

Ab initio studies of the potential of two pyrimidine derivatives to perform as photo-switch systems

Editorial

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Abstract: The six lowest lying electronic singlet states of 8-(pyrimidine-2-yl)quinolin-ol and 2-(4-nitropyrimidine-2-yl)ethanol have been studied theoretically using the complete active space self-consistent-field (CASSCF) and Møller-Plesset second-order perturbation theory (MP2) methods. Both molecules can be viewed as consisting of a frame and a crane component. As a possible mechanism for the excited-state relaxation process a intramolecular hydrogen transfer promoted by twisting around the covalent bond connecting the molecular frame and crane moieties has been considered. Based on this idea we have attempted to derive abstracted photochemical pathways for both systems. Geometry optimizations for the construction of hypothetical reaction coordinates have been performed at the MP2 level of theory while the CASSCF approach has been employed for the calculation of vertical excitation energies along the pathways. The results of the calculations along the specific twisting displacements investigated in this study do not support the notion of substantial twisting activity upon excitation of any of the five excited states at the planar terminal structures of the torsion coordinates of both molecules. However, the present analysis should be considered only as a first, preliminary step towards an understanding of the photochemistry of the two candidate compounds. For example, we have not performed any excited state geometry optimizations so far and the estimates of vertical excitation energies do not take dynamical electron correlation into account. Further work on this subject is in progress.

PACS (2008): 31.50.-x, 33.15.-e

Keywords: ab initio calculations • molecular switches • electronic states • pyrimidine derivatives

1. Introduction

The dynamics taking place in a molecule after absorbing a photon is usually studied in the framework of the Born-Oppenheimer adiabatic approximation [1, 2], which separates the motion of the rapidly moving electrons

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and the slowly moving nuclei. In this scheme the nuclei move on a single potential energy surface created by the faster moving electrons. Although this scheme is sufficient to treat certain types of chemical and physical processes, this approximation may break down in many important situations. Dynamical events that violate the Born-Oppenheimer adiabatic approximation are classified as nonadiabatic processes and they are characterized by a coupling of the nuclear and electronic motions. Strongly nonadiabatic phenomena are distinguished by a massive energy exchange between electrons and nuclei. Nonadiabatic effects are particularly pronounced if nuclear wave packets are passing through so-called conical intersections (CIs) of two or more potential energy surfaces [3–8]. CIs between electronic potential energy surfaces (PES) play a key mechanistic role in internal conversion processes [4–6]. In several important cases like dissociation, proton transfer, isomerization processes of polyatomic molecules or radiationless deactivation of electronic excited states [9–14] the CIs can provide a very efficient channel for ultrafast interstate crossing on the femtosecond time scale (internal conversion). A typical photochemical reaction that may involve strongly nonadiabatic relaxation dynamics at CIs is for instance the photoinduced switching of a molecule between two stable and well-separated conformers [15].

Since molecular switches have potential applications in a lot of areas, the search for them is of great interest nowadays [15–28]. Because of their small size, switches play an important role in miniaturization [19], permitting ultrahigh density data storage on a molecular level. Molecular switches are the simplest molecular electronic devices that can also be used to regulate the flow of electrons (for example between nanotubes) by application of external stimuli (e.g., light). Feringa and co-workers managed to develop a light-driven unidirectional molecular motor based on a switchable system [19]. Molecular switches have potential applications in medicine too, since they can be employed to control the drug release in cells. They are also applied to the imaging of living cells.

The potential energy profiles of the ground and lowest lying excited singlet states are highly relevant for an examination of the switching properties of molecules. While studying molecular systems with the intention to find possible switching pathways, it is important to analyze potential microscopic processes that can connect the stable forms of the molecule. Eigenvalue crossings of adiabatic electronic states are of particular interest in this context. Molecular switches can in principle be realized via photoinduced reversible ring opening/closure reactions, cis-trans isomerization, photoinduced electron transfer, excited state intramolecular hydrogen transfer (ESIHT) processes or other mechanisms.

We will focus here on ESIHT reactions in 8-(pyrimidine-2-yl) quinolin-ol (PQol, Fig. 1) and 2-(4-nitropyrimidine-2-yl) ethenol (NPE, Fig. 2) which are promoted by the torsion of a crane fragment about a frame component. The isomerizations are initialized by the breaking of an existing intramolecular hydrogen bond at one site of the molecule and are completed by the formation of a new hydrogen bond at a different location.

