometry of the corresponding intermediate is assigned from the angle O_{17}–H_{18}–N_{20}. Fig. 5 represents the variation of this angle with a change in either of the reaction coordinates, namely, O_{17}–H_{18} and H_{18}–N_{20} distances. It is observed that along with a change in the O_{17}–H_{18} or H_{18}–N_{20} distances other structural parameters undergo a change during the process of proton transfer [26,29]. In the course of the proton transfer process, O_{17}–H_{18} distance gradually increases while the H_{18}–N_{20} distance decreases passing through a transition state (TS). Thus, on plotting the angle O_{17}–H_{18}–N_{20} against the two assumingly independent reaction coordinates a crossover point between the two reaction trajectories is obtained at a O_{17}–H_{18} distance of 1.27 Å and H_{18}–N_{20} distance of 1.24 Å where the angle O_{17}–H_{18}–N_{20} is 149.5°. Approach from either side leads to the con-

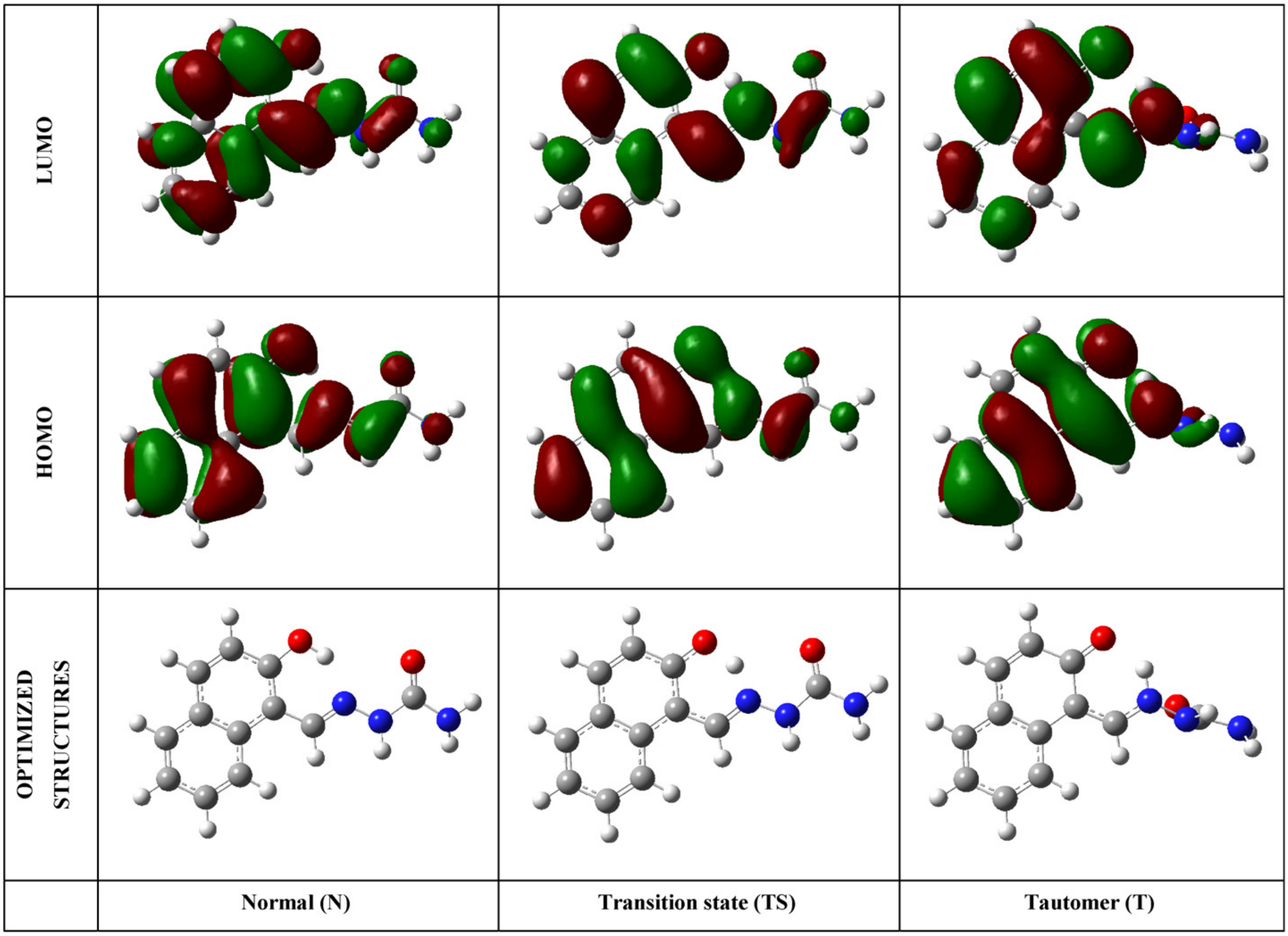


Fig. 6. Optimized structures and HOMO–LUMO pictures of the normal (N), transition state (TS) and the tautomer (T) of 2HNS.

