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Photophysics of Schiff Bases: Theoretical Study of Salicylidene Methylamine

Joanna Jankowska,^[c] Michał F. Rode,^[a] Joanna Sadlej,^{*,[b]} and Andrzej L. Sobolewski^{*,[a]}

The proton-transfer reaction in a model aromatic Schiff base, salicylidene methylamine (SMA), in the ground and in the lowest electronically-excited singlet states, is theoretically analyzed with the aid of second-order approximate coupled-cluster model CC2, time-dependent density functional theory (TD-DFT) using the Becke, three-parameter Lee–Yang–Parr (B3LYP) functional, and complete active space perturbation theory CASPT2 electronic structure methods. Computed vertical-absorption spectra for the stable ground-state isomers of SMA fully confirm the photochromism of SMA. The potential-energy profiles of the ground and the lowest excited singlet state are

calculated and four photophysically relevant isomeric forms of SMA; α , β , γ , and δ are discussed. The calculations indicate two S_1/S_0 conical intersections which provide non-adiabatic gates for a radiationless decay to the ground state. The photophysical scheme which emerges from the theoretical study is related to recent experimental results obtained for SMA and its derivatives in the low-temperature argon matrices (J. Grzegorzek, A. Filarowski, Z. Mielke, *Phys. Chem. Chem. Phys.* **2011**, *13*, 16596–16605). Our results suggest that aromatic Schiff bases are potential candidates for optically driven molecular switches.

1. Introduction

Aromatic Schiff bases belong to a broad family of molecular systems whose photophysics is determined by the excited-state intramolecular proton-transfer (ESIPT) reaction.^[1–3] Photochromic Schiff bases^[4] represent a special group of ESIPT systems, whose depopulation routes of the excited molecule are particularly complex. Besides the PT reaction cycle, returning the system to its original state through the back-PT, a large portion of molecules may be trapped in the ground state as metastable photochromic species. The photochromism and the high photostability typical for ESIPT systems, opens the prospects of their possible applications in optically driven molecular memories and switching devices.^[1] The search for molecular switches based on light-induced conformational changes prompted by the ESIPT reaction is drawing special attention^[2,5–12] since the theoretical proposition of a long-distance intramolecular hydrogen-atom transfer due to this phenomenon.^[1]

Despite of its compact size, very little is known about the photophysical behavior of one of the simplest aromatic Schiff base, the salicylidene methylamine (SMA). The double bond CH=N of SMA enables a coupling between the hydrogen bond and the aromatic π -electron systems of the phenyl ring. This in turn leads to a shortening of the H bond, which could be classified as a low-barrier hydrogen bond (LBHB).^[13] The flattening of the potential-energy surface (PES) in direction of the proton motion may result in an observable proton-transfer phenomenon. Indeed, the photoexcitation of the *cis*-enol form of SMA leads to the population of the lowest $\pi\pi^*$ excited singlet state, which is followed by a proton transfer along an intramolecular hydrogen bond OH...N and results in the formation of the *cis*-keto conformer on the excited-state PES (Scheme 1). The $S_1(\pi\pi^*)$ *cis*-keto tautomer may either isomerize to the photo-

chromic product, the *trans*-keto conformer, or it can return back to the initial ground-state *cis*-enol conformer by a thermal or photochemical process. The process of depopulation of the excited $^1\pi\pi^*$ of SMA is interesting and controversial not only due to the existence of few conformers of the enol and keto forms, but also because of the possibility of the conical intersections (CIs) with the ground state before or after proton transfer.

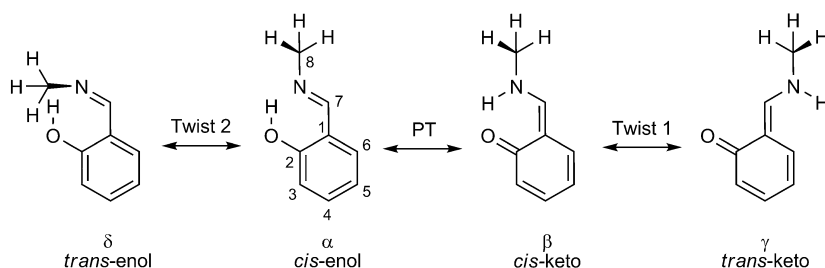
Only few papers are devoted to theoretical study on small Schiff bases. Zgierski and Grabowska^[14] showed that the enol and keto conformers of SMA are non-planar in the ground electronic state. The first optically allowed electronic transition leads to the $\pi\pi^*$ excited singlet state. It was found that the *cis*-keto form, more stable in the $^1\pi\pi^*$ state than the *cis*-enol, can decay to the $^1n\pi^*$ state, and through the internal conver-

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Scheme 1. Photophysically relevant structures of SMA.

sion may populate one of the *trans*-keto conformers. A small energy barrier for the ESIPT ($1.62 \text{ kcal mol}^{-1}$) was calculated on the PES of the first excited singlet state. The ESPIT reaction is thus possible and may occur between the planar *cis*-enol and *cis*-keto conformers.

