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Excited-State Intramolecular Proton Transfer: Photoswitching in Salicylidene Methylamine Derivatives

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

The effect of chemical substitutions on the photophysical properties of the salicylidene methylamine molecule (SMA) (J. Jankowska, M. F. Rode, J. Sadlej, A. L. Sobolewski, *ChemPhysChem*, **2012**, *13*, 4287–4294) is studied with the aid of ab initio electronic structure methods. It is shown that combining π -electron-donating and π -electron-withdrawing substituents re-

sults in an electron-density push-and-pull effect on the energetic landscape of the ground and the lowest excited $\pi\pi^*$ and $n\pi^*$ singlet states of the system. The presented search for the most appropriate SMA derivatives with respect to their photo-switching functionality offers an efficient prescreening tool for finding chemical structures before real synthetic realization.

1. Introduction

There exists a variety of bistable and multistable systems among organic molecules. The stable forms of a given system may constitute different tautomer or isomer structures and, in many cases, may reversibly be switched from one to another by an external stimulus, such as electron transfer, an external electric field,^[1] or optical excitation.^[2–4] Of these stimuli, light represents the most advantageous stimulus and offers very high spatial and temporal resolution that allows for true remote control of the switching. To ensure a selective and reversible optical switching between two stable forms upon irradiation with different wavelengths of light, the forms must possess distinguishably different absorption spectra. This property is termed molecular photochromism. It is now well established that this molecular property may guarantee access to optical switches and memories operating at a single-molecule level and, therefore, meets requirements for real nanophotonic devices for future electronics.^[5]

Over the years, most research effort in this field has been focused on two classes of intramolecular reactions related to photochromism. These are 1) ring-closing and ring-opening reaction in diarylethenes,^[6] fulgide derivatives^[7] and spiro-oxazines,^[8] and 2) *cis-trans* isomerization reactions in azoben-

zene^[2] and stilbenes (see Refs. [9 and 10]). More recently, a new class of photochromic systems subjected to a light-induced intramolecular proton-transfer (PT) process has been invoked.^[11–17] In recent decades, systems that exhibit the phenomenon of excited-state intramolecular proton transfer (ESIPT) have been of considerable applied interest as photostabilizers and sunscreens for the protection of organic polymers and biological tissues against damage that can be caused by the UV component of sunlight.^[18–21] Of these systems, photochromic Schiff bases^[22] represent a special group of ESIPT systems, for which depopulation routes of the excited molecule are particularly complex. In addition to the closed-PT reaction cycle returning the system to its original state through back-PT, as it is typical for ESIPT-based photostabilizers, a large portion of molecules may be trapped in the ground state as metastable photochromic species. The photochromism and the high photostability intrinsic for ESIPT systems open the perspective of their possible applications in optically driven molecular memories and switching devices.^[11–12, 23–27]

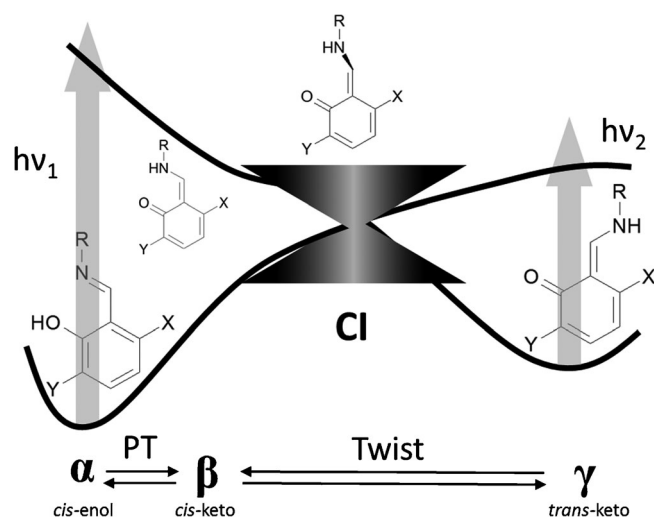
A qualitative photophysical scheme for optically driven molecular switches based on the ESIPT phenomenon was proposed by us recently.^[11, 14] The system is generally composed of two covalently bound molecular moieties, that is, the proton-donating and the proton-accepting units, and its operating mechanism is shown in Scheme 1. It involves several well-defined steps: 1) optical excitation to the lowest excited singlet state (S_1) induces a barrierless proton-transfer reaction between the proton-donating and proton-accepting molecular units, then 2) by twisting around the covalent (double) bond that connects the units, the system reaches the S_1/S_0 conical intersection (CI) around the perpendicular conformation and, eventually, 3) strong nonadiabatic coupling in the CI(S_1/S_0) drives the system back to the ground state in which the proton may either return to the proton-donating unit and thus close the photocycle, or the system can continue the twisting motion that results in formation of a photochromic species.

[a] J. Jankowska
College of Interfaculty Individual Studies in
Mathematics and Natural Sciences, University of Warsaw
Żwirki i Wigury 93, 02-089 Warsaw (Poland)

[b] J. Jankowska, Prof. J. Sadlej
Faculty of Chemistry, University of Warsaw
Pasteura 1, 02-093 Warsaw (Poland)
Fax: (+48) 22 822 59 96
E-mail: sadlej@chem.uw.edu.pl

[c] Dr. M. F. Rode, Prof. A. L. Sobolewski
Institute of Physics, Polish Academy of Sciences
Aleja Lotników 32/46, 02-668 Warsaw (Poland)
Fax: (+48) 22 843 09 26
E-mail: sobola@ifpan.edu.pl

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Scheme 1. General photoswitching scheme in SMA-based molecular systems; CI = conical intersection, PT = proton transfer.

