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On the Mechanism of Photoinduced Dihydroazulene Ring-Opening Reaction

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Abstract

The photoinduced ring-opening reaction is a key process in the functioning of dihydroazulene/vinylheptafulvene (DHA/VHF) photoswitches. Over the years, the mechanism of this reaction has been extensively debated. Herein, by means of nonadiabatic trajectory dynamics simulations and quantum chemistry calculations, we present the first detailed and comprehensive investigation on the mechanism of the photoinduced ring-opening reaction of DHA. The results show the crucial role of the excited-state ring planarization process for the bond breaking. Our dynamics simulations [show](#) that the DHA ring opening is an ultrafast reaction that does not follow exponential kinetics but exhibits ballistic dynamics. Upon photoexcitation, the planarization occurs within 300-500 fs. This leads to the ring-opening reaction and concurrent decay of the molecule to the ground state within 100 fs through an $S_1 \rightarrow S_0$ internal conversion process towards forming the VHF isomer. These results are consistent with previous ultrafast time-resolved experiments and lead to a thorough understanding of the DHA/VHF photoconversion.

TOC Graphic

The limited access to fossil fuels makes solar energy conversion and storage one of the great goals and challenges of this century. Among the many existing methods for sunlight conversion like artificial photosynthesis¹ and photovoltaic devices², to name a few, the strategy for conversion and storage of solar energy into the chemical bonds of metastable photoisomers has attracted great attention. Dihydroazulene (DHA) has been considered for a long time a promising candidate for solar energy harvesting, storage and release.³⁻⁹ Upon light absorption, the DHA molecule is excited from the electronic ground state (S_0) to the lowest-lying singlet excited state (S_1), corresponding to a $\pi\pi^*$ transition. The excited molecule undergoes a photoinduced high quantum yield ring-opening reaction, which leads to formation of the metastable *s-cis*-vinylheptafulvene (VHF) isomer through an S_1/S_0 conical intersection (CI).¹⁰⁻¹³ The *s-cis*-VHF isomer can either undergo a thermal ring-closure reaction with a relatively large energy barrier (18-24 kcal/mol^{14,15}) to recapture the DHA or be transformed to the metastable *s-trans*-VHF isomer with a energy barrier of 6 kcal/mol¹⁵ via a thermal *cis-trans* isomerization process (Scheme 1).

Scheme 1: Schematic representation of the photoinduced DHA ring-opening reaction and thermal VHF *cis-trans* isomerization. The [DFT](#) calculated C1-C10 bond lengths are 1.6 Å, 3.3 Å and 4.4 Å for the DHA, *cis*-VHF and *trans*-VHF isomers, respectively, [at the M06/cc-pVDZ level of theory](#).

The fast initial step of DHA/VHF photoconversion is the ring-opening reaction. Over the years, this reaction has been experimentally investigated for different DHA derivatives. De Waele *et al.*¹² studied the ultrafast dynamics of 1,1-dicyano-2-(4-cyanophenyl)-1,8a-dihydroazulene (CN-Ph-DHA; R = CN-Ph in Scheme 1) in methanol using transient absorption spectroscopy and reported time constants of 1.2 ps and 13 ps for the excited-state ring-opening and $S_1 \rightarrow S_0$ internal conversion processes, respectively. Employing the

same spectroscopic technique, Ern *et al.*¹¹ observed that the whole process including ring-opening reaction and formation of ground-state VHF isomer happens in 0.6 ps for 1,2,3,8a,9-pentahydrocyclopent[a]azulene-9,9-dicarbonitrile (cp-DHA; R = cp in Scheme 1) in acetone. More recently, the first gas-phase measurement was carried out by Schalk *et al.*¹⁰ on the 2-phenyl-1,8-dihydroazulene-1,1-dicarbonitrile derivative (Ph-DHA; R = Ph in Scheme 1) using time-resolved photoelectron spectroscopy. They reported a time constant of 320 ± 50 fs for the ring-opening process. These experimental studies indicate that the ring-opening reaction is strongly dependent on the environment and substitution on the rings. To understand and most importantly control this reaction, it is crucial to get profound knowledge about its mechanism. However, complications and difficulties in the interpretation of ultrafast experiments restrict our current understanding. Theoretical approaches are powerful and complementary tools to extend our knowledge in this regard. In this work, we present the first comprehensive and detailed theoretical investigation on the photoinduced mechanism of the DHA ring-opening reaction. We mention that recently, ring-opening reactions of organic molecules, such as 1,3-cyclohexadiene, have received great attention.^{16,17}