In the present work, the PQol and NPE molecules were theoretically investigated as potential molecular switch systems by using different levels of electronic structure theory. Based on the suggestion of Ref. [28], we have started the calculations with the larger PQol molecule. The torsion of the pyrimidine crane fragment relative to the two-ring frame component (Fig. 1(b)) can be considered as the key displacement contributing to the reaction

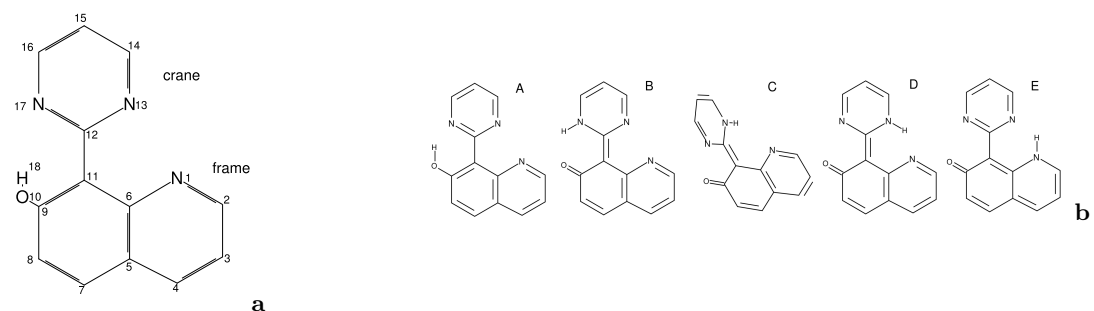


Figure 1. Ground-state equilibrium geometry of the PQol molecule (a) and its different geometries appearing along the ESIHT reaction path (b). (A-B): Planar intramolecular hydrogen transfer; (C): Intermediate twisted geometry; (D-E): Planar intramolecular hydrogen transfer.

path.

The ground state equilibrium structures of the terminal planar isomers have been determined by geometry optimizations employing the Møller-Plesset second-order perturbation theory (MP2) [32] method provided by the MOLPRO code [29]. For the construction of a hypothetical reaction pathway, the frame-crane torsional angle has been fixed at regular intervals, the other dihedral angles have generally been frozen and the nuclear frame has been relaxed in the S_0 state in the space of the remaining internal degrees of freedom, again utilizing the MP2 approach. At the resulting grid points, vertical excitation energies and oscillator strengths were calculated with the complete active space self-consistent-field (CASSCF) formalism [33–37] implemented in the MOLPRO[29] package. The results obtained so far are not consistent with the properties projected for a molecular photoswitch system. However, further theoretical examinations are necessary to obtain a more comprehensive picture of the photochemistry of PQol.

As a next step we have focused on the second molecule (NPE) which can be considered as a simplified version of PQol. NPE serves primarily as a test system for the calibration of the electronic structure approach since the reduced size significantly facilitates the *ab initio* calculations. We have designed a hypothetical switching coordinate for NPE in analogy to the procedure applied to PQol and have investigated the potential energy and transition dipole moment functions of the six lowest lying singlet states of the molecule along this pathway. Like in the case of PQol we also find for NPE that the computational results do not provide evidence for photoswitching activity of NPE, but additional investigations are necessary before any dependable conclusions can be made.

The subsequent sections of this paper are arranged as follows. The methodology and computational details of the *ab initio* calculations are explained in Sec. 2, Sec. 3 presents and discusses the results for the two studied systems. Conclusions are given in Sec. 4.

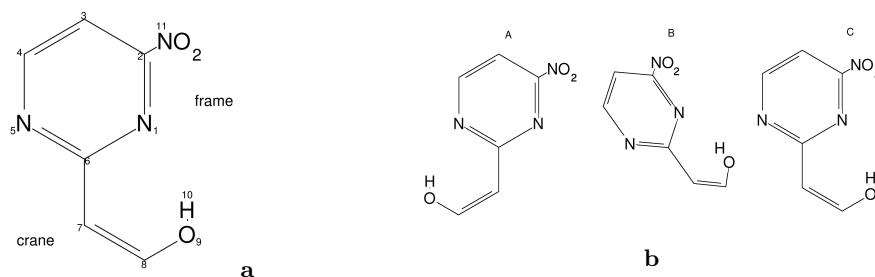


Figure 2. Ground-state equilibrium geometry of NPE molecule (a) and its different geometries appearing along the ESIHT reaction path (b). (A): Starting planar geometry; (B): Intermediate twisted geometry; (C): Terminal planar geometry.