The dynamic study of the photochromism of both model aromatic Schiff bases SMA and salicylideneaniline (SA) was performed with the aid of the Heidelberg multi-configuration time-dependent Hartree method (MCTDH) by Ortiz-Sanchez et al.^[7,8] in the ground and first excited singlet $\pi\pi^*$ states. The calculations predict a time scale of 11 fs for the hydrogen and 25 fs for deuterium transfer in SMA,^[7] while in SA it is estimated to 49.6 fs for the proton transfer.^[8] The proton-transfer reaction from the O to the N atom in the ground state is endoergic, with an energy barrier of $5.9 \text{ kcal mol}^{-1}$ and a reverse reaction-energy barrier of $0.9 \text{ kcal mol}^{-1}$.

Recently, the photoisomerization of the two simple aromatic Schiff bases, SMA and its chlorosubstituted derivative (SMAC), was thoroughly studied in low-temperature argon matrices by Grzegorzek et al.^[15] This work contains the first experimental results which demonstrate the occurrence of an ESIPT process and the excited-state rotation for keto and enol tautomers of the SMAC base. Twelve minima on the ground electronic state potential-energy surface of SMA were found by DFT/B3LYP/6-311++G(2d,2p) geometry optimization. However, only the product of the rotational isomerization reaction of the “native” enol tautomer, stabilized by an intramolecular O–H...N bond, was observed for SMA, but no ESIPT-related keto conformer was identified.^[15] The latter was observed for the SMAC derivative. These data provoke new questions about the mechanistic aspects of the phenomenon which govern and differentiate photophysics of those systems.

The main goal of our study herein is twofold: first, to describe the photoinduced isomerization of the aromatic Schiff base by calculations of the potential-energy-profiles of the ground state and the lowest excited singlet state along the minimum energy path, and second, to give an answer to the question, whether the Schiff base could play the role of a molecular switch driven by a photoinduced proton-transfer process. The outline of the article is as follows: In the Methods of Calculations Section we describe a brief account of computational details of the present study. Section 2 presents the results and the discussion of the calculations. Finally, a summary of our investigations is presented in Section 3, together with the conclusions.

Methods of Calculations

To explore the landscape of the ground (S_0) and first singlet excited state (S_1) of SMA, the MP2 and CC2 methods, respectively, were employed. The optimization and reaction-paths calculations were performed with the use of the cc-pVDZ basis set,^[16,17] which is known to be adequate to describe both organic molecules and their hydrogen-bonded systems.

The stationary structures were found by ascertaining that all harmonic frequencies were real. The vibrational zero-point energy (ZPE) was used for the correction of the computed relative electronic energy of the isomers. To compare our results with an earlier computational study,^[15] the relevant ground-state minima were additionally optimized at the DFT/B3LYP/cc-pVDZ level.

To confirm the presence of the S_1/S_0 CIs, as indicated by the CC2 method in a certain area of the PES, optimization of the CI geometry was performed with the aid of the CASSCF/cc-pVDZ method. The active space for these calculations consisted of six electrons distributed over six orbitals.

To check the credibility of the single-reference CC2 method, additional CASPT2 single-point calculations were carried out at the critical geometries of the energetic landscape (namely, at the equilibrium and transient structures) determined by MP2 (S_0) and CC2 (S_1) methods. The complete set of the CASSCF/CASPT2 results is presented in Tables 2, 3, and S1 in the Supporting Information along with the description of the active space used in these calculations.

The vertical electronic absorption spectra were calculated: 1) with the CC2 method^[18] and the aug-cc-pVTZ^[17] basis set for the MP2/cc-pVDZ-optimized geometry and 2) with TD-DFT/B3LYP and aug-cc-pVTZ basis set for the DFT/B3LYP/cc-pVDZ optimal structures. Since the CC2 method is the scheme of choice for the investigation of excited-state minimum-energy reaction paths, thanks to an effective implementation of analytical gradients, the TD-DFT method was used hereafter only to bridge our results with the previous DFT^[15] and TD-DFT^[14] results on SMA.

All geometry optimizations, reaction-paths, and UV absorption spectra calculations were carried out using the TURBOMOLE^[19] suite of programs, while the vibrational harmonic frequencies, CI optimizations and transition-state calculations were performed using the Gaussian 09 program,^[20] while for the CASSCF/CASPT2 calculations the MOLPRO package^[21] was used.

