

Ab initio studies of two pyrimidine derivatives as possible photo-switch systems

Research Article

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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 an 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.

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1. Introduction

The dynamics taking place inside a molecule after absorbing a photon is usually studied within the framework of the Born–Oppenheimer adiabatic approximation [1, 2],

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1 which separates out the motion of the rapidly moving elec-
2 trons and the slowly moving nuclei. In this scheme the
3 nuclei move on a single potential energy surface created
4 by the faster moving electrons. Although this scheme is
5 sufficient to treat certain types of chemical and physical
6 processes, this approximation may break down in many
7 important situations. Dynamical events that violate the
8 Born-Oppenheimer adiabatic approximation are classified
9 as non-adiabatic processes and are characterized by a
10 coupling of the nuclear and electronic motions. Strongly
11 non-adiabatic phenomena are distinguished by a massive
12 energy exchange between electrons and nuclei, and are
13 particularly pronounced if nuclear wave packets are pass-
14 ing through so-called conical intersections (CIs) of two or
15 more potential energy surfaces [3–8]. CIs between elec-
16 tronic potential energy surfaces (PES) play a key mech-
17 anistic role in internal conversion processes [4–6]. In sev-
18 eral important cases such as dissociation, proton transfer,
19 isomerization processes of polyatomic molecules or radia-
20 tionless deactivation of electronic excited states [9–14] the
21 CIs can provide a very efficient channel for ultrafast inter-
22 state crossing on the femtosecond time scale (internal con-
23 version). The photo-induced switching of a molecule be-
24 tween two stable and well-separated conformers is a typ-
25 ical example of photochemical reactions and may involve
26 strongly non-adiabatic relaxation dynamics at CIs [15].

27 Molecular switches have potential applications in many
28 areas and are thus an area of great research interest [15–
29 28]. Due to their small size, switches play an important
30 role in miniaturization [19] by permitting ultra-high den-
31 sity data storage on a molecular level. Molecular switches
32 are the simplest molecular electronic devices that can also
33 be used to regulate the flow of electrons (for example be-
34 tween nanotubes) by the application of external stimuli
35 (e.g., light). Feringa and co-workers managed to develop
36 a light-driven unidirectional molecular motor based on a
37 switchable system [19]. Molecular switches have poten-
38 tial applications in medicine as well, since they can be
39 employed to control the drug release in cells. They are
40 also used when living cells are imaged.

42 The potential energy profiles of the ground and lowest
43 lying excited singlet states are highly relevant for an ex-
44 amination of the switching properties of molecules. While
45 studying molecular systems with the intention of finding
46 possible switching pathways, it is important to analyze po-
47 tential microscopic processes that can connect the stable
48 forms of the molecule. In this context, eigenvalue cross-
49 ings of adiabatic electronic states are of particular interest.
50 Molecular switches can in principle be achieved through
51 photo-induced reversible ring opening/closure reactions,
52 cis-trans isomerization, photo-induced electron transfer,
and excited state intramolecular hydrogen transfer (ES-

IHT) processes.

53
54 One basic requirement for a molecular switch is bista-
55 bility, *i.e.* the appearance of two (and only two) well
56 separated minima of a molecule. The idea is that the
57 system can reversibly be transferred between the two iso-
58 mers by applying an external stimulus, in particular, light
59 of a well defined energy. This property is a condition, but
60 it is not sufficient. Several other requirements have to be
61 fulfilled for such a bistable system to perform as a molec-
62 ular switch. The most important ones are: (i) The two
63 well-defined minima have to be separated from each other
64 by a sufficiently large energy barrier in order to avoid
65 thermal interconversion; (ii) The molecule has to possess
66 photochromic properties, *i.e.*, the two stable conformers
67 must absorb photons at different wavelengths. In addition,
68 the energies of the lowest lying transitions with sufficient
69 oscillator strength of the two vertical excitation profiles
70 have to be sufficiently different in order to differentiate
71 between the two conformers; (iii) The two isomers should
72 have barrierless access to the CI (between the ground and
73 first excited states) from the Franck-Condon region of the
74 corresponding excited states.