Using the criteria for aromaticity, it can be realized that DHA derivatives in the S_0 state are not aromatic, however, *s-cis*-VHF isomers are. This is because in the S_0 state DHA is not planar conjugated and thus violates the Hückel rules. For a ring to be planar conjugated, the hybridization of all carbon atoms must be sp^2 . However, in the S_0 state of DHA, the C1 and C10 are sp^3 hybridized. By excitation of the molecule to the S_1 state, an electronic transition occurs from the π orbital of the seven-membered ring to a π^* orbital of the five-membered ring (see Figure S3), which leads to formation of a planar aromatic cycloheptatrienyl cation and increased π -conjugation, and therefore, stability of the molecule in the excited state. Based on this, we will argue that the ring-opening process occurs through several steps: (i) After excitation from the S_0 state, the non-planar seven-membered ring begins the planarization. (ii) This results in the cleavage of the C1-C10 bond and change of hybridization of the C1 and C10 atoms from sp^3 to sp^2 , as well as formation

of an open-shell diradical intermediate, which has been recently observed experimentally¹⁸.

(iii) The ring-opening reaction takes place and enhances the π -conjugation system of the molecule to form the metastable VHF isomer. Thus, the ring planarization is hypothesized to be an essential prerequisite for the bond breaking and the ring-opening reaction. To support our arguments, we perform excited-state nonadiabatic trajectory surface hopping (TSH) dynamics simulations, including all nuclear degrees of freedom, using the SHARC 2.0 program package¹⁹ to explore the dynamical aspects of this reaction, and electronic structure calculations to provide a static 2-dimensional (2D) S_1 excited-state potential energy surface (PES). To make the calculations practical, we substitute the phenyl group in the parent molecule (Ph-DHA) with a hydrogen atom to create our model system (H-DHA). We justify the chosen model system by similar vertical excitation energies for the H-DHA and Ph-DHA molecules (with a deviation of around 10%) leading to the same excited state (see Table S1).

Figure 1: Temporal evolution of the r_{C1-C10} bond length of the H-DHA obtained from analysis of the trajectories at the SA(4)-CASSCF(10,10)/cc-pVDZ (left) and TD-M06/cc-pVDZ (right) levels of theory. The dashed parts of the trajectories show the dynamics in the S_0 state. The dotted horizontal lines represent the r_{C1-C10} bond length from the ground-state CASSCF and DFT optimizations of VHF. The thick black line in the right panel represents $\langle r_{C1-C10}(t) \rangle$, obtained by averaging the time-dependent bond length $r_{C1-C10}(t)$ over all ring-opening trajectories.

We employ the multiconfigurational complete active space self-consistent field (CASSCF) method, which is the most-used approach for describing the S_1/S_0 CI.^{16,17,20,21} However, in contrast to the multistate complete active space second-order perturbation (MS-CASPT2)

and time-dependent density functional theory (TDDFT) methods, the vertical excitation energy obtained from the CASSCF calculation is much higher than the experimental value (Table S1). This is the consequence of wrong excited state ordering due to the lack of dynamic electron correlation in the CASSCF method. The CASSCF excited state ordering at the Franck-Condon (FC) geometry can be seen from Table S2, which shows that the optically allowed state is S_3 possessing the same character as S_1 at the TDDFT level. On the other hand, this may not be true when the trajectories leave the FC region and explore other parts of the PESs. For this reason, we carry out excited-state TSH dynamics simulations at the SA(4)-CASSCF(10,10)/cc-pVDZ level by propagating 50 trajectories up to 1 ps. The photoexcitation is described as an instantaneous FC transition where initial conditions are importance-sampled from the Wigner distribution functions²² of the ground-state normal modes of DHA (see Supporting Information for the details). Figure 1, left panel, illustrates the time evolution of the r_{C1-C10} bond length obtained from analysis of the CASSCF propagated trajectories. Unexpectedly only 4 trajectories (8%) lead to the ring-opening reaction and internal conversion to the S_0 state. These results indeed show the disability of the CASSCF method to *quantitatively* describe the DHA ring-opening reaction yield and the necessity to include dynamic electron correlation. For the 4 trajectories that do exhibit ring opening, after photoexcitation, we see an "induction time"²³⁻²⁶ of 300-500 fs, reflected by the C1-C10 bond oscillation, before initiation of the bond stretching. This is followed by an irreversible ring-opening reaction and formation of the H-VHF isomers via the $S_1 \rightarrow S_0$ internal conversion. By taking the point at which the C1-C10 distance stops to oscillate and undergoes an irreversible elongation, we define a bond length of $r_{C1-C10} \sim 2 \text{ \AA}$ for the start point of the ring-opening reaction.