The most important requirements for a molecular photo-switch are:

- 1) A molecule must have at least two stable minima (isomers) on the potential-energy surface (PES) of the ground electronic state. These minima should be separated by a substantial energy barrier to exclude thermal interconversion.
- 2) The isomers must absorb light at different wavelengths (photochromism) and absorption spectra should allow their selective excitation.
- 3) Each isomer must possess barrierless access to the S_1/S_0 conical intersection from the Franck–Condon (FC) area of the excited-state PES. The energy gradient in S_1 pointing toward the CI point is a desirable feature because it supports fast and unidirectional transformation after selective excitation of a particular isomeric form.
- 4) The energy difference between the isomers in the ground state should be small enough to maintain a similar density of their vibronic states at the S_1/S_0 conical intersection, the factor that drives the system in the direction of a particular minimum.
- 5) The photoswitching transformation between the two isomers should either be unique or be significantly more probable (faster) than any other photoinduced reaction in the system.

The above conditions may be fulfilled by proper chemical tuning of the proton-donating and proton-accepting moieties of the ESIPT system.

In our recent work, the photophysics of SMA was investigated by means of quantum-chemical methods. The results of the computations gave new insight into the interpretation of the experimental findings reported in Ref. [28]. In this system, the aromatic ring of phenol plays the role of the proton-donating unit and the $-C=N-CH_3$ group at the 2-position of the ring acts as the proton-accepting moiety. This is in line with the require-

ments for the molecular photoswitch, the mechanism of which is based on the ESIPT phenomenon.

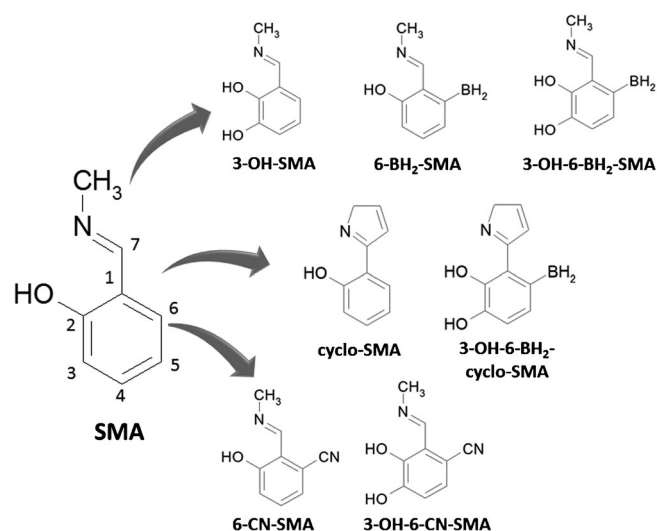
The photophysical scheme that emerges from our studies and from previous results presented for SMA and the similar molecular system of salicylideneaniline (SA)^[29–30] seems to be universal for aromatic Schiff base molecules. These results indicate the promising features of aromatic Schiff bases to serve as effective optical switches, but have also revealed some weaknesses of these systems. From the perspective of molecular photoswitching, their positive features are 1) good photochromism, which allows for selective optical excitation of both tautomeric forms and 2) a sizable barrier between them in the ground state, which provides a remarkable thermostability of the photoproduct. General weaknesses of SMA and SA are 1) a relatively high energy difference between the switchable photochromic forms and 2) diverse conformers produced by thermally induced rotations around single bonds. Moreover, although the S_1/S_0 conical intersection seems to be accessible in a barrierless fashion from the FC region of both corresponding isomeric forms, the energy gradient in the S_1 state, which could act as a driving force for the back transformation, is rather small.

The main goal of the present study is a theoretical search for chemical modifications of the parent SMA system that will improve or eliminate the above-mentioned limitations of the SMA molecule to serve as a photoswitch and at the same time will preserve its positive features. This will be done in the first stage by applying different electron-donating and electron-withdrawing groups to the aromatic ring, with the same proton-accepting moiety ($-C=N-CH_3$) in SMA. In the second stage, a modification of the proton-accepting moiety will be considered. Herein, we examine substituents that play the role of the electron-withdrawing groups, such as $-CN$ (moderate) and $-BH_2$ (strong) π -electron acceptors, and strong π -electron-donating groups, such as $-OH$. The main effect of the latter group is an increase in electronic occupancy of the π orbitals at the *ortho* and *para* positions in the substituted benzene ring (see Ref. [31]).

Herein, the following systems are studied in the course of modeling the optical switch: 3-[(*E*)-(methylimino)methyl]-catechol (3-OH-SMA), 3-hydroxy-2-[(*E*)-(methylimino)methyl]-phenylborane (6-BH₂-SMA), 3,4-dihydroxy-2-[(*E*)-(methylimino)methyl]-phenylborane (3-OH-6-BH₂-SMA), 3-hydroxy-2-[(*E*)-(methylimino)methyl]-benzonitrile (6-CN-SMA), 3,4-dihydroxy-2-[(*E*)-(methylimino)methyl]-benzonitrile (3-OH-6-CN-SMA), and as an example of changing the proton-accepting moiety attached to the frame, 2-(pyrrol-2-yl)phenol (cyclo-SMA) and 3,4-dihydroxy-2-(pyrrol-2-yl)phenylborane (3-OH-6-BH₂-cyclo-SMA). The geometrical structures of the ground-state global minima of these systems are shown in Scheme 2.

Methods of Calculations

The potential-energy (PE) landscapes of the ground and first singlet excited state of the SMA derivatives were explored by using the MP2 and simplified version of singles and doubles coupled cluster (CC2)^[32–33] methods, respectively. In geometry optimization



Scheme 2. SMA derivatives under investigation.

and reaction-path calculations, the correlation-consistent split valence double zeta basis set with polarization functions on all atoms (cc-pVDZ) was used.^[34] For calculations of the vertical electronic absorption spectra, the use of the CC2 method with the aug-cc-pVTZ^[35] basis set (at the MP2/cc-pVDZ-optimized ground state) was a compromise between the known fact of the minor impact of the augmented functions on the molecular geometry^[36] and their relative importance for energy calculations. The performance of the chosen single-reference electronic structure methods was previously benchmarked against the multi-reference CASPT2 approach (see Ref. [27] and the Supporting Information). The stationary structures found by using geometry optimization were supported, for the ground state, by harmonic frequency analysis (performed at the MP2/cc-pVDZ level of theory). The vibrational zero-point energy (ZPE) was used for correction of the computed relative electronic energy of the isomers.

