

Relaxation of the excited *N*-(2-hydroxy benzylidene) aniline molecule: An *ab initio* and TD DFT study

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MS received 19 November 2009; revised 9 August 2010; accepted 20 October 2010

Abstract. The photophysical behaviour of *N*-(2-hydroxy benzylidene) aniline or most commonly known as salicylideneaniline (SA) has been investigated using the *ab initio* and DFT levels of theory. The quantum chemical calculations show that the optimized non planar enol (C_1) form of the SA molecule is the most stable conformer in the ground state and is marked by the twisting of the phenolic and anilino rings of the molecule. The geometry optimizations and the subsequent frequency calculations of the excited singlet electronic states of the various tautomeric forms of SA molecule were performed with the CIS level of theory. A detail theoretical investigation on the relaxation dynamics of the SA molecule has been presented. Possible explanation on the excitation wavelength dependence of the photochromic yield of the molecule is also reported.

Keywords. Excited state intramolecular proton transfer (ESIPT); time dependent density functional theory (TD DFT); photochromism; natural population analysis (NPA); molecular electrostatic potential (MESP); Potential energy curve (PEC).

1. Introduction

Photochromism, which is defined as a light-induced reversible colour change, occurs when a molecule, upon absorption of a photon, undergoes rapid tautomerization associated with an ultrafast change of the nature of the electronic excited state. Organic compounds, revealing photochromic properties have been a growing subject of contemporary research interest because of their potential applications as rewritable memory storage devices,¹ molecular machines,² optical switches, display sensors³ and in non linear optics.⁴ Most commonly studied photochromic compounds mainly involve photochemical ring closure–ring opening reaction, *cis-trans* isomerization or excited state intramolecular proton transfer (ESIPT). ESIPT is complementary to the excited state intermolecular proton transfer, the subject of photoexcited state proton transfer reaction. Understanding of the ESIPT process has invoked colossal interest among the photo physicists because of its applications in the development of laser dyes,⁵ photo

stabilizers⁶ and scintillation counters.⁷ Moreover, ESIPT reactions are used as optical probes for biomolecules⁸ and in the investigation of biological environment.⁹ The ESIPT reaction occurs in the molecular systems where the closed proximate proton donor and acceptor groups are connected in general by a six-member hydrogen bond network. Aromatic anils are a typical class of photochromic materials involving both ESIPT and *cis-trans* isomerization to form an orange-red coloured photoproduct from the colourless molecules upon UV radiation. *N*-(2-hydroxy benzylidene) aniline or most commonly known as salicylideneaniline (hereafter SA) is the simplest compound of aromatic anils that is known to possess both the above mentioned properties.

The photochromism of SA has been known for more than 20 years,^{10–15} but understanding the dynamical aspect of the photochromic mechanism and the formation of possible intermediate structures in the process are still not clear. Almost all the existing literatures^{11,12,14–20} agree the deactivation from the first excited state enol conformer of the molecule and the vibrationally hot *cis-keto* tautomer as the

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common precursor to form the vibrationally cold fluorescing state and the final photoproducts. However, despite of theoretical and experimental investigations, the exact route of relaxation of excited SA molecule is not clearly understood. Moreover, the rationale concerning the excitation wavelength dependence photochromic product^{15,21} has not been explained and needs to be investigated in more detail. Few theoretical calculations have been published to explain the phenomenon regarding the nature of excited common precursor and the photochromic transient.^{19, 20} In this paper, we report a detailed theoretical investigation on the relaxation dynamics of the SA molecule. Possible explanation on the excitation wavelength dependence of the photochromic yield of the molecule, as suggested by Rosenfeld *et al*²¹ is also presented here.

2. Theoretical calculations

The theoretical calculations were carried out using Gaussian 03 suit of program.²² Optimization of the ground state geometries of the enol and the keto forms of the SA molecule and the calculations of the vibrational frequencies for the respective optimized structures were done by *ab initio* Restricted Hartree-Fock (RHF) and density functional levels of theory. The Pople split valance basis set with polarization function 6-31G(d,p) and with added diffused function 6-31+G(d,p)²³ were applied for the *ab initio* and DFT calculations. The B3LYP i.e. Becke three hybrid exchange²⁴ and Lee-Yang-Parr correlation functional (LYP)²⁵ were utilized in the DFT calculations in conjunction with the same basis set as used for the *ab initio* calculations. Information pertaining to the ESIPT of the SA molecule was obtained by calculating the Franck Condon (here after FC) transition energies for the HF/6-31+G(d,p) and 6-31G(d,p) optimized ground state structures at the Configuration Interaction Single (CIS)/6-31+G(d,p) and 6-31G(d,p) level of theory. FC transition energies for excited enol and excited keto forms of the molecule were also calculated with the TD DFT level of theory at the optimized B3LYP/6-31+G(d,p) and 6-31G(d,p) level ground state geometries. The strength of the intramolecular hydrogen bonding of the enol (C₁) form of the SA molecule was estimated from the difference in SCF energies between the optimized molecular structure of the enol (C₁) form of the SA molecule with hydroxy group rotated by 180° and the energy of optimized enol (C₁) form of

the molecule in ground state using both the *ab initio* and DFT calculations.