75 We will focus here on ESIHT reactions in 8-(pyrimidine-
76 2-yl) quinolin-ol (PQol, Fig. 1) and 2-(4-nitropyrimidine-
77 2-yl) ethenol (NPE, Fig. 2) which are promoted by the
78 torsion of a crane fragment about a frame component. The
79 isomerization is initialized by the breaking of an existing
80 intramolecular hydrogen bond at one site of the molecule
81 and is completed by the formation of a new hydrogen bond
82 at a different location.

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

91 The ground state equilibrium structures of the terminal
92 planar isomers have been determined by geometry opti-
93 mizations employing the Møller-Plesset second-order
94 perturbation theory (MP2) [31] method provided by the
95 MOLPRO code. For the construction of a hypothetical re-
96 action pathway, the frame-crane torsional angle has been
97 fixed at regular intervals, the other dihedral angles have
98 generally been frozen and the nuclear frame has been
99 relaxed in the S_0 state in the space of the remaining in-
100 ternal degrees of freedom, again utilizing the MP2 ap-
101 proach. At the resulting grid points, vertical excitation
102 energies and oscillator strengths were calculated with the
103 complete active space self-consistent-field (CASSCF) for-
104 malism [32–36] implemented in the MOLPRO package.

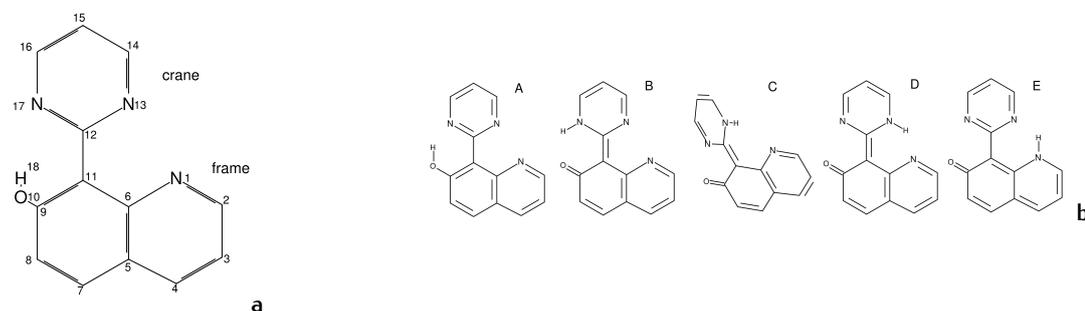


Figure 1. Ground-state equilibrium geometry of the PQol molecule (a) and its different geometries appearing along the ESIHT reaction path (b). (A-B): Planar intramolecular hydrogen transfer; (C): Intermediate twisted geometry; (D-E): Planar intramolecular hydrogen transfer.

The results obtained so far are not consistent with the properties projected for a molecular photo-switch system. However, further theoretical examinations are necessary to obtain a more comprehensive picture of the photochemistry of PQol.

For the next step we have focused on the second molecule (NPE) which can now 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 *ab initio* calculations. We have designed a hypothetical switching coordinate for NPE analogous 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. As in the case of PQol we also find for NPE that the computational results do not provide evidence for the photo-switching 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 provided in Sec. 4.

2. Computational details

The CASSCF and MP2 calculations were performed with the MOLPRO program package¹. Molecular structures and orbitals were visualized using Molden [29]. The ground state equilibrium geometries of both molecules were optimized at the MP2 level of theory. The full aug-