The PE landscape of investigated electronic states of the SMA derivatives was obtained according to the following procedures: 1) The minimum-PE profiles for the ground and the excited states were determined by optimization of the molecular geometry for fixed values of a given reaction coordinate parameter. 2) The vertical-PE profiles of the ground state were obtained from single-point CC2/cc-pVDZ calculations at the minimum-PE geometries of a given excited state. 3) Along the proton-transfer (PT) coordinate, the molecule was kept planar by imposing C_s symmetry (the only exception to this rule was the 3-OH-6-BH₂-cyclo-SMA system, for which C_s symmetry was used). The C_s symmetry constraint allowed for independent optimization of the lowest excited state in each of the two symmetry representations, $A'(\pi\pi^*)$ and $A''(n\pi^*)$.

For all quantities computed by using the CC2 method, the single-point CC2 energy of the ground-state global minimum (α -structure) was chosen as a reference value.

Geometry optimizations and calculations of the reaction paths and the UV absorption spectra were carried out by using the TURBO-MOLE^[37] suite of programs, whereas the calculations of the vibrational harmonic frequencies, search for the S_1/S_0 conical intersections, and transition-state optimizations were performed with use of the Gaussian 09 program package.^[38]

2. Results and Discussion

2.1. Ground- and Excited-State Structures of Relevant Derivatives of SMA

The chemical structures of the molecules studied herein and their atom numbering system are presented in Scheme 2. In agreement with our previous work,^[27] the primary photo-physical reaction for these molecular systems is the excited-state intramolecular transfer of the proton from the hydroxyl group of the nominal α form (*cis*-enol form) to the imino group, which results in formation of an oxo-amino β -tautomer (*cis*-keto form). The intramolecular reaction coordinate relevant for the PT process should describe the position of the proton with respect to the oxygen and the nitrogen atoms along the hydrogen bridge. Therefore, the OH separation was chosen as the reaction coordinate for the PT reaction. The β form of SMA, formed in the course of the ESIPT process, may further evolve on the PES of the S_1 state to the *trans*-keto conformer (γ) by twisting around the $C^1=C^7$ bond. This system evolution is accompanied by an ultrafast internal conversion to the ground state at the geometry close to the perpendicular orientation of this moiety with respect to the molecular frame, at which the CI between the S_1 and S_0 states is found. The relevant intramolecular coordinate for this reaction is the $C^2-C^1=C^7-N$ dihedral angle, which changes its value within the 0 to 180° range. Photophysical structures relevant for the photo-process are shown in Scheme 1. This simplified PE scheme allows for reversible optical switching between the two ground-state stable isomers of SMA, α and γ , because at the CI(S_1/S_0) the system may alternate between these two forms.

2.1.1. Modeling the Landscape of the Ground State

The α and γ isomeric structures of the SMA derivatives shown in Scheme 1 represent stable minima on the ground-state PES, whereas the β form spontaneously relaxes toward the α form upon optimization. The γ conformer is generally less stable than the global enol minimum (α form) and thus represents a local minimum on the ground-state PES. The relative energies of the crucial structures investigated herein are presented in Table 1 (for Cartesian coordinates, see Table SI4 in the Supporting Information). Note that the zero-point energy (ZPE) correction changes these numbers only marginally.

Two parameters describing the ground-state energetic landscape are crucial for molecular photoswitching performance. These are 1) close isoenergeticity of both α and γ tautomers (small E_γ , defined as the ZPE-corrected energy difference between α and γ) and 2) a sufficiently high barrier between them to prohibit thermal interconversion (from both directions; $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \alpha$). Because the second criterion is ensured in this type of reaction (twisting around a double bond in the ground state requires a significant amount of energy; see Table 1), this section is devoted to the issue of γ -tautomer stabilization versus the α form.

An additional difficulty when adjusting the landscape of the ground state is that any substitution to the SMA molecule

Table 1. Relative energy of crucial photochemical structures of investigated SMA derivatives.

Derivative	$S_0^{[a]}$			$S_1^{[b]}$
	γ (ZPE) [eV]	$\alpha \rightarrow \gamma$ (ZPE) [eV]	$\gamma \rightarrow \alpha$ (ZPE) [eV]	β [eV]
SMA	0.96 (0.95)	2.11 (2.09)	1.14 (1.13)	2.88 (1.34)
3-OH-SMA	0.72 (0.73)	1.90 (1.90)	1.18 (1.17)	2.69 (0.60)
6-BH ₂ -SMA	0.88 (0.88)	1.86 (1.85)	0.98 (0.96)	2.95 (0.56)
3-OH-6-BH ₂ -SMA	0.55 (0.58)	1.58 (1.59)	1.03 (1.01)	2.87 (0.31)
cyclo-SMA	1.01 (0.99)	2.02 (2.00)	1.01 (1.01)	–
3-OH-6-BH ₂ -cyclo-SMA	0.53 (0.54)	1.37 (1.37)	0.84 (0.83)	–
6-CN-SMA	0.78 (0.78)	1.89 (1.88)	1.11 (1.09)	3.08 (0.67)
3-OH-6-CN-SMA	0.50 (0.53)	1.66 (1.67)	1.16 (1.14)	–

[a] Ground-state (S_0) γ -minimum energy and the $\alpha \leftrightarrow \gamma$ transformation barriers (values in brackets are the same values corrected with ZPEs) optimized at the MP2/cc-pVDZ level. [b] Excited-state (S_1) structures: local minimum β optimized at the CC2/cc-pVDZ level (fluorescence energies are given in brackets).

should conserve the excitation selectivity of the system. For the best switching performance, the UV absorption spectrum should be distinguishable for each of the stable tautomeric forms, so that the system can be photoswitched forward and backward reversibly.^[5] As shown in reference [27], the selectivity condition is fulfilled for the bare SMA system because its UV spectrum possesses distinguishable excitation energies: 4.11 and 2.93 eV for α and γ tautomeric forms, respectively (see Figure 1). The weak point of bare SMA with respect to photo-switching is related to the S_0 energy difference between the isomeric forms ($E_\gamma = 0.95$ eV, see Table 1), which is rather too large to ensure an effective population of γ at the CI(S_1/S_0), which is the point of bifurcation of the system.