The TD DFT calculations can not be applied to accomplish the optimized geometries of the excited state/states of the molecule using Gaussian 03.²² The geometry optimizations and the subsequent frequency calculations of the excited singlet electronic states of the various tautomeric forms of SA molecule are thus performed with the CIS level of theory. In the process of geometry optimization for the fully relaxed or tight criterion method, convergence of all the calculations and the absence of imaginary values in the wave numbers confirmed the attainment of local minima on the potential energy surface. For a quantitative understanding of the transition state (TS), standard static quantum chemical technique has been used.²⁶

The excited state optimized geometries were used to perform single point calculations with the aid of HyperchemTM 8.03 software²⁷ using 6-31G(d,p) basis set in order to visualize the total electron density contour maps and 2D and 3D molecular electrostatic potential isosurface. Molecular structures, as obtained from *ab initio* calculations in the ground and in the excited states were visualized using Molden 4.1 software.²⁸

3. Results and discussions

3.1 Ground and excited singlet low lying state of the various forms of SA molecule

The geometry optimization under fully relaxed condition of the different forms of SA molecule exhibit preferential stability with the twisting of the two (ca. phenolic and anilino) rings in the electronic ground state. The ground state molecular structures of the enol (C₁), *cis-keto* (C₁), and *trans-keto* (C₁) forms of the SA molecule optimized under completely relaxed condition are shown in figures 1a–c. The ground state geometries at the global minima of the potential energy surface of the various forms of SA molecule as obtained from the *ab initio* calculations using 6-31+G(d,p) [6-31G(d,p)] basis set divulge that the anilino ring of the enol (C₁) conformer is found to be twisted by 45° [44°] with respect to the plane containing the phenolic ring in conjugation with the atoms C8N2C1C3. This result is in accordance with the theoretical prophecy as reported by Zgierski *et al*¹⁹ and also from the X-ray crystallographic data reported elsewhere^{10,29} For *cis-keto*

(C_1) and *trans*-*keto* (C_1) forms of the SA molecule, the corresponding twisting angles are 31° [29°] and 152° [153°] respectively. The results of the ground state DFT calculations predict the corresponding torsional angles as 36° [35°] for enol (C_1), 7° [7°] for *cis*-*keto* ($C_1 \sim C_S$) and 163° [176°] for *trans*-*keto* ($C_1 \sim C_S$) conformers. However, DFT calculations predict somewhat smaller torsion of the anilino ring in the enol (C_1) form and a practically quasi planar *cis*-*keto* (C_S) and *trans*-*keto* (C_S) forms of the molecule. These results are in accordance with the report of Zgierski *et al.*¹⁹

The ground state energies for the different conformers of the SA molecule at their respective optimized geometries as obtained from *ab initio*/DFT calculations reveal that enol (C_1) form of the SA

molecule is the most stable one with energy ~ 0.36 [0.38]/ 0.20 [0.21] eV, as obtained using 6-31+G(d,p) [6-31G(d,p)] basis set, lower than that of the *cis*-*keto* (C_1) form. The *trans*-*keto* (C_1) form of the molecule is at 0.32 [0.32]/ 0.46 [0.48] eV higher in energy than the *cis*-*keto* (C_1) form.

A distance of < 2 Å between the donor and the acceptor atoms of the excited molecules is expected to favour the migration of proton resulting in the ESIPT process to spawn a phototautomer in the excited state.³⁰

Since the experimental manifestation of the FC transition energy is frequently associated with the absorption maximum, thus these FC excitation energies are compared with the maximum of absorption in the absorption spectra. However there is a difficulty in direct comparison with the experimental spectra as the theoretical data correspond to the isolated molecule, whereas the absorption spectra of the SA were recorded in solution medium.¹⁸ Hence the theoretical results are compared with the experimental results performed in aprotic non polar solvent. In cyclohexane, the absorption maximum was recorded to be around 350 nm.¹⁸ Excitation energy as obtained from CIS/6-31+G(d,p) [6-31G(d,p)] level of calculation is high ~ 5.12 [5.21] eV compared to the experimental results for the S_1 state of the enol (C_1) form of the SA molecule but the TD DFT calculation at the B3LYP/6-31+G(d,p) [6-31G(d,p)] optimized geometry yields the energy of 3.63 [3.65] eV for the same, which is in good agreement with the experimental value of 3.7 eV.^{31,32} Vertical excitation energies for the different conformers as estimated from *ab initio* and TD DFT calculations are shown in table 1.