2. Results and Discussion

2.1. Photophysically Relevant Isomers of SMA

The nominal (enol-imino) tautomeric form of SMA, abbreviated as “ α -form”, is shown in Scheme 1 with the enumeration of the atoms indicated. The transfer of the proton from the hydroxyl group to the imino group results in the formation of an oxo-amino tautomer denoted as β -form in Scheme 1. This is expected to be the primary photophysical reaction for this molecular system as discussed above. The intramolecular reaction coordinate relevant for the PT process should describe the po-

sition of the mobile proton with respect to the oxygen and the nitrogen atoms along the hydrogen bridge. In the following we chose the OH distance as the reaction coordinate for the PT reaction.

The photoexcitation of SMA could, however, additionally trigger a torsional motion around the C₁C₇ or C₇N double bonds in the same way as it occurs upon the photoexcitation of systems, such as ethylene,^[22] stilbene,^[23,24] or azobenzene.^[25] This kind of motion plays a key role in photochemistry since it may lead to an intersection between the excited state and the ground state after twisting of the double bond by about 90°, leading to an ultrafast deactivation of the excited state through an internal conversion (IC) to the ground state. In fact, the importance of such torsions for the IC process in ESIPT-triggered systems has been suggested previously based on spectroscopic investigations.^[26,27] Recent calculations on salicylic acid^[2] closely related to SMA and on other ESIPT systems^[1,5,6,28] show that such a torsion actually may occur. Femtosecond experiments performed for one of these compounds [7-(2-pyridyl)indole] confirm these theoretical predictions.^[28]

For the case at hand, the β -form (*cis*-keto) of SMA, formed in the course of the ESIPT process, may further isomerize to the *trans*-keto conformer (γ -form in Scheme 1) by a twisting around the C₁C₇ double bond. The relevant intramolecular coordinate for this reaction is the C₂C₁C₇N dihedral angle which is expected to vary from 0° (β -form) to 180° (γ -form). Moreover, the nominal α -form (*cis*-enol) may also isomerize to the *trans*-enol by a twisting around the C₇N double bond (δ -form in Scheme 1). The relevant intramolecular coordinate for this reaction is the C₁C₇NC₈ dihedral angle.

The geometry optimization performed at the MP2/cc-pVDZ level showed that three of the four isomeric structures of SMA shown in Scheme 1, namely α , γ , and δ , represent minima on the ground-state PES, while the *cis*-keto (β -form) spontaneously relaxes to the nominal *cis*-enol (α -form) upon optimization. This is a qualitatively different result to previous DFT calculations^[7,15] in which the *cis*-keto (β) form was predicted as a stable minimum on the ground-state PES.

The γ and δ conformers represent local minima on the ground-state PES and are, at the MP2 level, less stable with respect to the global minimum (α -form) by 92.9 kJ mol⁻¹ (0.96 eV) and 58.2 kJ mol⁻¹ (0.60 eV), respectively. The ZPE correction changes these numbers only marginally, to 92.1 kJ mol⁻¹ for the γ -form and to 57.4 kJ mol⁻¹ for the δ -form. Optimization of the saddle points (SPs) between these structures and the global minimum results in a barrier of 201.4 kJ mol⁻¹ for the γ -form ($\alpha \rightarrow \gamma$ transition) and of 148.6 kJ mol⁻¹ for the δ -form ($\alpha \rightarrow \delta$ transition). These numbers change only marginally when calculated with the CASPT2 method performed at the MP2-optimized geometries (Table S1).

The vertical-absorption spectra computed at the CC2/aug-cc-pVTZ level for the three stable ground-state isomers of SMA are collected in Table 1 and are graphically visualized in Figure S1. Inspection of these data shows that there is a little difference between the absorption spectra of the α - and δ -forms, as it is expected in view of similar electronic conjugation pat-

Table 1. Vertical excitation energy (ΔE), oscillator strength (f) and electric dipole moment (μ) of the α -, γ -, and δ -forms of SMA, computed at the CC2/aug-cc-pVTZ level for the MP2/cc-pVDZ optimized structures.

α	State	ΔE [eV]	f	μ [Debye]
	S ₀	0.00 ^[a] 0.00 ^[b]	–	2.46
	¹ $\pi\pi^*$	4.11	0.1016	1.73
	¹ $n\pi^*$	4.98	0.0002	4.61
	¹ $\pi\pi^*$	5.16	0.1423	1.95
	¹ $\pi\sigma^*$	5.54	0.0025	5.88
	¹ $\pi\pi^*$	5.82	0.5157	2.02
	¹ $\pi\sigma^*$	5.96	0.0026	1.65
γ	State	ΔE [eV]	f	μ [Debye]
	S ₀	0.96 ^[a] 0.95 ^[b]	–	6.03
	¹ $n\pi^*$	2.93	0.0003	3.10
	¹ $\pi\pi^*$	3.05	0.2680	6.42
	¹ $\pi\sigma^*$	4.40	0.0009	6.87
	¹ $\pi\pi^*$	4.66	0.1332	5.23
	¹ $\pi\sigma^*$	5.06	0.0064	5.66
	¹ $\pi\sigma^*$	5.15	0.0001	9.51
δ	State	ΔE [eV]	f	μ [Debye]
	S ₀	0.60 ^[a] 0.60 ^[b]	–	1.26
	¹ $\pi\pi^*$	4.55	0.0535	2.55
	¹ $n\pi^*$	4.78	0.0024	2.37
	¹ $\pi\pi^*$	5.53	0.0500	4.93
	¹ $\pi\sigma^*$	5.81	0.0069	2.12
	¹ $\pi\pi^*$	6.00	0.0498	3.02
	¹ $\pi\sigma^*$	6.19	0.3193	1.47