As stated above, any chemical modification of the SMA structure must conserve excitation selectivity of the absorption spectrum, which is the necessary condition for reversibility of phototautomerization process. The calculated vertical excitation energies along with the simulated UV absorption spectra for all studied SMA derivatives are gathered in Figure 1 and Tables SI1 and SI2 of the Supporting Information and are compared with those of the bare SMA molecule.

Electron-Donating Substituents

The hydroxy (-OH) and amine (-NH₂) substituents are known as strong π -electron donors.^[31] Both were examined and tested in previous studies and were found to exert a remarkable influence on the excited-state energetic landscape.^[5,14,17] Here, the 3-OH substitution to the bare SMA molecule (3-OH-SMA) is presented as the first step to improve the photoswitchable performance. The 3-position was chosen for -OH group substitution because the π -electron-donating substitution at the position *ortho* to the proton-donating -OH functional group in 7-hydroxyquinolines occurred to give the most exoergic effect of the excited-state proton-transfer reaction.^[14] This suggestion was later successfully used by us in modeling another molecular photoswitch based on 3-hydroxy-picolinic acid.^[5] From inspection of Table 1, it can be seen that, as desired, this relatively minor structural modification decreases the E_γ value by 0.24 eV in comparison with the parent SMA molecule. The simulated UV absorption spectrum based on vertical excitation

energies and oscillator strengths computed for the α and γ conformers of the 3-OH-SMA system is presented in Figure 1. Its shape indicates that the excitation selectivity is maintained after 3-OH substitution, however, an important change in the absorption spectrum can be noted in comparison to the spectrum of bare SMA. To depopulate the α tautomer of 3-OH-SMA selectively, one should excite its second excitation band ($\pi\pi^*$ state) at 4.97 eV because there is an apparent absorption window

for the second γ tautomer at around 5 eV. The first excitation band of the α form at 3.88 eV is very weak and is entirely overlapped by the second $\pi\pi^*$ band of the form γ . In turn, the γ form may be switched back when its first absorbing band at 2.92 eV is excited.

Electron-Withdrawing Substituents

As discussed above, the π -electron-donating substitution at the 3-position improves the S_0 energetics of the molecular switch. In this section, the effect of the π -electron-withdrawing substituents on the S_0 -state energetic landscape is investigated. The 6-position of the proton-donating moiety (the *para* position with respect to the 3-position) was selected as the most suitable for electron-withdrawing substitution because, as shown in previous studies,^[14,39] the push-and-pull effect of electron-density shifts is most effective if both groups are substituted at opposite positions of the molecule. Moreover, the electronegative group placed at the considered position (*ortho* with respect to the proton-accepting unit) may stabilize the γ form through formation of intramolecular hydrogen bonds. Before merging the two effects in one, a new model molecule, the single electron-withdrawing substitution will be discussed first.

The strong (-BH₂) and medium (-CN) electron-withdrawing groups were substituted at the 6-position of the proton-donating moiety to form 6-BH₂-SMA and 6-CN-SMA molecules, respectively (see Scheme 2). In both compounds, a medium stabilization of the γ versus α conformer is observed in comparison with the parent SMA molecule. The stabilization is larger in the 6-CN-SMA molecule, for which the E_γ value is decreased by 0.18 eV to a value of 0.78 (see Table 1). It should be also stressed that the UV absorption spectra of these molecules conserve the excitation selectivity for both tautomeric forms of the system. The first excitation bands ($^1\pi\pi^*$) of a given tautomer might effectively be used to switch it to another form and vice versa. Also note that the addition of the -BH₂ group red-shifts the whole spectrum.