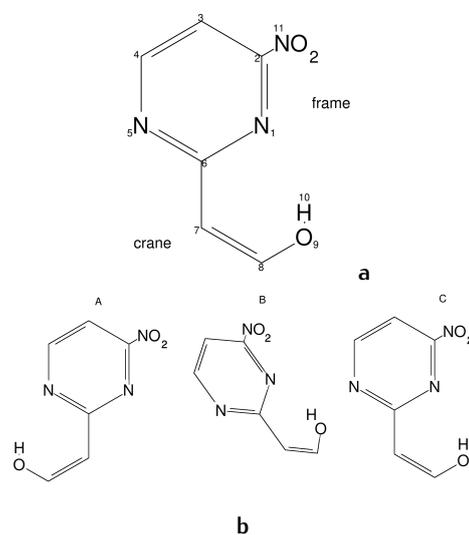


Figure 2. Ground-state equilibrium geometry of NPE molecule (a) and its different geometries appearing along the ESIHT reaction path (b). (A): Starting planar geometry; (B): Intermediate twisted geometry; (C): Terminal planar geometry.

cc-pVDZ basis set [30] 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) [37] 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 the core orbitals of the C, N and O atoms.

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

For NPE, we have defined two active spaces, in the

¹ MOLPRO is a package of *ab initio* programs written by H.-J. Werner et al.

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 pair 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.

A single active space, CAS(15/22), given by 22 valence electrons distributed over 15 orbitals is utilised for PQol. 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 twist pathway.

The excited state intramolecular hydrogen transfer (ESIHT) process has been investigated for both NPE and PQol to obtain 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 a product of the excited state relaxation mechanism. For the construction of the reaction path the frame-crane torsion angle α (the $N_1C_6C_7C_8$ dihedral angle, see Fig. 2(a)) has been chosen for NPE. For fixed values of this torsion angle and assuming the other dihedral angles all remain constant, the internal coordinates were varied. In the case of the PQol molecule only the initial, final and the $\alpha = 90^\circ$ geometries were optimized (here α is the $C_9C_{11}C_{12}N_{13}$ dihedral angle, see Fig. 1(a)). Using this data a linearly interpolated transit path was calculated.

More details on the selection of the active orbitals for CASSCF calculations and the definition of reaction pathways for both NPE and PQol will be given elsewhere [38, 39].

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 photo-switch functionality of PQol (see Fig. 1(a)). Based on electronic structure information Ref. [15] proposes the possibility of excited state intramolecular hydrogen transfer (ESIHT) being promoted by the frame-crane torsion (α). This photochemical mechanism is assumed 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 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 represents 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 fixing 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 have been found on the PEP of the ground state and they are separated from each other by a barrier exceeding 1 eV, which is sufficiently large to prevent thermal interconversion of the molecule, a necessary condition for a photo-switch 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).

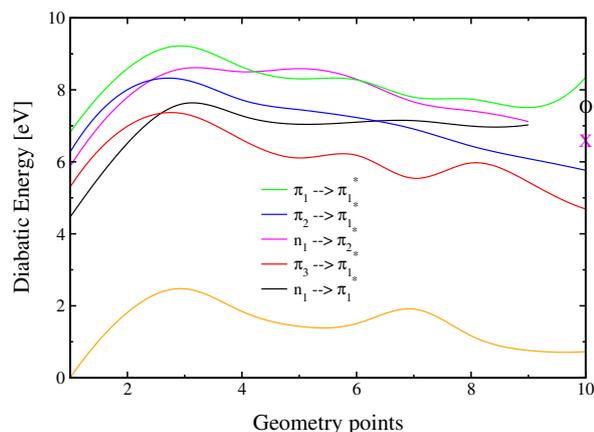


Figure 3. Potential energy profiles of the six lowest lying singlet states of PQol (with diabatic connection at eigenvalue crossings) obtained at the state-averaged CASSCF(15/22)/aug-cc-pVDZ+ECP level of theory.

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.

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 wavelengths λ_1 and λ_2 , respectively. In order for this molecule to perform as a photoreversible switchable system another necessary condition has to be fulfilled: the wavelengths λ_1 and λ_2

have to be reasonably different. The implication hereof is 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 by 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 since the oscillator strength of the first excited state is practically zero.

In order to further investigate the photo-switch 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. As further substantiation of this Fig. 3 indicates that no 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 $n \rightarrow \pi^*$ excitation is not present at that point (since the lone pair on N1 doesn't exist), therefore a direct diabatic connection cannot be made.