[a] MP2/cc-pVDZ S₀ energy, relative to the global minimum (α). [b] MP2/cc-pVDZ S₀ ZPE-corrected energy, relative to the global minimum (α).

terns in both isomers, while the spectrum of the γ -form is significantly (by about 1 eV) shifted to the red. Thus, the photochromism of SMA is fully confirmed by our results.

For the above comparison we chose the results calculated at the CC2/aug-cc-pVTZ level. However, Table 2 illustrates the influence of the methods and the basis sets in vertical-absorption calculations. As it was expected, the CASPT2 vertical-excitation energies are lower than the CASSCF values in the same DZ basis set, while the CC2 vertical-excitation energies are slightly higher than the CASPT2 ones in this basis set. On the other hand, the change of the basis set from DZ to TZ and the addition of augmented functions in CC2 calculations yielded vertical-excitation energies that are all much closer to the experimental values.

The CC2/cc-pVDZ optimization of the first excited singlet state of SMA resulted in only two stable structures out of the four isomers shown in Scheme 1. These are the *cis*-keto and the *trans*-keto conformers (β - and γ -forms in Scheme 1). The *cis*-enol structure (α -form) spontaneously relaxes through the PT reaction into the *cis*-keto tautomer (β -form) in the course of the optimization, while the S₁ state of the δ -form crosses the ground state upon the spontaneous twisting around the C₇N double bond. The S₁-optimized minima of the β - and γ -forms are energetically almost degenerate to each other with an adiabatic energy of 2.88 and 2.94 eV, respectively. The possible

Table 2. Comparison of vertical-excitation energies [eV] of the α - and γ -forms of SMA (C_1 -symmetry), computed at the CASSCF^[a]/cc-pVDZ, CASPT2^[b]/cc-pVDZ, CC2/cc-pVDZ, CC2/aug-cc-pVDZ and CC2/aug-cc-pVTZ level for the MP2/cc-pVDZ optimized structures with available experimental data.^[29] Corresponding oscillator strengths calculated at the CC2/aug-cc-pVDZ level of theory.

	CASSCF/DZ ^[b]	CASPT2/DZ ^[b]	CC2/DZ ^[b]	CC2/aDZ ^[c]	CC2/aTZ ^[d]	<i>f</i>	Exp.
α							
S_1 ($^1\pi\pi^*$)	5.28	3.92	4.21	4.14	4.11	0.1016	~3.97
S_2 ($^1n\pi^*$)	6.00	4.70	5.19	5.04	4.98	0.0002	
S_3 ($^1\pi\pi^*$)	6.60	4.82	5.43	5.19	5.16	0.1423	~4.91
γ							
S_1 ($^1n\pi^*$)	3.56	2.99	3.07	2.93	2.93	0.0003	
S_2 ($^1\pi\pi^*$)	4.06	3.03	3.29	3.05	3.05	0.2680	~3.10

[a] The active space for multi-configurational calculations involved eight electrons distributed over eight orbitals (six of π - and two of σ -type). [b] DZ stands for cc-pVDZ. [c] aDZ stands for aug-cc-pVDZ. [d] aTZ stands for aug-cc-pVTZ.

fluorescence from these minima is predicted to be strongly red shifted with respect to their absorption spectra and the main emission energy is predicted to be about 1.54 and 1.04 eV, that is, to lie in the near infrared (NIR) range of the spectrum.

2.2. Potential-Energy Profiles and Conical Intersections

The minimum potential-energy (MPE) profiles of SMA in the S_0 state and in the lowest excited $^1\pi\pi^*$ and $^1n\pi^*$ states, determined along the PT (OH distance) and along the torsion of the methyl group ($C_1C_7NC_8$ dihedral angle) and of the methylamine group ($C_2C_1C_7N$ dihedral angle) are shown in Figure 1. The minimum energy profiles (—) were obtained by optimization of molecular geometry for fixed values of the reaction coordinate for the ground and the excited state, performed respectively at the MP2/cc-pVDZ or CC2/cc-pVDZ level of theory. In addition,