2. Computational details

The CASSCF and MP2 calculations were performed with the MOLPRO program package [29]. Molecular structures and orbitals were visualized using Molden [30]. The ground state equilibrium geometries of both molecules were optimized at the MP2 level of theory. The full aug-cc-pVDZ basis set [31] was used for the description of NPE. In the case of NPE, additional CASSCF calculations have been performed by replacing the core orbitals of the aug-cc-pVDZ basis set on C, N and O atoms by effective core potentials (ECPs) [38] in order to examine the accuracy of this approximation. For the MP2 and CASSCF computations of PQol we have exclusively utilized the combination of aug-cc-pVDZ basis functions for the representation of valence orbitals with ECPs for core orbitals on C, N and O atoms.

In the CASSCF calculations of both molecules, the six lowest lying electronic singlet states were computed by including them with equal weights in the CASSCF energy functional.

For NPE, we have defined two active spaces, in the smaller CASSCF calculations, which were limited to the planar isomers, 12 electrons are distributed over 10 orbitals (CAS(10/12)), while a more extensive 18 electron / 13 orbital active space (CAS(13/18)) has been defined for the calculations along the reaction pathway in order to account for the mixing of orbital types induced by the torsional distortion. The CAS(13/18) includes the following orbitals: 4π , 2 lone pairs on the N atoms, 3σ localized between the frame and crane and 4 unoccupied π^* orbitals. The orbital classification corresponds to both planar isomers, at nonplanar conformations the π and σ character of certain orbitals may not be conserved.

For PQol we use only one active space, CAS(15/22), given by 22 valence electrons distributed over 15 orbitals. The 15 orbitals were chosen as 8π orbitals, 3 lone pairs on the nitrogen atoms and 4 unoccupied π^* orbitals (again, orbital assignment is only strictly valid at the planar structures of PQol). The vertical excitation energies, oscillator strengths and dipole moments were determined by the CASSCF method at the MP2-optimized ground-state equilibrium geometries along the twisting pathway.

The excited state intramolecular hydrogen transfer (ESIHT) process has been investigated for both NPE and PQol to obtain information on a possible photochemically relevant reaction path. Therefore, for the ground state calculations we have to consider two planar, stable isomers of both systems, one representing the initial form and

the other corresponding to the structure of the molecule as the product of the excited state relaxation mechanism. For the construction of the reaction path the frame-crane torsion angle α has been chosen for NPE, and for fixed values of this torsion angle and of the other dihedral angles all remaining internal coordinates were varied. In the case of the PQol molecule only the initial, final and the $\alpha = 90^\circ$ geometries were optimized. Using these data a linearly interpolated transit path was calculated.

More details on the selection of the active orbitals for CASSCF calculations of both NPE and PQol and on the definition of reaction pathways will be given elsewhere [39, 40].

The calculations were carried out on the Titan Rock Cluster at the University of Oslo and at the Jülich Supercomputing Centre on an Intel Xeon X5570 Cluster JUROPA.

3. Results and discussion

In this section the results of electronic structure studies will be reported and discussed for both PQol and NPE.

3.1. The PQol molecule

We begin with an examination of the potential photoswitch functionality of PQol (see Fig. 1(a)). Based on electronic structure information Ref. [15] proposes the possibility of excited state intramolecular hydrogen transfer (ESIHT) promoted by the frame-crane torsion (α). This photochemical mechanism is supposed to connect the two stable, planar forms of the molecule (see Fig. 1(b)). More specifically, Ref. [15] suggests that the ESIHT process is induced by the torsion of the molecular crane (pyrimidine ring) relative to the two-ring frame component. The projected driving coordinate for the hydrogen transfer is the $C_9C_{11}C_{12}N_{13}$ dihedral angle. Initially, a $O_{10} - H_{18} \cdots N_{17}$ hydrogen bond is formed at the educt geometry. After absorbing light this hydrogen bond breaks up and the new $O_{10} \cdots H_{18} - N_{17}$ bond forms, and the crane part of the molecule subsequently starts to rotate around the $C_{11} - C_{12}$ double bond. This photochemical process implies that the value of the dihedral angle (α) changes from 0° to 180° degree. At the final position of the dihedral angle ($\alpha = 180^\circ$) firstly the $N_{17} - H_{18} \cdots N_1$ hydrogen bond is formed, but this geometry still represent an intermediate conformer. The final structure is realized by reformation of this hydrogen bond to establish the $N_{17} \cdots H_{18} - N_1$ connection. In this final state the H_{18} atom is reattached to the molecular frame although now in a different position.