The very limited collection of data obtained in this section does not suggest effective photo-switch 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, in relative terms, a 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

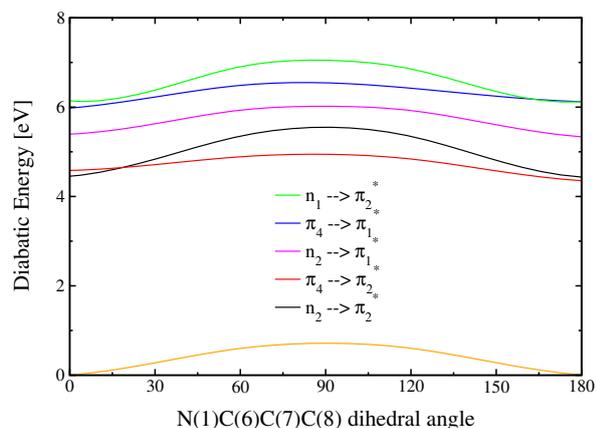


Figure 4. Potential energy profiles of the six lowest lying singlet states of NPE obtained at the state-averaged CASSCF(13/18)/aug-cc-pVDZ level of theory. Potential energy functions are diabatically connected at eigenvalue crossings.

the driving coordinate for the hydrogen transfer reaction is the α N₁C₆C₇C₈ 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° , 60° , 90° , 120° , 150° , 180°). During the geometry optimizations along the reaction path all the parameters were varied except for the dihedral angles. After determining the two planar 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 tabulated 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, but larger molecules. By comparing the transition energies between the ground and first excited states at the two stable forms it can be calculated that they are shifted relative to each other by only ca. 0.2 eV. This is hardly sufficient to meet one of the criteria that determines the photo-switch performance of a molecule.

Further we computed the five lowest lying excited singlet states at the optimized ground state structures to investi-

gate 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 are apparent. There are also no avoided crossings between the ground and first excited states along this coordinate.

4. Conclusions

In this paper we have investigated two pyrimidine derivatives as possible photo-switch systems. 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 as photochemical mechanism by which the two conformers of both NPE and PQol can isomerize. Based on this concept detailed numerical electronic structure studies have been performed. 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, along with other properties.

The analysis of the results obtained for both systems so far indicate that PQol and NPE are ineffective photo-switch 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 photo-switch property of molecules will usually not be utilized in the gas phase but rather in condensed phase environments. It is well known that

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
$1A'' \{n_2 \rightarrow \pi_2^*\}$	4.555	4.346	0.00834	0.00818	3.783
$2A' \{\pi_4 \rightarrow \pi_2^*\}$	4.583	4.400	0.04360	0.04561	6.410
$2A'' \{n_2 \rightarrow \pi_1^*\}$	5.530	5.451	0.00182	0.00123	2.029
$3A' \{\pi_4 \rightarrow \pi_1^*\}$	5.845	5.877	0.40933	0.38698	7.093
$3A'' \{n_1 \rightarrow \pi_2^*\}$	6.567	6.248	0.00272	0.00410	4.167
conformer C (180° dihedral angle)					
$1A'$	0.000	0.000	—	—	5.135
$2A' \{\pi_4 \rightarrow \pi_2^*\}$	4.562	4.507	0.01373	0.02908	7.603
$1A'' \{n_2 \rightarrow \pi_2^*\}$	4.736	4.576	0.00787	0.00791	8.703
$2A'' \{n_2 \rightarrow \pi_1^*\}$	5.408	5.336	9.5×10^{-6}	3×10^{-6}	7.308
$3A' \{\pi_4 \rightarrow \pi_1^*\}$	5.764	5.788	0.47319	0.46132	7.271
$3A'' \{n_1 \rightarrow \pi_2^*\}$	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.

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 photo-isomerization performance of both candidate molecules consideration of environmental effects would hence also be relevant.

It is therefore highly likely that more extended studies may in fact reveal that PQol and NPE are interesting photo-switch systems. However, based on the present status of this investigation this appears somewhat unlikely.

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