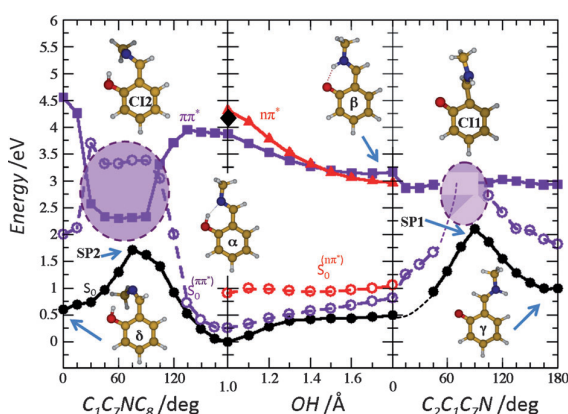


Figure 1. Energy profiles of SMA in the S_0 state (full circles) and in the excited states: $^1\pi\pi^*$ state (squares) and $^1n\pi^*$ state (triangles), determined at the CC2/cc-pVDZ level (MP2/cc-pVDZ for the ground state) along the minimum-energy path (solid) for the proton transfer from the enol α -form (central panel), the methylamine group torsion (right panel), and the methyl group torsion (left panel). $S_0^{(S1)}$ (empty circles) denotes the energy of the ground state calculated along the minimum-energy path of the appropriate excited state (dashed curves). Shaded ellipses denote area where the CC2 iteration cycle ceases to converge due to degeneracy of the S_1 and the S_0 states. Black diamond marks the vertical excitation energy of the α -form.

the vertical PE profiles of the ground state calculated at the optimized geometry of a given excited state were determined (-----). Hence $S_0^{(\pi\pi^*)}$ denotes the energy of the S_0 state calculated along the reaction path optimized in the $^1\pi\pi^*$ state, and so forth.

For the PT reaction (the central panel of Figure 1) we assumed the molecule to maintain the C_s symmetry, which allows independent optimization of the lowest excited state in each of the two irreducible representations of the C_s symmetry group,

$A'(\pi\pi^*)$ and $A''(n\pi^*)$. The results showed that after optical excitation of the α -form to the first excited singlet state ($\pi\pi^*$) a spontaneous (barrierless) ESIPT reaction is expected to occur. The CC2 result was confirmed by the CASPT2 calculation (Table S1), however, the ESIPT reaction is a bit less exoergic at this level of theory. At a point close to $R_{OH} \sim 1.4\text{--}1.5 \text{ \AA}$ the $\pi\pi^*$ and $n\pi^*$ states intersect with each other, and a non-adiabatic switching to the $n\pi^*$ state may occur.

Since the torsion of the methylamine group breaks the C_s symmetry plane, only the lowest excited singlet state can be optimized along this coordinate (the right panel of Figure 1). Analysis of the electronic configurations involved into this transition allows its assignment to the $\pi\pi^*$ state. Although the C_1C_7 bond is a single bond in the α -form, after the proton transfer it changes into a nominally double bond of the β -form. One may notice upon inspection of Figure 1 (right panel) that while the twist causes a large increase in the ground-state energy, the excited-state energy seems to remain almost constant. In result, for the dihedral angle in the range $0^\circ\text{--}50^\circ$ and $110^\circ\text{--}180^\circ$, the ground- and excited-state energies computed at the optimized excited-state geometry sharply approach each other, and in the range $50^\circ\text{--}110^\circ$ the CC2 iteration cycle ceases to converge.

Qualitatively similar PE profiles are obtained when optimizing the reaction paths connecting the α - and δ -forms along the $C_1C_7NC_8$ dihedral angle which is shown in the left panel of Figure 1. Once again, only few points can be computed near to the terminal ends of the excited-state minimum-energy path, due to the abrupt rise of the ground-state energy. Unlike in the case discussed above, there is no stable point in the S_1 state present along this MEP.^[30] The MEP of the ground state computed along these two twisting coordinates show remarkable barriers ($\approx 1 \text{ eV}$) near the perpendicular orientation of the relevant double bonds which separate the γ - and δ -isomers from the nominal α -form.

The above finding indicates the presence of a S_1/S_0 CI in the vicinity of the perpendicular twisting of the C_7N and C_1C_7 double bonds of the respective α - and β -forms. The biradical nature of the structures which are formed at the CI precludes their characterization with the aid of a single-reference elec-

tronic structure theory method, such as CC2 or TD-DFT, for instance. Indeed, the CI optimization performed at the CASSCF/cc-pVDZ level starting from these geometrical structures confirmed the presence of a CI between the ground and the first excited state close to the perpendicular orientation of the $C_1C_7NC_8$ dihedral angle in the α -form (CI1) and of the $C_2C_1C_7N$ dihedral angle in the β -form (CI2). The optimized structures of the S_1/S_0 CIs are shown as inserts in Figure 1 and their Cartesian geometries are given in the Supporting Information.