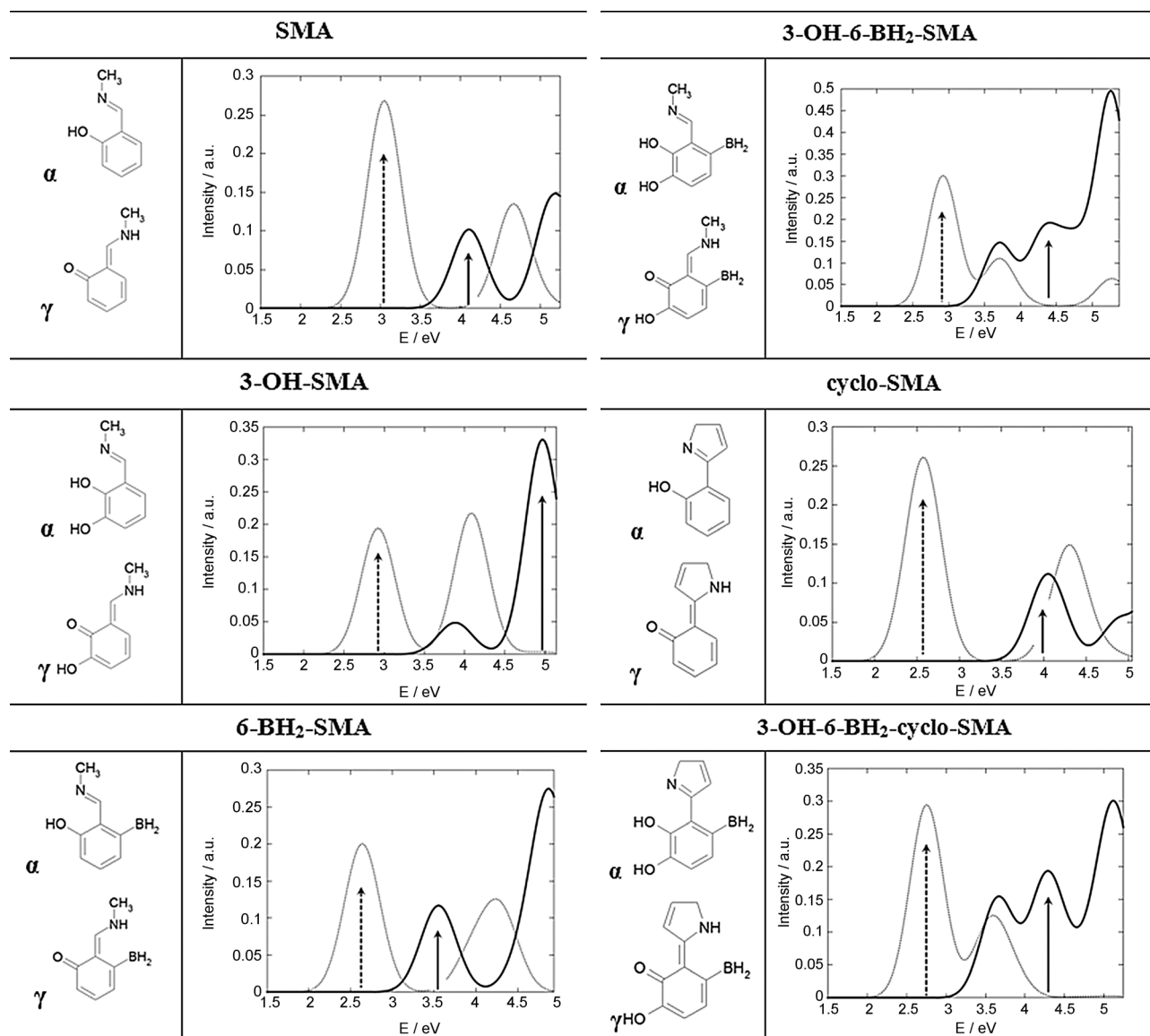


Figure 1. Absorption spectra of α and γ forms of all investigated SMA derivatives. The solid lines are the absorption spectrum of the α form and the dotted lines are the absorption spectrum of γ . The plotted curves are Gaussian functions with full-width at half-maximum (FWHM) set to 0.5 eV. The arrows mark absorption bands that may be used for photoswitching.

Merging of the Electron-Donating and Electron-Withdrawing Structural Modifications

Considering the effect of single π -electron-donating and -withdrawing substitutions on the ground-state energetics, in this section the effect of simultaneous substitutions of the electron-donating and electron-withdrawing groups to the molecular frame on the S_0 landscape is discussed. According to the results presented in preceding sections, the three singly substituted derivatives of SMA (3-OH-SMA, 6-BH₂-SMA, and 6-CN-SMA) are quite promising in this context. Thus, two additional molecular systems, 3-OH-6-BH₂-SMA and 3-OH-6-CN-SMA, were constructed by merging the 3-OH substitution with one of the π -electron-withdrawing groups (-BH₂ or -CN) substituted at the 6-position of the proton-donating moiety.

These doubly substituted systems have three important features in common. First, the E_{γ} parameter decreases remarkably for the doubly substituted molecules to a value of approximately 0.5 eV from the value of 0.95 eV for the parent SMA molecule (see Table 1). This stepwise change in the S_0 energy landscape is illustrated on the energy diagrams for the respective systems presented in Figure 2. Second, the UV absorption spectra of 3-OH-6-BH₂-SMA and 3-OH-CN-SMA molecules preserve the excitation selectivity. Although the first absorption band of the α conformer is overlapped by the second absorption band of the γ form, there is an apparent window at approximately 4.5 eV in the absorption spectrum of 3-OH-6-BH₂-SMA and at approximately 5.5 eV for 3-OH-6-CN-SMA, at which the α conformer may be switched selectively to the γ form by excitation to higher electronic states. The third important fea-