Figure 2: Time evolution of the average electronic state populations along the TDDFT trajectories for the S_0 and S_1 states. Note that the role of the S_2 state in the population decay dynamics is negligible and not shown here.

In order to describe the ring-opening reaction yield quantitatively, an alternative choice for the CASSCF method is MS-CASPT2. However, the lack of analytical nuclear gradients in the available TSH codes and expensive computational cost hamper us to perform the dynamics at this level, [although we note that there are a few recent nonadiabatic TSH dynamics studies that have applied MS-CASPT2 using a local implementation of analytic energy gradients.](#)^{27–29} Therefore, we make use of the (TD)DFT method as a practical alternative to CASSCF. It is well-known that the TDDFT method fails in the vicinity of the S_1/S_0 CI due to the single-reference character of the ground-state wavefunction.^{20,30} A well-established strategy^{31–35} for such cases is to analyze the trajectories until the energy gap between S_0 and S_1 reaches a pre-defined threshold and consider this point as an indication for the $S_1 \rightarrow S_0$ internal conversion. Herein, based on the observations from the CASSCF ring-opening trajectories, we apply a forced irreversible hop to the S_0 state when the energy gap reaches the threshold value and allow the trajectories to continue their exploration into the ground state. [Note that the applied strategy of forced hops most likely makes the results biased towards the formation of VHF isomers and thus the obtained quantum yield for the ring-opening](#)

reaction should be considered as an upper bound. We set 0.15 eV for the threshold guided by the CASSCF simulations and the fact that at this energy gap there is a high probability for the $S_1 \rightarrow S_0$ internal conversion. We propagate 64 trajectories at the TD-M06/cc-pVDZ level of theory and analyze the results (see Supporting Information for the computational details). As shown in Figure 1, right panel, in 90% of the simulated trajectories the irreversible ring-opening reaction occurs, while 2 trajectories undergo the ring-closure and in 4 trajectories, ring opening does not occur and no dissociation is observed in the S_1 state. Figure S4 represents the temporal distribution of the initiation of the ring opening at $r_{C1-C10} \sim 2 \text{ \AA}$ and subsequent internal conversion, extracted from the TDDFT dynamics simulations. These results show that after photoexcitation within 300-500 fs the C1-C10 bond stretching initiates (see Movie S1b), which is in perfect agreement with the timescale obtained from the 4 CASSCF ring-opening trajectories. Thus, despite of wrong description of the CASSCF method in the FC region, the validity of the ring-opening trajectories may be justified by the facts (1) that the predicted timescale for the initiation of the ring opening obtained from the CASSCF results agrees very well with the one extracted from the TDDFT simulations and with the experiment, and (2) that the average hopping geometries in the S_1/S_0 crossing seam region obtained are similar from the TDDFT and CASSCF trajectories (see Figure S7) – excluding the CASSCF trajectory with the very late hop to S_0 at around 750 fs (the blue trajectory in Figure 1). However, this trajectory shows ring-opening dynamics like the others. As seen from the fast expansion of r_{C1-C10} shown in Figure 1 and Movie S1b, the ring opening is an ultrafast reaction, happening in ~ 25 fs. For the average trajectory shown as the thick black line in Figure 1, the ring-opening process appears slower due to the variation in the onset of the ring opening. Thus, the ring opening exhibits "ballistic dynamics"²³⁻²⁶ that does not follow exponential kinetics. This ballistic dynamics can be also seen clearly from Figure 2 that shows $S_1 \rightarrow S_0$ population decay dynamics along the TDDFT trajectories for the first picosecond.

We identify from the dynamics (see Movie S1a and the normal mode analysis of all tra-

Figure 3: Time evolution of the φ dihedral angle of the H-DHA obtained from analysis of the trajectories at the TD-M06/cc-pVDZ level of theory. The thick black line represents $\langle\varphi(t)\rangle$, obtained by averaging the time-dependent dihedral angle $\varphi(t)$ over all trajectories. The dotted horizontal lines represent the φ dihedral angle from the ground-state DFT optimization.