Since the CI1 can be reached in an essentially barrierless way upon optical excitation of the nominal α -tautomer, this provides a route for an effective radiationless decay through IC to the ground state. The molecular geometry at the CI and the potential-energy profiles shown in Figure 1 suggest that the IC populates the ground state most probably near to the perpendicular conformation of the methylamine group which is a transition structure separating the nominal α -form from its photochromic isomer (γ -form). The transition-state optimization performed at the MP2/cc-pVDZ level confirmed this structure as a first-order saddle point (SP1) with a barrier of $109.4 \text{ kJ mol}^{-1}$ (ZPE corrected) separating the photochromic γ -isomer from the global minimum ($\gamma \rightarrow \alpha$ transition). Bifurcation of the wave packet at the SP1, which is achieved due to the $S_1 \rightarrow S_0$ non-adiabatic transition at the CI1, provides a mechanism for an effective population of the photochromic form of SMA.

A similar photophysical mechanism for the generation of the δ -form can be guessed upon inspection of the left panel of Figure 1, together with the relevant CI (CI2) and the SP (SP2) structures whose Cartesian coordinates are given in the Supporting Information. Apart from the proton-transfer process which, unlike in the case discussed in the previous paragraph, do not participate in this reaction pathway, the bifurcation of the wave packet at the SP2 geometry—non-adiabatically populated from the CI2—may result in the photogeneration of the δ -form. There is, however, a subtle difference in the initiation of these two reaction pathways which can be noticed upon a close inspection of Figure 1. Excitation of the nominal α -tautomer to the lowest $^1\pi\pi^*$ state places the wave packet at the PES with a significant gradient in direction of the PT reaction. This is expected to initialize the pathway toward the γ -form along the barrierless PE profile of the $S_1(\pi\pi^*)$. The competing pathway leading to the δ -form is protected by a small barrier of 5.2 kJ mol^{-1} (10.6 kJ mol^{-1} at the CASPT2 level), and additionally, the PES in vicinity of the top of this barrier is quite shallow. Moreover, the latter pathway would encompass the rotation of two parts of the molecule which are both heavier than the proton particle and thus, the evolution of the system along the twisting coordinate is expected to be slower than that along the PT coordinate.

A barrierless PE profile of the $S_1(\pi\pi^*)$ state in direction of the PT reaction and the small mass of the proton leads to the conclusion that the photophysics of SMA is dominated by the ESIPT reaction which eventually may result in the formation of the photochromic γ -form. This seems to be particularly true for an excitation at the red edge of the absorption band. However, excitation of SMA near the S_1 band maximum (the diamond symbol in Figure 1) provides enough energy to overcome the

small barrier along the reaction pathway leading to the CI2 and may result in formation of the δ -form. The relative partition of the photoexcited SMA between these two reaction pathways can only be estimated on the base of dynamic wave-packed simulations which are beyond the scope of this work.

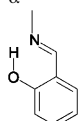
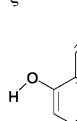
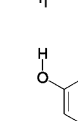
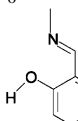
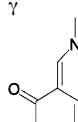

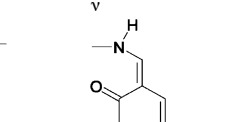
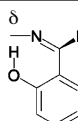
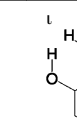
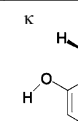
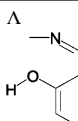
For the sake of completeness, to get a more accurate picture of the energy-level shape at points, where the change of the symmetry of the system from C_s to C_1 is present, we also performed C_1 symmetry optimizations of the first excited state (S_1) at $R_{OH}=1.0 \text{ \AA}$ and $R_{OH}=1.8 \text{ \AA}$ structures. This allowed us to assess the effect of vibronic coupling between the $\pi\pi^*$ and $n\pi^*$ states. It turned out to be insignificant for $R_{OH}=1.0 \text{ \AA}$, while for $R_{OH}=1.8 \text{ \AA}$ it resulted in a lowering of the S_1 -excited-state energy of about 0.1 eV.

2.3. Theoretical Predictions versus Experimental Observations

There is one additional important point that arises from the comparison of our theoretical results with the experimental findings of ref. [15]. The vibrational absorption (IR) spectrum of SMA (α -form) isolated in the low-temperature noble-gas matrix shows that the only product of its UV irradiation with a mercury lamp can be assigned to the enol conformer in which the hydroxyl and methylamine groups are rotated by 180° with respect to the α -form. The conformer is denoted in this paper as the ζ -form of SMA and its molecular structure is drawn in Table 4. The MP2/cc-pVDZ geometry optimization of this isomer resulted in the in-plane conformation of both the hydroxyl and the methylamine groups, thus restoring the C_s symmetry of the system. At this level of theory, the ζ -form of SMA is less stable by 40.8 kJ mol^{-1} (0.44 eV) than its nominal (α) form. This is, however, the next most stable form of SMA among the isomers investigated in this work (Table 3 and Table S1).