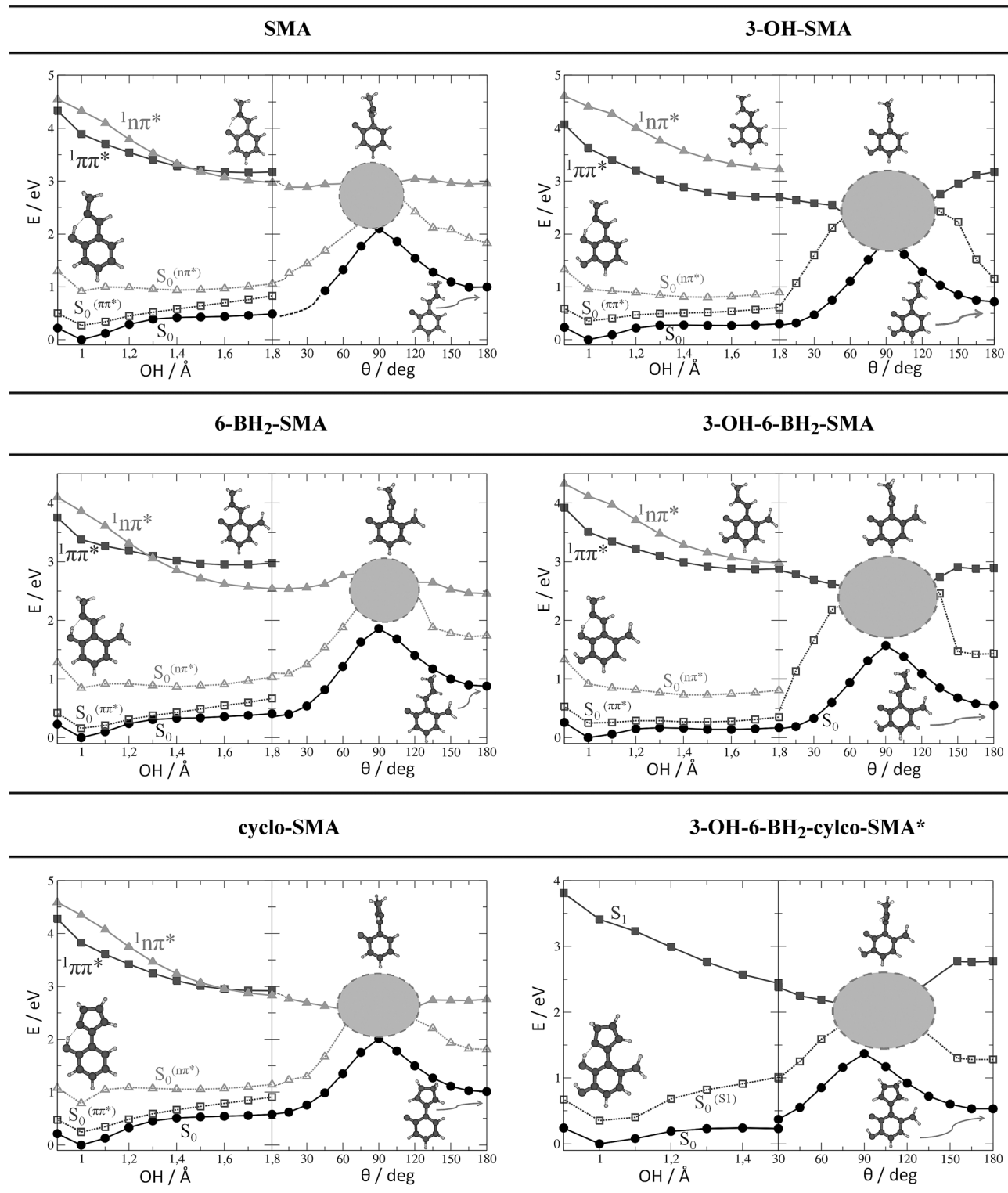


Figure 2. Energy profiles of SMA and its selected derivatives (3-OH-SMA, 6-BH₂-SMA, 3-OH-6-BH₂-SMA, cyclo-SMA, and 3-OH-6-BH₂-cyclo-SMA) in the S_0 state (●) and in the excited states: $^1\pi\pi^*$ state (■) and $^1n\pi^*$ state (▲), determined at the CC2/cc-pVDZ level (MP2/cc-pVDZ for the ground state) along the minimum-energy path (filled symbols) for the proton transfer from the enol α form (left panels) and the methylamine group torsion (right panels). S_0 ($\pi\pi^*$) and S_0 ($n\pi^*$) (□ and △, respectively) denote the energy of the ground state calculated along the minimum-energy path of the appropriate excited state (----). Shaded ellipses denote the area at which the CC2 iteration cycle ceases to converge due to degeneracy of the S_1 and the S_0 states. *: For the 3-OH-6-BH₂-cyclo-SMA system in both panels only the lowest singlet-excited state (S_1) PES has been investigated due to the lack of C_s symmetry during the PT

ture of all systems presented so far is a large $\alpha \rightarrow \gamma$ barrier (≈ 2 eV) and, which is even more important, a significant ener-

getic barrier for the reverse $\gamma \rightarrow \alpha$ transformation (≈ 1 eV) in the ground electronic state. These characteristics, together

with the low value of E_{γ} , ensure the thermal stability of both conformers.

From an electron-structure engineering perspective, the three S_0 energetic arguments discussed above allow us to pre-select the 3-OH-6-BH₂-SMA and 3-OH-6-CN-SMA systems as the most promising candidates for molecular photoswitching. Moreover, the 3-OH-6-BH₂-SMA compound should be considered as a system of choice because both its switching absorption bands lie in an energy range easily accessible under laboratory conditions ($\lambda \approx 425$ and 290 nm for γ and α absorption, respectively). However, as shown below, an additional parameter crucial for the photoswitching performance is the shape of the excited-state energy landscape.

2.1.2. Substituent Effect on the Excited-State Energy Landscape of SMA

Minimum potential-energy profiles of the ground electronic state (S_0) and of the lowest $^1\pi\pi^*$ and $^1n\pi^*$ excited-singlet states relevant for the photophysics of the SMA derivatives studied herein are presented in Figure 2 and Figure S11 in the Supporting Information. The PE profiles were calculated along two reaction coordinates, that is, the OH separation that describes the proton transfer from the *cis*-enol form to the *cis*-keto form (Figure 2, left panels) and the $C^2-C^1=C^7-N$ dihedral angle (θ) that describes the rotation of the proton-accepting group about the $C^1=C^7$ bond and transforms the *cis*-keto form into the *trans*-keto form (Figure 2, right panels).

The results presented in Figure 2 clearly show that after optical excitation of the α form to the first excited-singlet state ($^1\pi\pi^*$) a barrierless ESIPT reaction is expected to occur. The planar (C_s symmetry) *cis*-keto form (β) formed in this reaction is unstable and further decreases the S_1 state energy by twisting around the $C^1=C^7$ bond. Although the $C^1=C^7$ bond was a single bond in the ground state of the α form, it changes into a nominally double bond of the β form in the course of the PT reaction. Thus, the photophysics of the keto tautomer follow a pathway typical of ethylenic-like behavior, and for the geometry characterized by the $C^2-C^1=C^7-N$ dihedral angle being close to 90° the first excited-singlet state becomes degenerate with the ground state. Indeed, the S_1/S_0 conical intersection was localized in the vicinity of this conformation for all systems in this work. The relevant optimized structures of the CI(S_1/S_0) are shown as insets in Figure 1 and Figure S1 in the Supporting Information, whereas their Cartesian geometries are given in Table S13 in the Supporting Information.

The scale and the direction of the substituent effect on the PE landscape in the relevant states are discussed below.