stancy of the angle O_{17}–H_{18}–N_{20}, corroborating the uniqueness of the transition state (TS) (Fig. 5). This substantiates that either of the approaches visualize the progress of the IPT process although looking from different sides, and assures that one can safely monitor the course of the intramolecular prototropic reaction considering either of O_{17}–H_{18} or H_{18}–N_{20} distances as the reaction coordinate.

The experimental observations as well as the theoretical calculations, thus, assert that for the present molecular system (2HNS) the normal enolic form is the most stable form in the ground state and the intramolecular proton transfer process is exclusively an excited state phenomenon. The Mulliken charge distribution on the O_{17} and N_{20} centres further elucidate the fact. Assessment of the computed Mulliken charges on the optimized normal form of 2HNS shows a decrease in the charge density on the O_{17} atom upon photoexcitation from the ground to the excited first singlet state (-0.667 in S_0 to -0.658 in S_1). This is expected to reduce the binding strength between O_{17} and H_{18}. On the other hand, the negative charge density on the N_{20} atom increases upon photoexcitation, from -0.395 in S_0 to -0.408 in S_1. Both the effects work in the same direction to enhance the feasibility of the proton translocation from O_{17} atom to the N_{20} atom of 2HNS in the S_1 state and confirm the ESIPT reaction [26,29,39].

The supportive platform for the IPT reaction occurring in the excited state becomes more evident from the analysis of the electron density pictures of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) that provides a vivid representation of the electronic distribution on the normal form, the transition state and the tautomer form of 2HNS in the S_0 and S_1 states respectively (Fig. 6). It is apparent that the electronic distribution on the HOMO and LUMO are altered on being converted from the normal to the tautomeric form passing through the transition state (TS). For both the normal and the tautomeric forms HOMO and LUMO orbitals are of $\pi\pi^*$ character. As Fig. 6 depicts, the electron density on the HOMO in the normal form is concentrated on the O_{17} atom of the O–H group. In the LUMO, however, the electronic projection over the N_{20} atom is greatly enhanced at the cost of a reduction in the electron density on the O_{17} centre. This indicates a weakening of the O–H bond and a simultaneous enhancement in the basicity at the N_{20} centre suggesting a greater feasibility of the intramolecular proton transfer in the photoexcited state. Similarly, the HOMO–LUMO picture of the tautomeric form indicates non-existence of the tautomer in the ground state. Thus, the HOMO–LUMO orbital pictures imply that the intramolecular proton transfer is feasible in the excited state only but not in the ground state.

The novelty of the present article lies in establishing the excited state intramolecular proton transfer property of 2HNS, a newly synthesized bio-inorganic ligand. No information about the photophysical behavior of the said compound is available and extraction of such information would give a valuable addition to the scientific documentation. This article further enriches us with the idea that any of the suitably and logically chosen structural parameters giving the same value of the reaction parameters may serve as the reaction co-ordinate. For the present case, the course of the prototropic reaction may be monitored by choosing either R_{O-H} or R_{N-H} as the reaction coordinate.

The experimental observations supported by the theoretical calculations at the TDDFT level, thus infers that for 2HNS molecular system formation of the tautomer through IPT is exclusively an excited state phenomenon. The potential energy curve (PEC) along the proton transfer coordinate favors a low barrier tautomerization in the excited state leading to a largely red shifted emission band from the tautomer. Calculations suggest that both the thermodynamic (ΔH) and the kinetic (E_{act}) factors promote the IPT process in the S_1 state and not in the ground state.

5. Conclusions

The present work develops a comprehensive insight into the intramolecular proton transfer reaction of the biologically potent compound, 2-hydroxy-1-naphthaldehyde semicarbazone (2HNS), in n-heptane and methanol solvents based on both experimental findings and theoretical calculations at the TDDFT level. The experimental observations are well corroborated and rationalized from the calculations. The elaborate study reveals that:

2HNS exists in its enolic normal form in methanol, intermolecularly hydrogen bonded to the solvent, both in the ground and the excited state. In n-heptane, although it exists in the normal form in the ground state, upon photoexcitation it undergoes a rapid excited state intramolecular proton transfer (ESIPT) forming the tautomer species.