We have optimized the ground state geometries of PQol at the MP2 level of theory by freezing the torsion angle α at the values 0° , 90° , 180° . At $\alpha=180^\circ$, the terminal structure corresponding to H_{18} attached to N_1 as well as the upstream intermediate with $N_{17} - H_{18}$ bond have been optimized in S_0 with the MP2 method.

The geometry optimization of the $\alpha=90^\circ$ conformer has been performed by freezing α and all other dihedral angles at the adjustments of the planar conformers and by varying all other coordinates. The intermediate geometries have been determined by linear interpolation to obtain the ground state potential energy profile (PEP). In Fig. 3 the ground state PEP along the above discussed reaction path is displayed. Note that two, well-separated minima

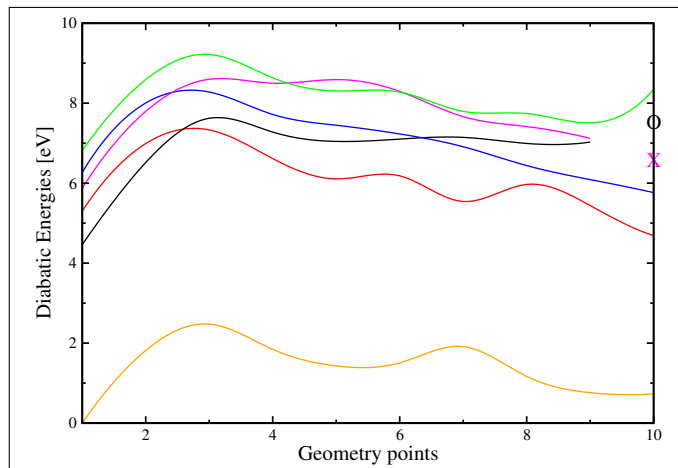


Figure 3. Potential energy profiles of the six lowest lying singlet states of PQol (with diabatic connection at eigenvalue crossings) obtained at the state-averaged CASSCF(15/22)/aug-cc-pVDZ+ECP level of theory.

Table 1. Vertical excitation energies (ΔE), given in eV, oscillator strengths (f), and dipole moments (μ), given in Debye of PQol calculated with the state-averaged CASSCF(15/22)/aug-cc-pVDZ+ECP approach at the ground state equilibrium (conformers No. 1 and 10) geometries.

State	ΔE (eV)	f osc. str.	μ (Debye)
conformer 1 (0°)			
1A'	0.000	—	1.222
1A'' { $n_1 \rightarrow \pi_1^*$ }	4.464	0.00278	4.964
2A' { $\pi_3 \rightarrow \pi_1^*$ }	5.302	0.39741	1.547
2A'' { $n_1 \rightarrow \pi_2^*$ }	5.873	0.00620	3.777
3A' { $\pi_2 \rightarrow \pi_1^*$ }	6.270	0.41769	0.805
4A' { $\pi_1 \rightarrow \pi_1^*$ }	6.814	0.25499	1.551
conformer 10 (180°)			
1A'	0.726 ^a	—	9.372
2A' { $\pi_3 \rightarrow \pi_1^*$ }	3.962	0.12066	6.612
3A' { $\pi_2 \rightarrow \pi_1^*$ }	5.038	0.44060	6.705
4A' { $\pi_3 \rightarrow \pi_2^*$ }	5.847	0.58983	4.657
5A' { $\pi_2 \rightarrow \pi_2^*$ }	6.799	0.74548	8.034
6A' { $\pi_1 \rightarrow \pi_1^*$ }	7.622	0.22044	6.605

^a Energy relative to the ground-state global minimum.

have been found on the PEP of the ground state and they are separated from each other by a barrier exceeding 1eV, which is sufficiently large to prevent thermal interconversion of the molecule, a necessary condition for a photoswitch system.