The optimized structural parameters of the various forms of SA molecule in the ground and in the first excited singlet state (S_1) as obtained from *ab initio* calculations and that from the X-ray crystallographic data^{10,29} are presented in Table S1 (supplementary information). After optimization of the first excited singlet S_1 state for the enol (C_1) form of the SA molecule at CIS/6-31+G(d,p) [6-31G(d,p)] level, it acquires $n \rightarrow \pi^*$ character¹⁹ with phenolic ring almost perpendicular to the anilino one. The optimized structure is shown in figure 2. CIS calculations further predict that the energy of S_1 state lies 1.81 [1.81] eV above the ground state of the enol (C_1) form of the molecule. However, for the *cis*-*keto* form of the SA molecule, S_1 state can be described by $\pi \rightarrow \pi^*$ configuration.¹⁹ The optimized S_1 state of the *cis*-*keto* (C_1) form shows planar (C_S) structure

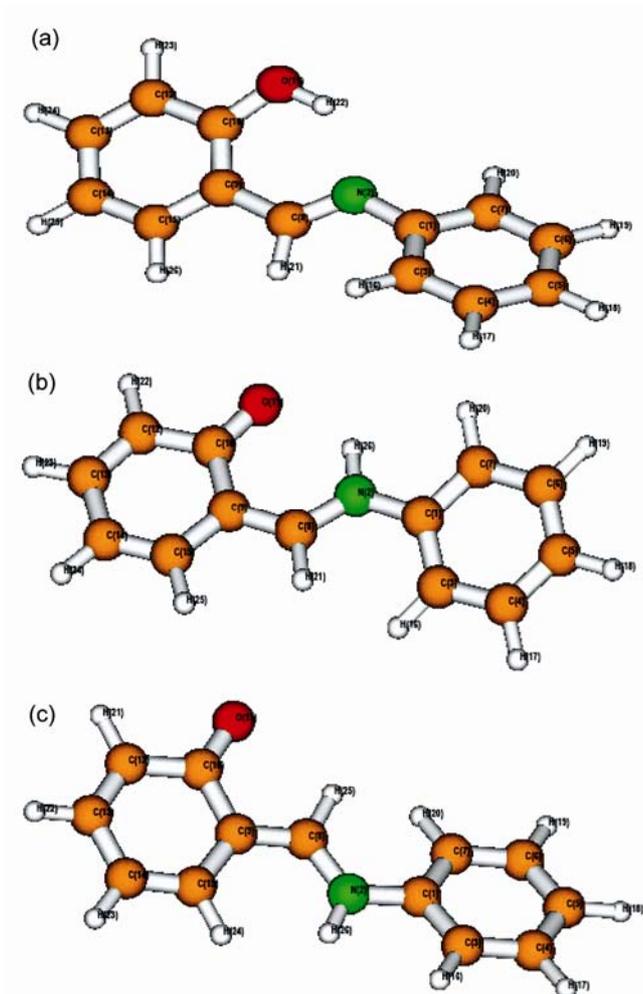


Figure 1. The ground state optimized molecular structure of the (a) enol (C_1), (b) *cis*-*keto* (C_1), and (c) *trans*-*keto* (C_1) forms of the SA molecule obtained from RHF/6-31G(d,p) level of theory.

Table 1. Franck condon excitation energies (ΔE^{FC}) calculated at CIS/6-31+G(d,p) [6-31G(d,p)] and TD-DFT/6-31+G(d,p) [6-31G(d,p)] levels of theory, and the excitation energies (ΔE^1) corresponding to the optimized geometry of S_1 state of the conformers at CIS/6-31+G(d,p) [6-31G(d,p)] level with respect to the optimized ground state energy of the enol (C_1) form of the molecule in eV.

Energy level	Method	Enol (C_1)	Enol (C_s)	<i>Cis-keto</i> (C_1)	<i>Cis-keto</i> (C_s)	Twisted <i>cis-keto</i> (C_1)	<i>Trans-keto</i> (C_1)
ΔE^{FC}	CIS	5.12 [5.21]	4.93 [5.07]	4.53 [4.70]	4.50 [4.64]	5.40 [5.55]	4.08 [4.99]
	TD-DFT	3.63 [3.65]	3.48 [3.56]	3.16 [3.24]	3.14 [3.24]	3.74 [3.85]	3.48 [3.52]
ΔE^1	CIS	1.81 [1.81]	3.95 [4.10]	–	3.95 [4.04]	2.36 [2.48]	–

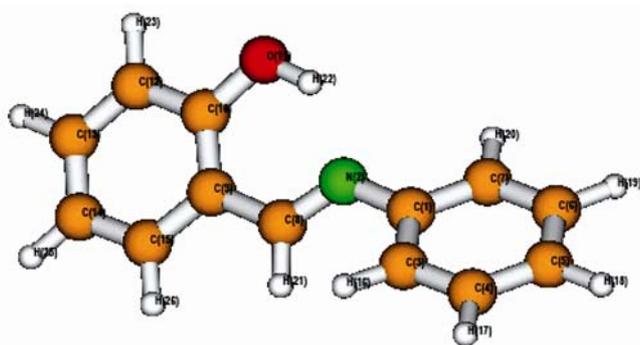


Figure 2. The optimized molecular structure of enol (C_1) form of SA molecule in the first excited singlet state obtained from CIS/6-31+G(d,p) level of theory.

which lies ~ 3.59 [3.66] eV above the ground state of the optimized *cis-keto* (C_1) form.