Quantum chemical calculations at the TDDFT level suggest that both the thermodynamic (ΔH) and the kinetic (E_{act}) factors favor the IPT reaction of 2HNS in the S_1 state and not in the ground state. A negative enthalpy of reaction (thermodynamic parameter) and an appreciable lowering in the activation barrier (kinetic parameter) in the lowest excited singlet state makes the IPT process feasible.

The calculations reveal that either of the O_{17}–H_{18} or H_{18}–N_{20} distances may be considered as the reaction coordinate to monitor the progress of the IPT reaction since both leads to the same prototropic species (normal and tautomer) and results in the same and unique transition state.

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References

[1] M. Kasha, Proton-transfer spectroscopy. Perturbation of the tautomerization potential, J. Chem. Soc. Faraday Trans. 2 (82) (1986) 2379–2392.

[2] A. Douhal, S.K. Kim, A.H. Zewail, Femtosecond molecular dynamics of tautomerization in model base pairs, Nature 378 (1995) 260–263.

[3] C.-L. Chen, C.-W. Lin, C.-C. Hsieh, C.-H. Lai, G.-H. Lee, C.-C. Wang, P.-T. Chou, Dual excited-state intramolecular proton transfer reaction in 3-hydroxy-2-(pyridin-2-yl)-4H-chromen-4-one, J. Phys. Chem. A 113 (2009) 205–214.

[4] M.P. Lukeman, P. Wan, A new type of excited-state intramolecular proton transfer: proton transfer from phenol OH to a carbon atom of an aromatic ring observed for 2-phenylphenol, J. Am. Chem. Soc. 124 (2002) 9458–9464.

[5] K. Weber, Über die enge beslehung der fluorescenzausloschung zur hemmung-photochemischer reaktionen, Z. Phys. Chem. B 15 (1931) 18–44.

[6] T. Förster, Fluoreszenzspektrum und wasserstoffionenkonzentration, Naturwissenschaften 36 (1949) 186–187.

[7] A. Weller, Fluorescence shifts of naphthols, Z. Elektrochem. 56 (1952) 662–668.

[8] S.J. Formosinho, L.G. Arnaut, Excited-state proton transfer reactions. II. Intramolecular reactions, J. Photochem. Photobiol. A: Chem. 75 (1993) 21–48.

[9] W. Frey, T. Elsaesser, Femtosecond intramolecular proton transfer of vibrationally hot molecules in the electronic ground state, Chem. Phys. Lett. 189 (1992) 565–570.

[10] J. Seo, S. Kim, S.Y. Park, Strong solvatochromic fluorescence from the intramolecular charge-transfer state created by excited-state intramolecular proton transfer, J. Am. Chem. Soc. 126 (2004) 11154–11155.

[11] F.A.S. Chipem, G. Krishnamoorthy, Comparative theoretical study of rotamerism and excited state intramolecular proton transfer of 2-(2′-hydroxyphenyl)benzimidazole, 2-(2′-hydroxyphenyl)imidazo[4,5-b]pyridine, 2-(2′-hydroxyphenyl)imidazo[4,5-c] pyridine and 8-(2′-hydroxyphenyl)purine, J. Phys. Chem. A 113 (2009) 12063–12070.

[12] S. Santra, G. Krishnamoorthy, S.K. Dogra, Excited-state intramolecular proton transfer in the anionic species of 2-(2′-acetamidophenyl)benzimidazole in aqueous medium, Chem. Phys. Lett. 327 (2000) 230–237.

[13] N. Sarkar, K. Das, S. Das, A. Datta, D. Nath, K. Bhattacharya, Excited-state intramolecular proton transfer of 2-(2′-hydroxyphenyl) benzimidazole in micelles, J. Phys. Chem. 99 (1995) 17711–17714.

[14] J. Catalan, F. Fabero, M.S. Guijarro, R.M. Claramunt, M.D.S. Maria, M.C. Foces-Foces, F.H. Cano, J. Elguero, R. Sastre, Photoinduced intramolecular proton

transfer as the mechanism of ultraviolet stabilizers: a reappraisal, J. Am. Chem. Soc. 112 (1990) 747–759.