The vertical excitation energies, oscillator strengths and dipole moments obtained at the optimized geometry of both conformers are presented in Table 1. The optical transition to the lowest excited singlet state at the terminal structure has a moderate oscillator strength in the UV range of the spectrum ($f = 0.12066$, $\Delta E = 3.962$ eV), while the first excited state is essentially dark in absorption from the ground state ($f = 0.00278$, $\Delta E = 4.464$ eV) at the educt geometry. However, for the second excited state the value of the oscillator strength is reasonably

large at this starting geometry ($f = 0.39741$, $\Delta E = 5.302$ eV).

Let us consider the two stable forms of our bistable molecule, and assume that it can be excited from the ground states to the first excited ones by λ_1 and λ_2 wavelengths, respectively. In order for this molecule to perform as a photoreversible switchable system another necessary condition has to be fulfilled. The λ_1 and λ_2 wavelengths have to be reasonably different. This means that the system should be switchable from one state to another by two photon energies that are markedly different from each other. As can be seen from Table 1, this requirement is fulfilled for PQol, but only in the special situation that the energies for transitions between ground and first excited state (at the product structure) as well as between ground and second excited state (at the initial structure) are shifted with respect to each other by more than 1.0 eV. At the educt geometry the second excited state has to be taken into account as the oscillator strength of the first excited one is practically zero.

In order to further investigate the photoswitch potential of this compound the energy profiles of the lowest lying excited singlet states have been evaluated as a function of the twisting coordinate. The profiles are shown in Fig. 3 with diabatic connections at eigenvalue crossings. While the ground state PEP shows a sufficiently large barrier between the two minima to prevent the system from thermal interconversion, the CASSCF calculations do not predict a stabilization of excited states at nonplanar conformations. Fig. 3 also does not indicate that an avoided crossing between the ground and first excited state exists along the pathway.

The presence of the circle and cross marks at the final geometry (point 10) is due to the fact that no $n \rightarrow \pi^*$ excitation is present at that point (since the lone pair on N1 doesn't exist), therefore direct diabatic connection cannot be made.

The very limited collection of data obtained in this section does not suggest effective photoswitch functionality of PQol. The system has two well-defined ground state minima which are separated from each other by a sufficiently large energy barrier to prevent thermally induced isomerization and the energy of relevant transitions of the two conformers are also different enough from each other for selective excitation of one isomer. However, the excited state energy profiles do not indicate the existence of nonplanar minima and the first excited state does not form a pronounced avoided crossing with the ground state potential as well.

3.2. The NPE molecule

NPE represents a simplified version of PQol, but a similar repulsion between nitrogen lone pair electrons can be excluded in the case of NPE. The smaller size of the system allows for a, in relative terms, more comprehensive active space. In addition, we were able to perform more detailed numerical studies. The coordinate characteristic for the reaction path is the torsion of the C_2OH_3 molecular crane about the molecular frame component. In this case the driving coordinate for the hydrogen transfer reaction is the α $N_1C_6C_7C_8$ dihedral angle.

In order to define the reaction coordinate we have optimized the ground state geometries at the MP2 level of theory for different values of the dihedral angle ($\alpha=0^\circ, 30^\circ, 60^\circ, 90^\circ, 120^\circ, 150^\circ, 180^\circ$). During the geometry optimizations along the reaction path all the parameters were varied except the dihedral angles. After determining the two planar

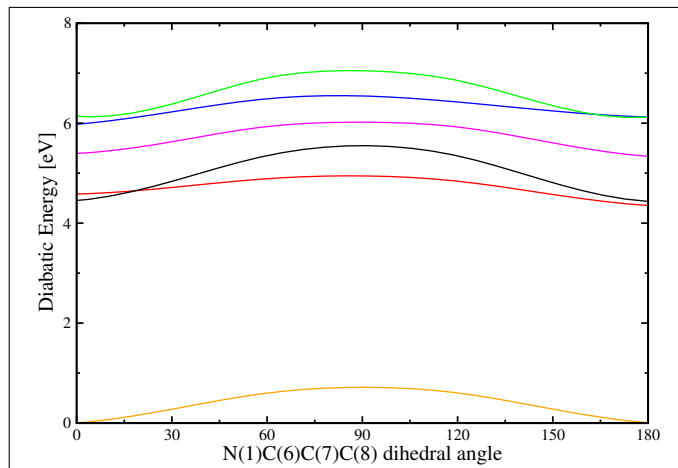


Figure 4. Potential energy profiles of the six lowest lying singlet states of NPE obtained at the state-averaged CASSCF(13/18)/aug-cc-pVDZ level of theory. Potential energy functions are diabatically connected at eigenvalue crossings.