It is clearly seen from table S1 (supplementary information), that in comparison to the ground state enol (C_1) conformer, the most noticeable changes of 93° [90°] rotated conformer in the first excited singlet state (figure 2), are characterized by the decrease in O11–H22 bond length from 0.955 Å to 0.945 Å [0.954 Å to 0.944 Å] with the augmentation in N2–H22 bond length from 1.898 Å to 2.945 Å [1.889 Å to 2.084 Å]. These type of variations in the bond lengths and the nature of the S_1 (n, π^*) orbital,¹⁹ with perpendicular orientation of the two rings, are adverse for the transfer of proton from O11 to N2 atom. Hence, S_1 state with the planar structure of enol (C_s) conformer of the SA molecule has been identified by confining the CIS calculation under symmetry restriction on the initially optimized ground state molecular structure of the enol (C_s) form of the molecule. Vertical FC excitation energy of this state for enol (C_s) form of the SA molecule as obtained from CIS/6-31+G(d,p) [6-31G(d,p)] calculation is estimated to be ~ 4.93 [5.07] eV, which enthrallingly is found to lie very close to the energy

of the FC state of enol (C_1) conformer ~ 5.12 [5.21] eV of the SA molecule (table 1).

The molecular structure of enol (C_s) form in the S_1 state is marked by the increase in the O11–H22 bond distance and corresponding decrease in the N2–H22 bond length in comparison to the ground state enol (C_1) form of the SA molecule. The trend of change of the O11–N2 bond distance for the excited state of enol (C_s) form is comparable with the *cis-keto* (C_s) form of the molecule as depicted in table S1 (supplementary information). This increase in O11–H22 bond length and shortening of N2–H22 and O11–N2 bond distances between excited state enol (C_s) and *cis-keto* (C_s) form of the SA molecule embrace a possible intramolecular proton transfer in the excited state.³³

The strength of the intramolecular hydrogen bond was determined by rotating the phenolic OH group out of the H bonded enol (C_1) conformer in the ground electronic state and computing the energy difference between the closed and the open conformer. The value of the intramolecular hydrogen bonding energy as estimated from *ab initio*/DFT calculation is 0.52/0.60 eV using 6-31G(d,p) basis set.

The transition state (TS) for intramolecular proton transfer in the S_1 state has been evaluated for enol (C_s) to *cis-keto* (C_s) form of the SA molecule. Standard static quantum chemical technique has been used to locate the TS structure of the molecule using the keyword Opt=QST2 in the route section of the Gaussian 03 input.²⁶ Apart from this, there are indeed various elegant methods (ca. isotropic average frequency dependent polarizability, *ab initio* molecular dynamics simulations, etc.) reported elsewhere,^{34,35} which confirm the TS structure of the molecule. However, this manuscript is primarily focused on the dynamical aspect of the photochromic mechanism of the salicylideneaniline (SA) molecule and on the formation of possible intermediate struc-

Table 2. Optimized ground state energies (ΔE^0) in eV at RHF/6-31+G(d,p) [6-31G(d,p)], B3LYP/6-31+G(d,p) [6-31G(d,p)] levels and optimized excited state energies (ΔE^1) at CIS/6-31+G(d,p) [6-31G(d,p)] level of the various conformers of SA with respect to the optimized ground state energy of enol (C_1) form of the molecule.