[15] P. Chou, D. McMorrow, T.J. Aartsma, M. Kasha, The proton-transfer laser. Gain spectrum and amplification of spontaneous emission of 3-hydroxyflavone, J. Phys. Chem. 88 (1984) 4596–4599.

[16] A.U. Acuna, A. Costela, J.M. Munoz, A proton-transfer laser, J. Phys. Chem. 90 (1986) 2807–2808.

[17] R.M. Tarkka, X. Zhang, S.A. Jenekhe, Electrically generated intramolecular proton transfer: electroluminescence and stimulated emission from polymers, J. Am. Chem. Soc. 118 (1996) 9438–9439.

[18] T. Nishiya, S. Yamauchi, N. Hirota, M. Baba, I. Hanazaki, Fluorescence studies of intramolecularly hydrogen-bonded o-hydroxyacetophenone, salicylamide, and related molecules, J. Phys. Chem. 90 (1980) 5730–5735.

[19] G. Zhang, H. Wang, Y. Yu, F. Xiong, G. Tang, W. Chen, Diamond photodetector response to deep UV excimer laser excitation, Appl. Phys. B: Lasers Opt. 76 (2003) 677–681.

[20] Y. Wu, X. Peng, J. Fan, S. Gao, M. Tian, J. Zhao, S. Sun, Fluorescence sensing of anions based on inhibition of excited-state intramolecular proton transfer, J. Org. Chem. 72 (2007) 62–70.

[21] A. Stynik, M. Kasha, Excited-state intramolecular proton transfer as a fluorescence probe for protein binding-site static polarity, Proc. Natl. Acad. Sci. U.S.A. 91 (1994) 8627–8630.

[22] T. Ozturk, A.S. Klymchenko, A. Capan, S. Oncul, S. Cikrikci, S. Taskiran, B. Tasan, F.B. Kaynak, S. Ozbey, A.P. Demchenko, New 3-hydroxyflavone derivatives for probing hydrophobic sites in microheterogeneous systems, Tetrahedron 63 (2007) 10290–10299.

[23] P. Purkayastha, N. Chattopadhyay, Role of rotamerisation and excited state intramolecular proton transfer in the photophysics of 2-(2′-hydroxyphenyl)benzoxazole, 2-(2′-hydroxyphenyl) benzimidazole and 2-(2′-hydroxyphenyl)benzothiazole: A theoretical study, Phys. Chem. Chem. Phys. 2 (2000) 203–210.

[24] D.S. English, K. Das, K.D. Ashby, J. Park, J.W. Petrich, E.W. Castner Jr., Confirmation of excited-state proton transfer and ground-state heterogeneity in hypericin by fluorescence upconversion, J. Am. Chem. Soc. 119 (1997) 11585–11590.

[25] G. Krishnamoorthy, S.K. Dogra, Excited state intramolecular proton transfer in 2-(2′-hydroxyphenyl)-3H-imidazo[4,5-b]pyridine: effect of solvents, J. Lumin. 92 (2001) 91–102.

[26] R.B. Singh, S. Mahanta, S. Kar, N. Guchhait, Photo-physical properties of 1-hydroxy-2-naphthaldehyde: a combined fluorescence spectroscopy and quantum chemical calculations, Chem. Phys. 331 (2007) 373–384.

[27] H. Mishra, S. Maheshwary, H.B. Tripathi, N. Satyamurthy, An experimental and theoretical investigation of the photophysics of 1-hydroxy-2-naphthoic acid, J. Phys. Chem. A 109 (2005) 2746–2754.

[28] J. Catalan, J.C. del Valle, J. Palomar, C. Diaz, J.L.G. Paz, The six-membered intramolecular hydrogen bond position as a switch for inducing an excited state intramolecular proton transfer (ESIPT) in esters of o-hydroxynaphthoic acids, J. Phys. Chem. A 103 (1999) 10921–10934.

[29] W. Frey, F. Laermer, T. Elsaesser, Femtosecond studies of excited-state proton and deuterium transfer in benzothiazole compounds, J. Phys. Chem. 95 (1991) 10391–10395.

[30] P. Chowdhury, S. Panja, S. Chakravorti, Excited state prototropic activities in 2-hydroxy 1-naphthaldehyde, J. Phys. Chem. A 107 (2003) 83–90.

[31] M. Moriyama, M. Kosuge, S. Tobita, H. Shizuka, Excited-state intramolecular proton transfer followed by *cis–trans* isomerization of (1-hydroxy-2-naphthyl)-s-triazine derivatives, Chem. Phys. 253 (2000) 91–103.