Our results discussed in the two previous sections, which are in line with the earlier studied Schiff base, salicylideneaniline,^[8] indicate on two photophysically relevant CIs (CI1 and CI2) which provide non-adiabatic gates for a radiationless decay to the ground state. IC through these CIs populates the ground state of SMA at the conformations near to the SPs (SP1 and SP2) which can be assigned to the transient structures for the formation of the respective γ - and δ -isomers from the native α -form. These transient structures have a relatively high energy since they involve an almost perpendicular conformation of the relevant double bond. All other isomers shown in Table 3 are related to each other, and to the photophysically relevant forms α , γ , or δ , by the rotation around the single bonds.^[31] As such, they are separated from each other by much smaller barriers. In other words, the photophysically induced rotations around the double bonds and the S_1/S_0 conical intersections near to the perpendicular conformations of the relevant dihedral angles split all nominally possible molecular rotamers into classes, as it is illustrated in Table 3. In view of the large barriers for rotations around the double bonds, an interconversion between different classes can only be induced

Table 3. Geometrical schemes of the three classes of stable ground-state isomers of SMA. ZPE-corrected energies relative to the α -isomer calculated at the MP2/cc-pVDZ level. Numbers in parentheses denote ZPE-corrected values obtained at the DFT/B3LYP/3-311G++(2d,2p) level of theory reported in the Supporting Information to ref. [15]. Numbers in square brackets show the energies of the most relevant structures calculated at the CASPT2^[a]/cc-pVDZ level. All values are in kJ mol⁻¹.

α class				
α	ζ	η	θ	
				
0.00 (0.00) [0.00]	40.84 (37.64) [36.98]	46.06 (42.88)	55.33 (52.61)	
γ class				
γ	μ	ν		
				
92.07 (63.38) [96.69]	101.38 (73.33)	102.02 (75.76)		
δ class				
δ	ι	κ	Λ	
				
57.44 (65.78) [54.69]	63.86 (64.17)	64.84 (66.78)	87.38 (68.48)	
[a] The active space for multi-configurational calculations consisted of eight electrons distributed over six orbitals (five of π - and one of σ -type).				

photophysically. On the other hand, small barriers separating rotamers within a given class allow for thermodynamically induced conversions.

In order to illustrate this effect, a one-dimensional minimum-energy cut through the PES that connects the SP1 with the ζ -form is shown in Figure 2. One can notice upon inspection of this figure, that from the point-of-view of the SP1 barrier, the energetic landscape leading to the single-bond twisted conformers (α , η , and ζ) is very flat. Thus, these isomers subject to an effective thermalization when the energy of the SP1 redistributes over intramolecular degrees of freedom, and eventually is transferred to the cold noble-gas matrix. Actually, at the CI1, where an IC to the ground state takes place, the system has an even much higher energy (≈ 3 eV), as it can be estimated from data shown in Figure 1. This energy is high enough to populate the photochromic γ -form, as it was discussed in Section 2.2. However, the free energy is expected to drive effectively the system in direction of the flat area of the PES where thermalization may lead to the formation of the experimentally observed ζ -form, as it can be noticed upon inspection of Figure 2.

In view of the above discussion, it is clear that the ζ -form can effectively be formed due to an optical excitation, as it is the lowest-energy isomer of SMA (except for the global mini-

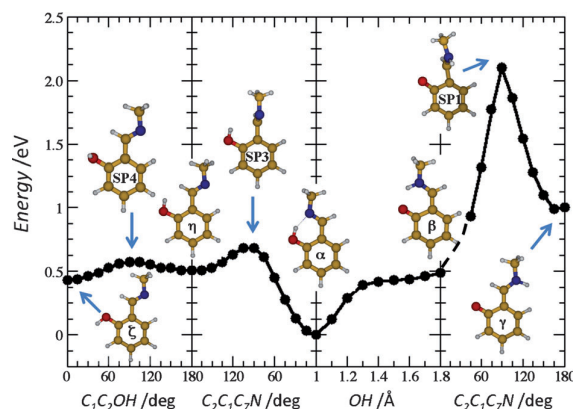


Figure 2. Energy profiles of SMA in the S_0 state determined at the MP2/cc-pVDZ level along the minimum-energy path for (from the left): the C_1C_2OH single-bond twist, the $C_2C_1C_7N$ single-bond twist, proton transfer (OH stretching), and $C_2C_1C_7N$ double-bond twist.

mum). The question is why the photochromic γ -form or other rotamers of this class are apparently not observed in the experiment of ref. [15]. These isomers are energetically accessible from the CI1, and once any of them is formed it is protected by a high barrier with respect to transformation to the native α -form, as it is illustrated in Figure 2. Some light is shed on this question by the inspection of data collected in Figure 3. It