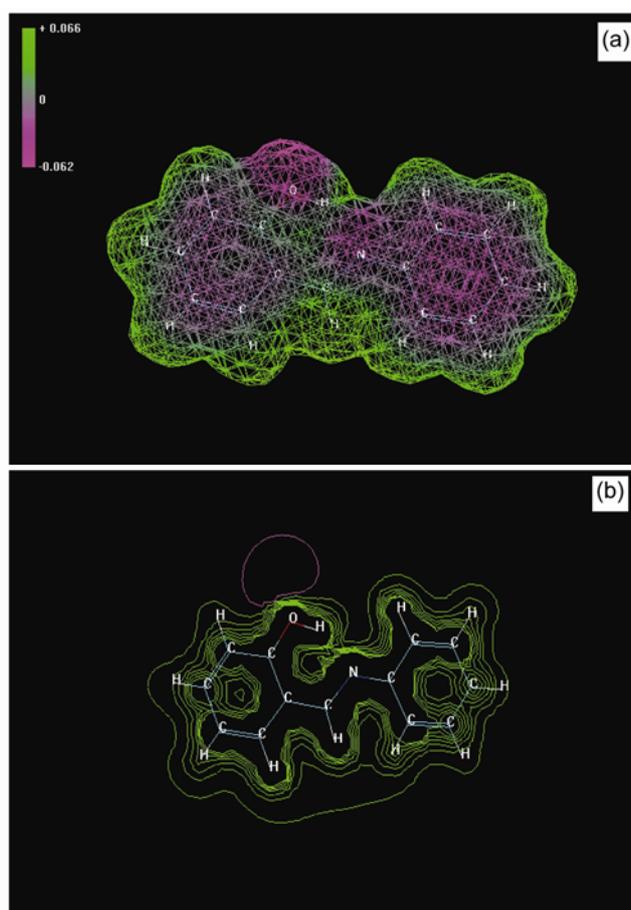
Energy level	Method/ basis set	Enol (C_1)	Enol (C_S)	<i>Cis-keto</i> (C_1)	<i>Cis-keto</i> (C_S)	Tw <i>cis-keto</i> (C_1)	<i>Trans-keto</i> (C_1)
ΔE^0	RHF/6-31+G(d,p) [RHF/6-31G(d,p)]	0.00	0.07 [0.07]	0.36 [0.38]	0.38 [0.39]	1.13 [1.16]	0.68 [0.70]
	B3LYP/6-31+G(d,p) [B3LYP/6-31G(d,p)]	0.00	0.03 [0.03]	0.20 [0.21]	0.20 [0.21]	1.03 [1.05]	0.66 [0.69]
ΔE^1	CIS/6-31+G(d,p) [CIS/6-31G(d,p)]	1.81 [1.81]	3.95 [4.10]	–	3.95 [4.04]	2.36 [2.48]	–

tures in the process. The molecular structure in the TS has been optimized through the calculation of the force constants. The results of the frequency calculation show only one imaginary vibrational frequency, which confirm that the optimized molecular structure represents the TS.²⁶ The energy disposition of the TS, the enol (C_S) and the *cis-keto* (C_S) forms of the molecule in the excited state (S_1) are shown in figure S1 (supplementary information). The CIS calculation of the TS has come out to be ~ 0.30 eV above the energy of the optimized S_1 excited enol (C_S) form of the SA molecule.

3.2 Discussion

Table 2 shows the ground state SCF energies at HF and DFT levels and the first excited state energies at CIS and TD DFT levels for the various tautomeric forms of SA molecule with respect to the optimized enol (C_1) ground state energy. TD/B3LYP/6-31+G(d,p) [6-31G(d,p)] Energies for S_1 state has been calculated at the optimized CIS level of theory. It is also observed that the energies of the various conformers calculated at TD DFT level are in the same order as that obtained from the CIS calculations. Here, we restrict our discussion with the results as obtained from HF and CIS level of theories only.

From energy data as shown in table 1, it is observed that the FC excitation energy for the enol (C_1) form is 5.12 [5.21] eV and for *cis-keto* (C_1) form of the molecule, it is 4.53 [4.70] eV. The FC state of the excited enol (C_S) form is ~ 0.19 [0.14] eV lower than that of the enol (C_1) form of the SA molecule. This theoretical result further connote the possibility of ES IPT from planar S_1 ($\pi \rightarrow \pi^*$) state of the enol (C_S) form to the S_1 ($\pi \rightarrow \pi^*$) state of the planar *cis-keto* form (C_S) of the SA molecule.

**Figure 3.** (a) 3D mapped MESP isosurface, (b) 2D MESP contour map of enol (C_S) form of SA molecule (Isosurface: 0.008).

Charge densities, computed using natural population analysis (NPA), on the atoms involved in the ES IPT process, reveal that there is a considerable change in charge density on O11 atom (-0.663465 e to -0.723896 e) while the charge densities on N2 and the related H atoms (N2: -0.770317 e to

-0.782459 e, H: $+0.421119$ e to $+0.4011468$ e) remain almost impervious in going from enol (C_S) to *cis-keto* (C_S) form of the SA molecule. The change of charge density of the O11 atom ($\Delta q = +0.06$ e) implies the transfer of charge to the N–H bond which is essential to form *cis-keto* (C_S) conformer from enol (C_S) conformer.²⁸ These results are in accordance with the 2D contour maps displaying the total electronic charge densities of the enol (C_S) and *cis-keto* (C_S) forms of the molecule shown in figure S2 (supplementary information) (a) and (b) respectively. Figures 3a and 4a show the 3D mapped isosurface of the molecular electrostatic potential (MESP) of the enol (C_S) and *cis-keto* (C_S) forms of the SA molecule. The corresponding 2D contour maps of the projected surface on the respective molecular planes are shown in figures 3b and 4b, respectively. Substantial increase in the negative MESP values particularly around the O11 atom are observed for the *cis-keto* (C_S) form in comparison to the enol (C_S) form of the SA molecule (figures 3 and 4). The modification of the MESP features in the