[32] Sahadev, R.K. Sharma, S.K. Sindhwani, Stabilities of some bivalent transition-metal ions with 2-hydroxy naphthaldehyde semicarbazones and thiosemicarbazones in dioxane–water mixtures – a potentiometric study, Monatsh. Chem. 123 (1992) 1099–1105.

[33] Sahadev, R.K. Sharma, S.K. Sindhwani, Chelation behaviour of biologically activeo-hydroxy naphthaldehyde derivatives with bivalent metal ions in different solvents: a potentiometric study, Proc. Indian Acad. Sci. (Chem. Sci.) 105 (1993) 103–110.

[34] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, New York, 1980.

[35] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman Jr., J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.01, Gaussian, Inc., Wallingford, CT, 2004.

[36] S.P. De, S. Ash, S. Dalai, A. Misra, A DFT-based comparative study on the excited states intramolecular proton transfer in 1-hydroxy-2-naphthaldehyde and 2-hydroxy-3-naphthaldehyde, J. Mol. Str.: Theochem. 807 (2007) 33–41.

[37] S. Mahanta, R.B. Singh, D. Nath, N. Guchhait, Photophysical properties of 2,3,6,7-tetrahydro-8-hydroxy-1H, 5H-benz[*i*,*j*] quinolizine-9-carboxaldehyde: Evidence of excited state intramolecular proton transfer but not of intramolecular charge transfer process, J. Photochem. Photobiol. A: Chem. 197 (2008) 62–73.

[38] S. Mahanta, R.B. Singh, S. Kar, N. Guchhait, Evidence of coupled photoinduced proton transfer and intramolecular charge transfer reaction in para-N,N-dimethylamino orthohydroxy benzaldehyde: spectroscopic and theoretical studies, Chem. Phys. 354 (2008) 118–129.

[39] B.K. Paul, S. Mahanta, R.B. Singh, N. Guchhait, A DFT-based theoretical study on the photophysics of 4-hydroxyacridine: single-water-mediated excited state proton transfer, J. Phys. Chem. A 114 (2010) 2618–2627.

[40] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648–5652.

[41] C. Lee, W. Yang, R.G. Parr, Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 785–789.

[42] J. Catalan, J. Palomar, J.L.G. de Paz, Intramolecular proton or hydrogen-atom transfer in the ground and excited states of 2-hydroxybenzoyl compounds, J. Phys. Chem. A 101 (1997) 7914–7921.

[43] M.J. Paterson, M.A. Robb, L. Blancafort, A.D. DeBellis, Theoretical study of benzotriazole UV photostability: ultrafast deactivation through coupled proton and electron transfer triggered by a charge-transfer state, J. Am. Chem. Soc. 126 (2004) 2912–2922.

[44] L. Onsager, Electric moments of molecules in liquids, J. Am. Chem. Soc. 58 (1936) 1486–1493.

[45] C.J.F. Bottcher, Theory of electronic polarization, vol. 1, Elsevier, Amsterdam, 1983.

[46] D.D. Perrin, Dissociation Constants of Organic Bases in Aqueous Solution, Butterworths, London, 1965, Supplement, 1972.

[47] K.-C. Wu, Y.-M. Cheng, Y.-S. Lin, Y.-S. Yeh, S.-C. Pu, Y.-H. Hu, J.-K. Yu, P.-T. Che, Competitive intramolecular hydrogen bonding formation and excited-state proton transfer reaction in 1-[(diethylamino)-methyl]-2-hydroxy-3-naphthaldehyde, Chem. Phys. Lett. 384 (2004) 203–209.

[48] S. Tobita, M. Yamamoto, N. Kurahayashi, R. Tsukagoshi, Y. Nakamura, H. Shizuka, Effects of electronic structures on the excited-state intramolecular proton transfer of 1-hydroxy-2-acetonaphthone and related compounds, J. Phys. Chem. A 102 (1998) 5206–5214.

[49] D.R. Richardson, P.V. Bernhardt, Crystal and molecular structure of 2-hydroxy-1-naphthaldehyde isonicotinoyl hydrazone (NIH) and its iron(III) complex: an iron chelator with anti-tumour activity, J. Biol. Inorg. Chem. 4 (1999) 266–273.

[50] A.L. Sobolewski, W. Domcke, *Ab initio* study of excited-state intramolecular proton dislocation in salicylic acid, Chem. Phys. 232 (1998) 257–265.