equilibrium structures of the molecule (at $\alpha=0^\circ$ and $\alpha=180^\circ$) we investigated the six lowest lying singlet states of the molecule employing the CASSCF(13/18) method. For efficiency reasons we investigate the performance of the replacement of $1s$ basis functions on C , N and O atoms by ECPs by comparison with CASSCF(10/12) results obtained at the terminal structures of NPE with the full aug-cc-pVDZ basis set.

Employing ECPs reduces the number of basis functions in the aug-cc-pVDZ basis representation from 321 to 309. The vertical excitation energies, oscillator strengths and dipole moments obtained with and without ECP approximation are collected in Table 2 for the two planar equilibrium geometries. The values presented are in good agreement with each other. Based on these results it can be expected that if the ECP approximation works for this small system it will also work for similar, larger molecules.

By comparing the transition energies between the ground and first excited states at the two stable forms it can be noticed that they are shifted relative to each other by only ca. $0.2eV$. Most probably this will hardly be sufficient to meet one of the criteria that decide on the photoswitch performance of a molecule.

We further computed the five lowest lying excited singlet states at the optimized ground state structures to investigate if any of them would be stabilized by the torsion. The obtained PEPs, with diabatic connections at eigenvalue crossings, are displayed in Fig. 4. The ground state PEP shows a sufficiently large barrier between the two ground state minima to prevent the system from thermally induced isomerization. However, like in the case of PQol, no stabilization of excited states at nonplanar conformations can be diagnosed. There are also no avoided crossings between the ground and first excited states along this coordinate.

Table 2. Vertical excitation energies (ΔE), given in eV, oscillator strengths (f) (obtained with and without ECP), and dipole moments (μ), given in Debye of NPE calculated with the CASSCF(10/12)/aug-cc-pVDZ method (applying maximum possible weights for the respective states in the wave function optimization) at the ground state equilibrium geometries of the planar conformers with 0° and 180° dihedral angles.

State	ΔE (eV)		f oscillator str.		μ (Debye)
	no ECP	with ECP	no ECP	with ECP	
conformer A (0° dihedral angle)					
1A'	0.018 ^b	0.020 ^c	—	—	3.365
1A'' {n ₂ →π ₂ [*] }	4.555	4.346	0.00834	0.00818	3.783
2A' {π ₄ →π ₂ [*] }	4.583	4.400	0.04360	0.04561	6.410
2A'' {n ₂ →π ₁ [*] }	5.530	5.451	0.00182	0.00123	2.029
3A' {π ₄ →π ₁ [*] }	5.845	5.877	0.40933	0.38698	7.093
3A'' {n ₁ →π ₂ [*] }	6.567	6.248	0.00272	0.00410	4.167
conformer C (180° dihedral angle)					
1A'	0.000	0.000	—	—	5.135
2A' {π ₄ →π ₂ [*] }	4.562	4.507	0.01373	0.02908	7.603
1A'' {n ₂ →π ₂ [*] }	4.736	4.576	0.00787	0.00791	8.703
2A'' {n ₂ →π ₁ [*] }	5.408	5.336	9.5x10 ⁻⁶	3x10 ⁻⁶	7.308
3A' {π ₄ →π ₁ [*] }	5.764	5.788	0.47319	0.46132	7.271
3A'' {n ₁ →π ₂ [*] }	6.647	6.415	0.00181	0.00145	6.003

^b Energy relative to the ground-state global minimum without using ECP.

^c Energy relative to the ground-state global minimum in case of using ECP.

4. Conclusions

One basic requirement for a molecular switch is bistability, i.e. the appearance of two (and only two) well separated minima of a molecule. The idea is that the system can reversibly be transferred between the two isomers by applying an external stimulus, in particular, light of well defined energy. This property is a condition, but it is not sufficient. Several other requirements have to be fulfilled for such a bistable system to perform as a molecular switch. The most important ones are: (i) The two well-defined minima have to be separated from each other by a sufficiently large energy barrier in order to avoid thermal interconversion; (ii) The molecule has to possess photochromic properties, i.e., the two stable conformers must absorb photons at different wavelengths. In addition, the energies of the lowest lying transitions with sufficient oscillator strength of the two vertical excitation profiles have to be sufficiently different in order to differentiate between the two conformers; (iii) The two isomers should have barrierless access to the CI (between the ground and first excited states) from the Franck-Condon region of the corresponding excited states.