Excited-State Properties of the 3-OH-SMA, 6-BH₂-SMA, and 3-OH-6-BH₂-SMA Systems

Our previously reported investigation of the SMA energetic landscape^[27] showed a pronounced exoergic effect for the PT reaction in the S_1 state (of $\approx +0.7$ eV for the $^1\pi\pi^*$ state). A similar pattern is observed for all SMA derivatives investigated herein. In all studied cases, this reaction is barrierless and

involves a potential-to-kinetic energy transformation of about 1.3, 0.7, and 1.0 eV for the 3-OH-SMA, 6-BH₂-SMA, and 3-OH-6-BH₂-SMA systems, respectively. The PT reaction thus involves a ballistic motion of the proton in the S_1 state and is expected to occur on the femtosecond timescale. For all investigated compounds, the lowest excited-singlet state, close to the FC region of the PES, is of $\pi\pi^*$ character. However, the energy of the $^1n\pi^*$ state also stabilizes remarkably along the PT reaction coordinate and may participate in the reaction. The PE profile of the $^1n\pi^*$ state varies with respect to the $^1\pi\pi^*$ state in a somewhat different manner for different derivatives. Although it runs in parallel fashion with respect to the $^1\pi\pi^*$ PE profile for the 3-OH-SMA system, it exhibits the $^1n\pi^*/^1\pi\pi^*$ apparent crossing (both states were independently optimized) around $R_{OH} \approx 1.2$ Å for the 6-BH₂-SMA derivative and becomes isoenergetic with the $^1\pi\pi^*$ state of the *cis*-keto (β) form for the doubly substituted 3-OH-6-BH₂-SMA system. The comparison of these cases with SMA (for explicit energy values see Table S15 in the Supporting Information) leads to the conclusion that the -OH substituent, which is a π -electron-donating and σ -electron-withdrawing group,^[31] at the proposed position strongly stabilizes the $^1\pi\pi^*$ state versus $^1n\pi^*$ along the PT reaction coordinate. This observation is in line with a previous theoretical study of photophysics of 7-hydroxy-quinoline derivatives.^[14] In contrast, for the σ -electron-donating -BH₂ group, the stabilization effect acts mainly on the $^1n\pi^*$ state. The combination of these substitutions results in a combined effect on the 3-OH-6-BH₂-SMA PESs of the investigated excited states.

After the proton transfer occurs, the system arrives at a rather flat region of the S_1 PES. Now the relevant reaction coordinate becomes a rotation around the $C^1=C^7$ bond, that is, the twist motion that breaks the C_s symmetry of the system and causes an electronic mixing between previously distinguishable $n\pi^*$ and $\pi\pi^*$ states. In effect, only the lowest excited-singlet state can be optimized. The single-reference (CC2) method used for the excited-state geometry optimization becomes less reliable for the region at which the excited-singlet state approaches the ground state. Thus, this area of the reaction path is highlighted by an ellipse (see Figure 2 and Figure S1 in the Supporting Information).

For all three systems analyzed in this section, a shallow local minimum in the S_1 state was found (β form). In all cases its structure can be characterized by proton transfer from oxygen (initial hydroxyl group) to the nitrogen atom at an almost planar orientation of the proton-donating and proton-accepting units (for exact geometrical structures, see Table S13 in the Supporting Information). The energy of the minimum depends only marginally on the substitution and ranges from 2.69 to 2.95 eV for the analyzed molecules (see Table 1).

In the PES region related to the rotation around the $C^1=C^7$ bond, one may observe modest differences between PES shapes for different substitutions. Thus, for bare SMA the rotation causes only minor changes in the potential energy of the S_1 state (within ≈ 0.1 eV) and so, keeping in mind the above-mentioned weakness of the CC2 method in handling near-degeneracy effects, it might be considered to be a barrierless process. A very similar picture is also found for the 6-BH₂-SMA

system. For the 3-OH-SMA and 3-OH-6-BH₂-SMA compounds, one can find a small gradient toward perpendicular conformation of the system at which an intersection between the S₁ and S₀ states was found for all derivatives studied herein.

Optimization of the lowest-energy CI(S₁/S₀) was performed at the CASSCF(6,6)/cc-pVDZ (averaging over two states) level of theory with the use of Gaussian 09 program package.^[38] In all cases, the active space included six electrons distributed over six molecular orbitals, three HOMOs and three LUMOs, computed at the guessed geometry of the intersection. The pictures of orbitals included in the active space are presented in Table SI6 in the Supporting Information. Because the CASSCF method accounts only for the static part of electron correlation, it was impossible to place the energy of the optimized CI(S₁/S₀) point on the photoreaction energetic landscape obtained at the CC2 level.

The S₁ PE profiles discussed above along the PT coordinate and the rotation about the C¹=C⁷ bond ranging from 0 to about 90° might be considered as relevant for the α-to-γ phototransformation. However, to investigate the possibility of switching in the opposite direction, one should also consider the S₁ PES to the right from the CI point (corresponding to 90–180° C²–C¹=C⁷–N rotation). After excitation of the *trans*-keto γ form at the appropriate wavelength (see Table SI2 in the Supporting Information for exact values) the system arrives at a very flat S₁ PES area. For the SMA molecule, we found that the S₁ energy remains almost unchanged during the rotation around the C¹=C⁷ bond (all calculated points lie within a ≈0.1 eV energy range). On the one hand, this means that access to the CI(S₁/S₀) from both sides of the investigated PE profiles is practically barrierless. On the other hand, to assure efficient performance of any molecular photoswitch a significant gradient from the FC region toward the CI is necessary. Otherwise, the system may be trapped in the FC area for a longer time, which brings a risk of other competing photochemical and/or photochemical processes to occur. The search to overcome this drawback is one of our main topics of interest in this work.

The most promising substitution effect on the desired shape of the S₁ PES was observed for the 3-OH-SMA derivative of SMA. The electron-donating group substituted into the proton-donating moiety resulted in a remarkable stabilization of the first excited-singlet state (by about 0.5 eV) in the CI(S₁/S₀) area with respect to the parent system. In turn, an opposite effect was observed for the 6-BH₂-SMA derivative. The boryl group substitution at the 6-position results in the rise of a small energy barrier (≈0.2 eV) and the state conserves nπ* character near the perpendicular conformation. For the combined substitution in 3-OH-6-BH₂-SMA, the energy landscape again experiences the additive effect of both substitutions. After a flat behavior within the FC area the PE profile of the S₁ state stabilizes when approaching the twisted CI (the net drop in potential energy equals ≈0.2 eV). The lowest excited-singlet state is assigned as the ππ* state in this case.