jectories as shown in Figures S5 and S6) that the ring planarization occurs prior to the ring opening. To quantitatively characterize this process, we choose the C4-C10-C9-C8 dihedral angle (φ) of the seven-membered ring as a descriptor, since this φ angle in the equilibrium geometries of the H-DHA and *s-cis*-H-VHF are $\sim 65^\circ$ and $\sim 0^\circ$, respectively. Figure 3 illustrates the changes in the φ angle along time and clearly shows the ring planarization process occurring prior to the ring-opening reaction. An oscillation with a period of 200 fs (~ 170 cm^{-1}) is seen, which can be ascribed to motion of the molecule facilitating the planarization process. This is most clear from $\langle\varphi(t)\rangle$, the time-dependent dihedral angle $\varphi(t)$ averaged over all trajectories shown as the thick black line in Figure 3. De Waele *et al.*¹² also identified experimentally four low-frequency (150-330 cm^{-1}) torsional normal vibrational modes for CN-Ph-DHA, which contribute to the planarization and support the ring opening. We note that in addition to the above discussed 200 fs oscillations, we also observe faster large amplitudes motions in Figure 3 related to C-C vibrations; however, on average, these fast oscillations cancel out.

After the ring-opening reaction is initiated, the molecule decays very fast to the S_0 state

Figure 4: Relaxed 2D PES scan of the S_1 state along the φ dihedral angle and r_{C1-C10} bond length computed at the TD-M06/cc-pVDZ level of theory. The black solid line represents the minimum energy path. The energies are given relative to the S_0 minimum.

via the S_1/S_0 CI, while the C1-C10 bond keeps stretching towards forming the H-VHF isomers. The CASSCF and TDDFT simulations show that the decay process to the S_0 state occurs concurrently with the ring opening. Analysis of the TDDFT trajectories indicates that this process happens within 100 fs after initiation of the ring-opening reaction (see [Figures 2 and S4](#)). These results show a qualitative agreement between the CASSCF and TDDFT simulations and their consistency with the excited-state experimental observations by Schalk *et al.*¹⁰ and Ern *et al.*¹¹ for Ph-DHA and cp-DHA derivatives, respectively. The analyzed trajectories in the S_0 state show a *cis-trans* VHF interconversion on a sub-ps timescale, [as seen from the rapid oscillations of the trajectories within 600-900 fs in Figure 1](#), in very good agreement with the gas-phase experiment¹⁰. The reason that this process happens very fast is because the molecule possesses [kinetic energy](#) after decay to the S_0 and the simulations

Figure 5: Schematic illustration of the proposed reaction path from the FC region through the S_1/S_0 CI towards the *cis-trans* isomerization process. The reaction coordinate is a combination of the φ angle and r_{C1-C10} bond internal coordinates. The top structures are taken from the dynamics, with top view for the ring planarization and side view for the ring opening. The lines represent the underlying minimum energy path. The bottom DHA and VHF structures are obtained by DFT optimization.

as well as the gas-phase experiment do not enable energy dissipation to the environment (ground-state cooling). We note that since all nuclear degrees of freedom are included in the TSH dynamics, intramolecular vibrational energy redistribution (IVR) can happen. At longer times, this can in principle lead to intramolecular cooling of the dynamics in the reaction coordinate.

Our TSH dynamics simulations indicate that the planarization is a crucial process for the ring-opening reaction. To understand this, we calculated the S_1 excited-state PES of the H-DHA molecule (see Supporting Information for the computational details). Figure 4 shows the relaxed 2D excited-state PES along the φ dihedral angle and r_{C1-C10} bond length. As seen, due to the existence of high barrier regions (>0.7 eV at $\varphi > 20^\circ$), the favorable pathway for the bond breaking is only accessible through the ring planarization as shown by

the black solid line in Figure 4. We point out that in the dynamics, the molecule possessing **kinetic energy** does not follow the minimum energy path, which can be seen by the C1-C10 bond oscillation in Figure 1. This picture evidences an undeniable role of the planarization process as a bottleneck in the DHA ring-opening reaction. The results of static TDDFT calculations complement and explain the TSH dynamics simulations.

In Figure 5, we present the reaction path including the structural alterations, taken from a representative trajectory (top structures), from the photoexcitation towards the S_1/S_0 CI and *cis-trans* isomerization. Starting from the FC geometry in the S_1 state, the φ dihedral angle changes from $\sim 65^\circ$ to $\sim 0^\circ$ making the structure planar and removing the barrier for the ring-opening reaction. Thereafter, while the molecule keeps the ring planar, the r_{C1-C10} bond continues to dissociate, and the S_1 state approaches the S_0 state. The molecule undergoes internal conversion to the S_0 state, transforming into a mixture of VHF isomers with *cis-trans* interconversion occurring on a sub-ps timescale.

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