In this paper we have investigated two pyrimidine derivatives as possible photo-switch systems. As photochemical mechanism by which the two conformers of both NPE and PQol can isomerize we investigate excited state intramolecular hydrogen transfer (ESIHT) promoted by twisting around the covalent bond that connects the crane and frame parts of each molecule. Based on this concept detailed numerical electronic structure studies have been performed. Among other properties, the ground state equilibrium geometries of both stable forms, the potential energy functions of the six lowest lying singlet states along hypothetical reaction pathways, oscillator strengths and dipole moments were calculated.

The analysis of the results obtained for both systems so far does not indicate that PQol or NPE would be effective photoswitch systems. However, we emphasize that the investigations are still in an early state and far from being conclusive. We mention just three important aspects that are relevant for obtaining an improved picture of the photochemistry of PQol and NPE: (i) The isomerization coordinates defined for PQol and NPE in the present study are based on ground state optimizations and may therefore differ significantly from the regions of coordinate space that may actually be frequented by excited state wave packets. In other words, to obtain more realistic pathways we need to perform constrained excited state geometry optimizations with the frame-crane torsion-angle fixed at regular intervals. (ii) The CASSCF method takes only a very small part of dynamical electron correlation into account. However, inclusion of dynamical electron correlation in the electronic structure model is required to reach more realistic estimates in particular of vertical excitation energies. This can be accomplished e.g. by employing multiconfigurational perturbation theory or multireference configuration interaction method based on CASSCF reference functions. (iii) For applications, e.g. in electronics or medicine, the photoswitch property of molecules will usually not be utilized in the gas phase but in condensed phase environments. It is well known that interactions with matrix or solvent molecules can have a significant effect on the photophysics and photochemistry of the probe or solvent molecule (here, PQol or NPE). In order to assess the photoisomerization performance of both candidate molecules consideration of environmental effects would hence also be relevant.

It is therefore very well possible that more extended studies may in fact reveal that PQol and NPE are interesting photoswitch systems. However, based on the present status of this investigation this appears somewhat unlikely.

Acknowledgments

The authors thank for funding by the Norwegian-Hungarian bilateral project n° NO-1/2009. The support of the COST Action CM0702 CUSPFEL is gratefully acknowledged. This work has received continued funding from the Mohn Foundation (C. W.), the Centre for Theoretical and Computational Chemistry (CTCC) at the University of Tromsø and the Research Council of Norway (C. W.: Grant Nr. 177558/V30). Support of several visits at the University of Debrecen by the Hungarian Research Council is also acknowledged by C. W.. Thanks go also to Norwegian High Performance Computing (NOTUR) and the John-von-Neumann Institute, Research Center Jülich (Project ID ehu01) for providing computational resources on the titan and juropa clusters, respectively.

References

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- [1] M. Born, R. Oppenheimer, Ann. Phys. 84 (1927) 457.
 - [2] M. Born, K. Huang, The Dynamical Theory of Crystal Lattices; Oxford University Press: Oxford, UK, (1954).
 - [3] H. Köppel, W. Domcke, L. S. Cederbaum, Adv. Chem. Phys. 57 (1984) 59.