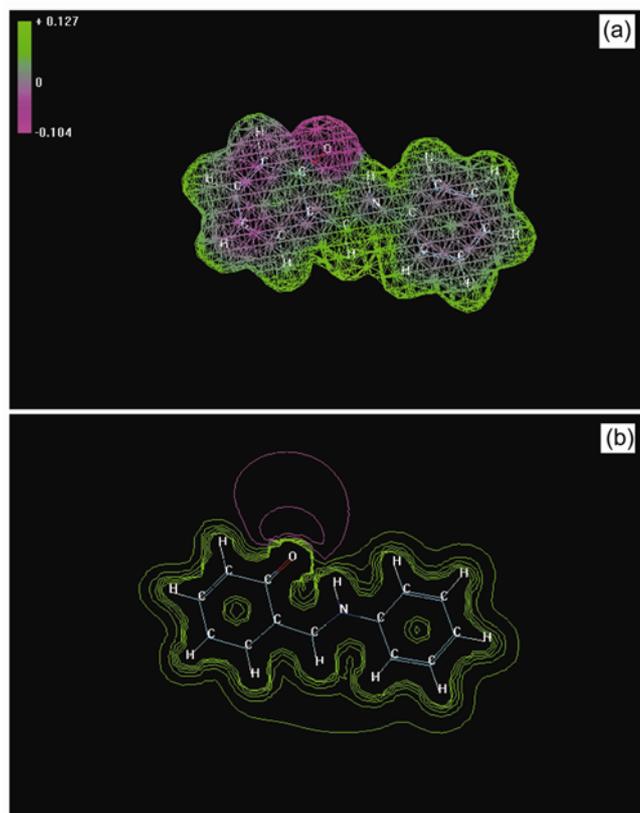


Figure 4. (a) 3D mapped MESP isosurface, (b) 2D MESP contour map of *cis-keto* (C_S) form of SA molecule (Isosurface: 0.008).

cis-keto (C_S) and the enol (C_S) forms of the SA molecule portend the ESIPT from enol (C_S) to *cis-keto* (C_S).³⁶

In order to comprehend the proton transfer process in further detail and to envisage the specific forms of the molecule involved in it, the adiabatic potential energy curves (PECs) of the various forms of the probe molecule in the ground state as well as in the excited S_1 state have been generated. They are shown in figure 5. The PEC for the ground electronic state and the first singlet excited state of the enol (C_1) and enol (C_S) forms of the SA molecule (figure 5) have been attained by varying the $r_{O11-H22}$ bond distance³⁷ and optimizing the structural parameter for each choice of $r_{O11-H22}$. The resulting potential energy profile for the ground state enol (C_1) form of the SA molecule [figure 5(i)] is characterized by an asymmetric double well, of which the former well is much more profound than the later. Considering this barrier energy ~ 0.65 eV as estimated from *ab initio* calculations, the possibility of ground state intramolecular proton transfer (GSIPT) from the enol (C_1) to the *cis-keto* (C_1) form of the molecule may be discarded. Moreover, the very weak intramolecular hydrogen bonding energy as estimated from *ab initio* and DFT calculations between N2 and H22 atoms of enol (C_1) conformer (vide supra) confirms the more stable ground state enol (C_1) form of the SA molecule. So the molecule

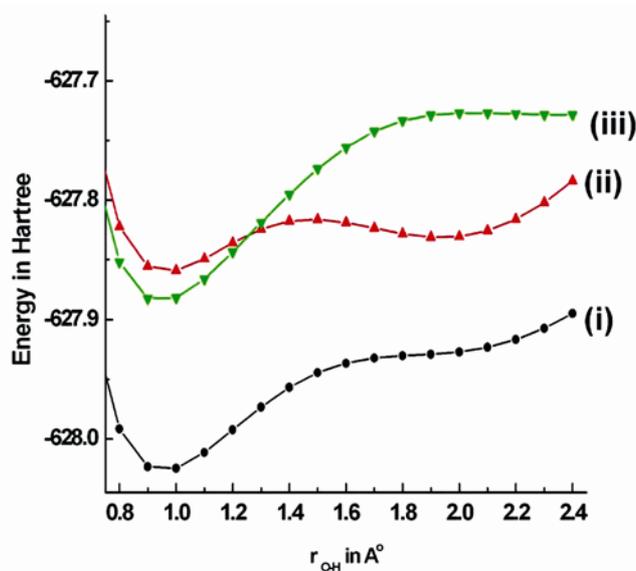


Figure 5. Potential energy curves of (i) enol (C_1) form of the SA molecule in ground state, (ii) enol (C_S) and (iii) enol (C_1) forms of the SA molecule in the S_1 state.

in the *cis-keto* (C_1) form can easily go back to the enol (C_1) form in the ground state.