Excited-State Properties of the 6-CN-SMA and 3-OH-6-CN-SMA Systems

In this section we discuss excited-state PE profiles of two other investigated molecules: 6-CN-SMA and 3-OH-6-CN-SMA, which exhibit perspective properties for future investigations.

For the 6-CN-SMA substitution (-CN group) the photophysical picture is very similar to the 6-BH₂-SMA case. During exoergic (≈1.1 eV within the ¹ππ* state) and barrierless PT process, a change in the relative position of ¹ππ* and ¹nπ* states is observed (see Figure SI1 in the Supporting Information). After passing the shallow minimum, the system arrives at relatively flat area around the CI(S₁/S₀) geometry, on both sides of which small barriers of approximately 0.25 eV can be observed (see Figure SI1 in the Supporting Information). This result supports the previously formulated conclusion on the effect of electron-withdrawing substitution on the molecular frame of SMA.

In the 3-OH-6-CN-SMA system, the combination of the -OH and -CN substitutions gives an almost identical effect to the picture found for the analogous 3-OH-6-BH₂-SMA compound. The potential-energy release during the PT reaction is about 1.3 eV. However, free optimization of the S₁ minimum starting from the FC region of the α form drives the system directly to the CI point (no flat minimum along this reaction path is found).

Excited-State Properties of Other SMA-Based Systems (cyclo-SMA and 3-OH-6-BH₂-cyclo-SMA)

Finally, we also investigated the excited-state behavior of the cyclo-SMA compound. In this case, the purpose of applied substitution was to block the photoinduced reaction of C=N bond twisting, which competes with ESIPT in the bare SMA molecule. This goal was achieved directly by closing the proton-accepting moiety with a 1-aza-1,3-cyclopentadiene ring in the proton-accepting moiety. This modification resulted in only small changes in other areas of the S₁ PES. During the PT reaction, a decrease in energy of the ππ* excited-singlet state (about 1.2 eV) was observed. As found for 3-OH-6-CN-SMA, in this case the search for the S₁ minimum (starting from the α form) also results in a barrierless relaxation to the CI(S₁/S₀) geometry. The excited-state PES in the FC region of the γ form resembles the shape found previously for SMA.

The cyclo-SMA substitution itself does not allow an efficient molecular photoswitching device to be built because, excluding the elimination of possible side photoreactions involving rotation around the C=N bond,^[27] it does not improve the defined photochemical parameters of interest with respect to the bare SMA system. However, one may consider a combination of the previously discussed substitutions on the proton-donating moiety with the proposed modification of the proton-accepting functional group. For this reason, we designed and checked the properties of the 3-OH-6-BH₂-cyclo-SMA system by merging the -OH, -BH₂, and proton-accepting unit substituents. The obtained results confirm our predictions concerning the additive nature of the electronic effects in the proton-accepting moiety and molecular frame. For 3-OH-6-BH₂-cyclo-

SMA, one finds strong stabilization of the γ form in the S_0 state ($E_\gamma = 0.53$ eV) accompanied by approximately 1.5 eV stabilization of the $\pi\pi^*$ state energy due to the PT reaction. Again, access to the CI is barrierless from both sides along rotation around the $C^1=C^7$ bond (no β minimum). The only important difference with respect to the previously discussed systems is the lack of the C_s symmetry during PT, which results from stronger steric repulsion between spatial proton-accepting and $-BH_2$ groups.

3. Conclusions

For all the investigated substitutions to the proton-donating moiety, we observed stabilization of the *trans*-keto form (γ) against the global minimum *cis*-enol form (α) in the ground S_0 state in comparison to the bare SMA system. The stabilization extent depends on the character of the substituent and is most pronounced for combined electron-donor/electron-acceptor substitution.

Analysis of the UV absorption spectra of the SMA derivatives reveals the impact of substituents on the absorption-peak positions. Although the photochromism between the α and γ forms is always preserved, the overlap of the lowest-in-energy bright states and their positions might be controlled by an appropriate choice of substitution; for example, the $-OH$ substitution at the 3-position affects mostly the position of higher excited states of the γ form, whereas the $-BH_2$ substitution at the 6-position shifts the whole spectrum to the lower energy range (here, by about 0.5 eV).

For all the investigated substitutions, the ESIPT process starting from the FC region is barrierless and exoergic in the S_1 state (by about 0.7–1.3 eV, depending on the substitution).

After the PT reaction, the investigated systems arrive at a flat region of the S_1 PES (some of them even exhibit a very shallow local minimum: the β form), and approach the conical intersection with the ground state by twisting around the $C^1=C^7$ bond. Note that there are minor differences for different substituents, but the CI(S_1/S_0) region is energetically accessible for each investigated system due to significant kinetic energy released in the course of the PT reaction.

The conical intersection between the S_1 and S_0 states around the perpendicular conformation is present for all substitutions.

In the S_1 PES region corresponding to higher values of the $C^2-C^1=C^7-N$ dihedral angle (rotation from the FC region of the γ form toward the CI), the electron-accepting substitutions ($-BH_2$, $-CN$) result in a moderate energy barrier whereas the electron-donating substituent ($-OH$) stabilizes the CI(S_1/S_0) region and thus imposes some exoergic character on this transformation.

The side photoreaction competing with ESIPT in SMA-like systems (rotation around the double $C=N$ bond) may be blocked by replacing the proton-accepting moiety with a closed aliphatic ring group. This substitution does not affect any other photochemical features of the system and can subsequently be combined with the electron-donor/electron-acceptor substitutions to the proton-donating moiety.

In summary, we reported a successful attempt to control the crucial photophysical properties of systems that may be used as molecular photoswitches, and we recommend push-and-pull substituted derivatives (analogous to 3-OH-6-BH₂-SMA or 3-OH-6-BH₂-cyclo-SMA) as promising candidates for an experimental realization of such molecular devices.

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