- [4] M. Baer, G. D. Billing, *The Role of Degenerate States in Chemistry*, Advances in Chemical Physics Vol. 124 Wiley-Interscience, New York, (2002).
- [5] W. Domcke, D. R. Yarkony, H. Köppel, Eds.; *Conical Intersections: Electronic Structure, Dynamics and Spectroscopy*; World Scientific: Singapore, (2004).
- [6] G. A. Worth, L. S. Cederbaum, *Annu. Rev. Phys. Chem.* 55 (2004) 127.
- [7] M. Baer, *Beyond Born Oppenheimer: Electronic Non-Adiabatic Coupling Terms and Conical Intersections*; Wiley: Hoboken, NJ, (2006).
- [8] S. Matsika, *Rev. Comp. Chem.* 23 (2007) 83.
- [9] M. Klessinger, J. Michl, *Excited States and Photochemistry of Organic Molecules*; VCH Publishers Inc.; New York, (1995).
- [10] P. Kukura, et al. *Science* 310 (2005) 1006.
- [11] S. Hahn, G. J. Stock, *Phys. Chem. B.* 104 (2000) 1146.
- [12] T. Schultz, et al. *Science* 306 (2004) 1765.
- [13] Z. Lan, L. M. Frutos, A. Sobolewski, W. Domcke, *Proc. Natl. Acad. Sci.* 105 (2008) 12707.
- [14] T. Andruniow, N. Ferre, M. Olivucci, *Proc. Natl. Acad. Sci.* 101 (2004) 17908.
- [15] A. L. Sobolewski, *Phys. Chem. Chem. Phys.* 10 (2008) 1243.
- [16] A. Aviram, M. A. Ratner, *Chem. Phys. Lett.* 29 (1974) 277.
- [17] J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science* 286 (1999) 1550.
- [18] Z. Yao, H. W. C. Postman, L. Balents, C. Dekker, *Nature* 406, (1999) 273.
- [19] *Molecular Switches*. Ed. by Ben L. Feringa, 2001 Wiley-VCH Verlag GmbH.
- [20] P. R. Hania, R. Telesca, L. N. Lucas, A. Pugzlys, J. van Esch, B. L. Feringa, J. G. Snijders, K. Duppen, *J. Phys. Chem. A* 106 (2002) 8498.
- [21] D. Guillaumont, T. Kobayashi, K. Kanda, H. Miyasaka, K. Uchida, S. Kobatake, K. Shibata, S. Nakamura, M. Irie, *J. Phys. Chem. A* 106 (2002) 7222.
- [22] D. Dulic, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. De Jong, T. N. Bowden, J. Van Esch, B. L. Feringa, B. J. Van Wees, *Phys. Rev. Lett.* 91 (2003) 207402.
- [23] J. Li, G. Speyer, O. Sankey, *Phys. Rev. Lett.* 93 (2004) 248302.
- [24] M. Zhuang, M. Ernzerhof, *Phys. Rev. B* 72 (2005) 073104.
- [25] C. J. Barrett, J. Mamiya, K. G. Yagerc, T. Ikeda, *Soft Matter*, 3 (2007) 1249.
- [26] H. Tamura, S. Nanbu, T. Ishida, H. Nakamura, *J. Chem. Phys.* 125 (2006) 034307.
- [27] L. Lapinski, M. J. Nowak, J. Nowacki, M. F. Rode, A. L. Sobolewski, *ChemPhysChem* 10 (2009) 2290.
- [28] M. F. Rode, A. L. Sobolewski, *J. Phys. Chem. A* 114, (2010) 11879.
- [29] Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schtz, M.; Celani, P.; Korona, T.; Rauhut, G.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Lloyd, A. W.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nickla, A.; Palmieri, P.; Pitzer,

- R.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. MOLPRO package.
- [30] G. Schaftenaar, J. H. Noordik, *J. Comput. Aid. Mol. Des.* 14 (2000) 123.
- [31] T.H. Dunning, Jr. *J. Chem. Phys.* 90 (1989) 1007.
- [32] C. Møller, M. S. Plesset, *Phys. Rev.* 46 (1934) 618.
- [33] B. H. Lengsfeld III, D. R. Yarkony, *Adv. Chem. Phys.* 82 (1992) 1.
- [34] B. O. Roos, *Adv. Chem. Phys.* 69 (1987) 399.
- [35] B. O. Roos, P. R. Taylor, P. E. M. Siegbahn, P. E. M., *Chem. Phys.* 48 (1980) 157.
- [36] H. J. Werner, *Adv. Chem. Phys.* 69 (1987) 1.
- [37] K. Ruedenberg, K., M. W. Schmidt., M. M. Gilbert, S. T. Elbert, *Chem. Phys.* 71 (1982) 41.
- [38] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* 80 (1993) 1431.
- [39] C. Woywod, A. Csehi, G. Halasz, K. Ruud, A. Vibok, submitted to *Phys. Chem. Chem. Phys.*
- [40] A. Csehi, A. Vibok, G. Halasz, K. Ruud, C. Woywod, to be published.