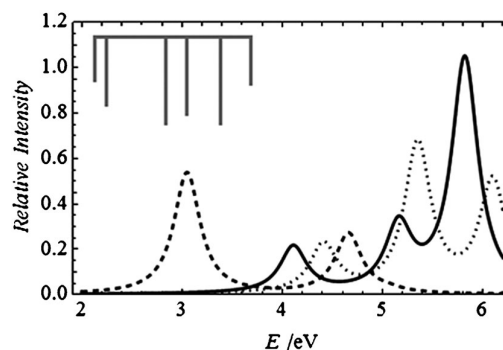
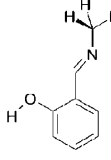


Figure 3. The UV absorption spectra of the α -form (solid line), the γ -form (dashed line), and the ζ -form (dotted line) of SMA. The sample emission spectrum of the mercury lamp is schematically shown in the upper left corner. Absorption spectra were calculated at the CC2/aug-cc-pVTZ level for the MP2/cc-pVDZ equilibrium geometry, and the computed stick spectra were broadened with a Lorentz function of 0.5 eV full width at half maximum.

collects the absorption spectra of isomeric α -, γ -, and ζ -forms of SMA computed at the CC2/aug-cc-pVTZ level at their respective equilibrium geometry. These spectra are additionally shown in Tables 1 and 4, and the spectra computed at the TD-DFT/aug-cc-pVTZ level of theory can be found in the Supporting Information. One can notice upon inspection of Figure 3 that the absorption spectra of the α - and ζ -forms are similar to each other as these forms have similar electronic conjugation patterns (they are interrelated by rotations around single bonds). The absorption spectrum of the photochromic γ -form

Table 4. Vertical-excitation energies (ΔE), oscillator strength (f), and electric dipole moment (μ) of the ζ -form of SMA, computed at the CC2/aug-cc-pVTZ level for the MP2/cc-pVDZ equilibrium geometry.

ζ	State	ΔE [eV]	f	μ [Debye]
	S_0	0.44 ^[a] 0.42 ^[b]	–	2.20
	$^1\pi\pi^*$	4.41	0.1059	4.20
	$^1n\pi^*$	4.61	0.0008	3.76
	$^1\pi\pi^*$	5.35	0.3276	3.43
	$^1\pi\sigma^*$	5.42	0.0007	9.92
	$^1\pi\sigma^*$	5.98	0.0051	10.05
	$^1\pi\pi^*$	6.10	0.2429	2.51

[a] MP2/cc-pVDZ S_0 energy, relative to the global minimum (α). [b] MP2/cc-pVDZ S_0 ZPE-corrected energy, relative to the global minimum (α).

is substantially different due to its different electronic conjugation. Additionally in Figure 3, a schematic emission spectrum of the mercury lamp used in the experiment of ref. [15] is shown.

Inspection of Figure 3 leads to the following conclusions: 1) the nominal α -form can be excited by the most blue line of the mercury lamp at the red edge of its absorption band, as expected, 2) the ζ -form is not excited under the experimental conditions, and it can accumulate in the course of experiment, 3) the absorption spectrum of the photochromic γ -form matches to a large extent the emission spectrum of the mercury lamp, thus if this isomer is formed, it is very effectively burned-out in the experiment. This provides an explanation of the mismatch between the theoretical predictions and the experimental observations.

3. Conclusion

The photophysics of the one of the simplest aromatic Schiff bases, SMA, has been studied with respect to the formation of stable photochromic species which can provide a template for the design of fast optically driven molecular switches. The photophysical scheme that emerges from our studies seems to be universal for molecular systems based on Schiff bases in view of earlier results presented for salicylideneaniline.^[8] The results of the theoretical investigations can be summarized as follows:

1. All isomers (tautomers and rotamers) of SMA studied in this work can be divided into three classes which are related to each other by proton transfer and/or rotation around the double bond. These processes are induced by electronic excitation and non-adiabatic return to the ground state at the respective CI, and may result in the formation of photochromic species which are protected by sizable barriers with respect to the nominal form. On the other hand, molecular transformations within a given class can be thermally induced due to the small barriers for rotations around single bond(s).^[31]
2. The photochromic species of SMA are only formed as a result of cooperation of the ESIPT process and the photo-induced rotation around the double bond. All other isomers

which are formed due to the thermodynamical rotations around single bonds or photodynamical rotations around double bonds (without ESIPT) have similar absorption spectra. Thus, these two kinds of isomers can effectively be transformed into each other by proper tuning of the excitation wavelength. In that sense aromatic Schiff bases are promising candidates for optically driven molecular switches.

3. Results of this work stress the need for monochromatic selective excitation of particular isomeric forms in low-temperature noble-gas matrix experiments in order to avoid the photochemical burning of products.

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- [31] An exception is the v-form which nominally relates to the parent γ-isomer by rotation around the C₁C₇ double bond, but the rotation around the C₇N single bond in the course of its non-adiabatic formation at the CI1 is expected to induce an effective back-PT reaction and its relaxation to the nominal α-form.

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