PEC of enol (C_1) form in the first excited state [figure 5(iii)] is characterized by a single minimum. Absence of double well in the potential energy surface for the enol (C_1) form of the molecule in the S_1 state may also rebuff the possibility of the ESIPT from the enol (C_1) to the keto form of the molecule. Interestingly, the PEC for the enol (C_S) form of the molecule in the S_1 state exhibits two prominent minima, one is for the enol (C_S) and the other is for the *cis-keto* (C_S) form of the SA molecule [figure 5(ii)]. The enol (C_S) and the *cis-keto* (C_S) forms of the molecule are separated by an energy barrier of ~ 0.30 eV. This small energy barrier between the two forms of the molecule may pledge the concomitance of both the forms of the molecule in the first singlet excited state. The PECs of enol (C_1) and enol (C_S) forms of the molecule in the first singlet excited state are found to intersect [figure 5(ii) and (iii)]. The intersection may thereby indicate a possibility of internal conversion (IC).³⁸ The IC may result in the twisting of the enol (C_1) form of the molecule in the S_1 state.

Proton transfer from excited enol (C_S) to the *cis-keto* (C_S) form of the SA molecule however will lead to the population of hot vibrational states of *cis-keto* (C_S) form of the molecule. Experimental investigation on the transient absorption spectra¹⁷ of the molecule revealed the presence of a band at ~ 420 nm, which is owed to the proton transferred *cis-keto* (C_S) form of the SA molecule in the S_1 state. The time dependent spectral blue shift and narrowing of the 420 nm band at the early time delay (~ 4 ps) after excitation has been explained by the intramolecular vibrational relaxation process of *cis-keto* form of the molecule.^{39,40} Barbara *et al*¹⁵ proposed a general explanation of this blue shifted band as unrelaxed vibrationally excited state *cis-keto* form of the molecule. The slender blue shift of the transient absorption band at ~ 420 nm in the initial time delay after excitation, may harmonize to the transient absorption band of some other conformer. From the *ab initio* calculation, it is observed that the SCF energy of the FC state of twisted *cis-keto* (C_1) form of the molecule calculated at the CIS level of theory is slightly higher (table 1) than that of the S_1 *cis-keto* (C_S) form of the molecule. However, the TD DFT calculation predicts that the FC state of these two forms is nearly same. The results from the *ab initio* and TD DFT calculation may por-

tend that initially formed *cis-keto* (C_S) conformer of the molecule after ESIPT undergoes torsion around C8–N2 bond to form twisted *cis-keto* (C_1) conformer which may result in the blue shift of 420 nm band in the transient absorption spectrum.³⁹ However, the DFT calculation predicts the same FC energy levels for these two conformers. The time constant ~ 400 fs observed in the blue shift of 420 nm band may be due to the torsional relaxation of *cis-keto* (C_S) form resulting in the generation of the twisted S_1 state *cis-keto* (C_1) in which the two rings are almost rotated by 80° . It has been published that the life time of torsional relaxation usually occurs within a few hundred femtosecond.^{41,42}

This twisted *cis-keto* conformer (C_1) of the molecule after fully relaxed optimization takes a conformer which lies only 1.23 [1.32] eV above its ground state and 1.66 [1.78] eV above the *trans-keto* (C_1) ground state (table 2) as obtained from *ab initio*/6-31+G(d,p) [6-31G(d,p)] level of theory. This twisted *cis-keto* (C_1) form is then may be converted either to the ground state of twisted *cis-keto* (C_1) or to the ground state of energetically favourable final photo chromic product of *trans-keto* (C_1) form. The probability of radiationless transition from this twisted conformation to the ground state of *trans-keto* (C_1) form should be very high because of the structural advantage of this conformer. The presence of twisted forms as photochromic transient has been reported elsewhere.^{16,29,32} Recent study by Zgierski *et al*¹⁹ have shown that S_1 (π , π^*) state of planar *cis-keto* (C_S) form can undergo a twist of $\sim 80^\circ$ to bestow an energetically favourable conformation, which can easily be converted to the final photochromic product. But it is really enigmatic to understand the experimental fact concerning the reliance of excitation energy on the formation of the final photochromic product.^{15,21}

An effort has been made to offer an explanation for excitation energy dependence of the photochromic yield. Excitation energy dependence photoproduct suggests the involvement of vibrationally hot *cis-keto* (C_S) form in the formation of final photo product.^{15,17,21} If vibrationally hot *cis-keto* (C_S) tautomer is formed, higher vibrational energy is sufficient to rotate the molecule to alleviate the formation of twisted *cis-keto* (C_1) form of the molecule thereby increasing the rate of formation of the photoproduct.

There must occur a competition between the formation of this twisted *cis-keto* (C_1) form and the

process of stabilization of the planar *cis-keto* (C_S) form of the molecule in the S_1 (π, π^*) state. If the *cis-keto* (C_S) in S_1 state after proton transfer is formed near to cold fluorescing state, vibrational relaxation leading to fluorescing state should dominate over the process of making torsion of the molecule.

The most efficient channel for relaxation of excited SA molecule has been proposed. The entire scheme is shown in figure 6. The FC excited enol (C_1) tautomer of the molecule or very closely situated its planar analogue [ca. enol (C_S)], undergoes a tautomeric proton transfer to the *cis-keto* (C_S) form and partly stabilizes to highly non planar enol S_1 (n, π^*) state.

The planar *cis-keto* (C_S) form partly through vibrational relaxation stabilizes to cold fluorescing state and partly undergoes a torsional relaxation to a stable twisted conformer leading to photochromic product. Thus photochromic product consists of two

possible photochromic structures ca. ground state of twisted *cis-keto* (C_1) and the ground state of *trans-keto* (C_1) form. Depending on the nature of the experimental condition the relative contribution of the individual form appears.

4. Conclusions

The photo physical behaviour of the various isomeric forms of SA molecule in the ground and in first singlet excited state has been investigated using the *ab initio* and DFT levels of theory. The optimized structural parameters of the various forms of the SA molecule in the ground and the first excited singlet (S_1) states, as obtained from the quantum chemical calculations are in good agreement with the X-ray crystallographic data. The trend of change of the O11–N2, N2–H22 and O11–N2 bond distances discarded the possibility of ESIPT process from enol (C_1) to *cis-keto* (C_S) form and suggested the prediction of the planar structure of enol (C_S) conformer in the S_1 state as the precursor for ESIPT. The information as obtained from the PECs confirm the possibility of the ESIPT process from the planar enol (C_S) to *cis-keto* (C_S) form in the S_1 state and discard the possibility of GSIPT. The 3D mapped isosurface of the molecular electrostatic potential (MESP) and the 2D contour maps displaying the total electronic charge densities of the enol (C_S) and the *cis-keto* (C_S) forms portend the possibility of ESIPT from enol (C_S) to the *cis-keto* (C_S) form of the SA molecule. The possibility of the internal conservation (IC) has been established from the intersection of the PECs of enol (C_1) and enol (C_S) forms in the S_1 state. The most efficient route of the relaxation of excited SA molecule leading to the formation of the final product has been envisaged. Excitation energy dependence of the photochromic yield has also been explained.

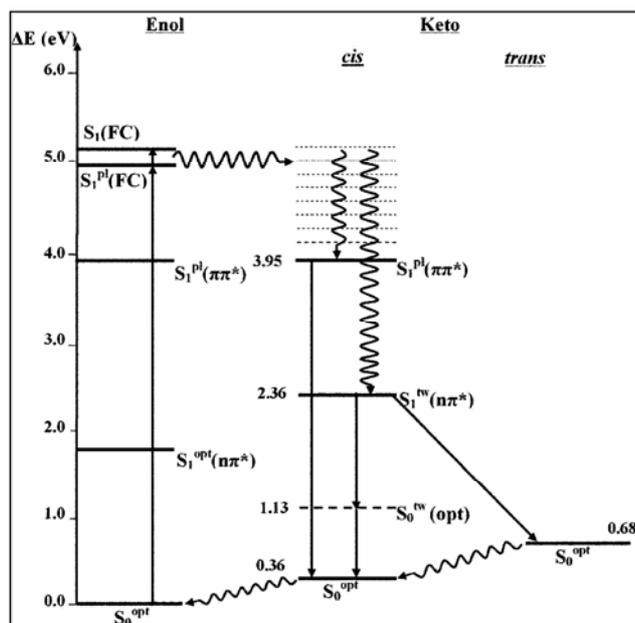


Figure 6. Energy levels of enol and keto tautomers of SA molecule as obtained from RHF/6-31+G(d,p) and CIS/6-31+G(d,p) levels of calculations and possible way of the production of photochromic products are shown in this diagram. The ‘FC’ level means the energy of vertical excitation of the C_1 and C_S enol tautomer. Superscripts ‘opt’, ‘tw’ and ‘pl’ denote the ‘optimized (C_1)’, ‘twisted’ and ‘planar’ structures respectively. Broken line energy level represented by S_0^{tw} (opt) is for the twisted *cis-keto* conformer. The energy of the optimized ground state of the C_1 enol form is taken as the reference level (table 1). Weavy arrows mark the radiationless transitions. Here all energies are in eV.

Supplementary information

For supplementary information table S1 and figures S1 and S2 see the website (www.ias.ac.in/chemsci).

Acknowledgements

Authors thank Dr. Nikhil Guchhait of Chemistry Department, University of Calcutta for fruitful discussion. Joydeep Chowdhury thanks University

Grants Commission (UGC), Government of India for financial support through the research project (MRP Project No: F. PSW-046/08-09 (ERO)).

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