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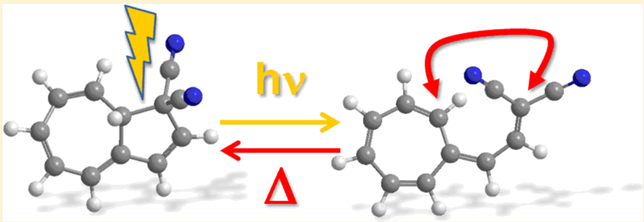
On the Condensed Phase Ring-Closure of Vinylheptafulvalene and Ring-Opening of Gaseous Dihydroazulene

Oliver Schalk,[†,‡,§] Søren L. Broman,[⊥] Michael Å. Petersen,[⊥] Dmitry V. Khakhulin,[¶] Rasmus Y. Brogaard,[⊥,#] Mogens Brøndsted Nielsen,[⊥] Andrey E. Boguslavskiy,[‡] Albert Stolow,[‡] and Theis I. Sølling*[,⊥]

[†]Stockholm University, AlbaNova University Center, Roslagstullsbacken 21, SE-10961 Stockholm, Sweden
[‡]National Research Council, Sussex Drive 100, K1A 0R6, Ottawa, Canada
[§]Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität, Oettingenstrasse 67, 80538 München, Germany
[⊥]Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark
[¶]European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP220, 38043 Grenoble, France
[#]Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States

Supporting Information



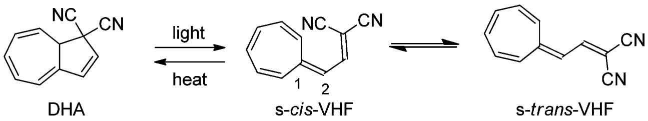
ABSTRACT: Dihydroazulenes are interesting because of their photoswitching behavior. While the ring-opening to vinylheptafulvalene (VHF) is light induced, the back reaction is known to proceed thermally. In the present paper, we show the first gas phase study of the ring-opening reaction of 2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (Ph-DHA) by means of time-resolved photoelectron spectroscopy which permits us to follow the ring-opening process. Moreover, we investigated *s-trans*-Ph-VHF in a series of transient absorption experiments, supported by ab initio computations, to understand the origin of the absence of light-induced ring-closure. The transient absorption results show a biexponential decay governed by a hitherto unknown state. This state is accessed within 1−2 ps and return to the ground state is probably driven through a *cis*−*trans* isomerization about the exocyclic $C_1{=}C_2$ double bond. The rapid decrease in potential energy disfavors internal rotation to *s-cis*-Ph-VHF, the structure that would precede the ring-closure reaction.

1. INTRODUCTION

Photoswitches are molecules which can reversibly change their physical properties such as electrical conductivity, refractive index, or luminosity upon absorption of a photon.[1−3] To be functional, the switches must meet certain criteria such as high quantum efficiency for both switching directions, high stability with respect to switching events, and a long lifetime in each configuration. For many applications, it is also important to control the wavelength at which the switches operate. Therefore, it is pivotal to understand the dynamics of competing processes, the electronic nature of the excited states involved, and their associated potential energy surfaces, such that solvent and substituent effects can be predicted and utilized.

Several classes of photoswitches have been discussed in the literature, including spirooxazines and spiropyranes,[4−7] fulgides,[8−10] and diarylethenes.[1,11,12] However, these all fail to meet at least one of the aforementioned criteria. A promising class of photoswitches are derivatives of 1,8a-dihydroazulene-1,1-dicarbonitrile (DHA, see Scheme 1) which undergo a light-induced ring-opening reaction to form the corresponding vinylheptafulvenes (VHF) with high quantum yields.[13] Because of the large structural difference between VHF and DHA, the system is thought to be particularly attractive. The VHF derivatives are returned to DHAs by a thermally assisted ring-closure, whereas VHF may isomerize around the bond between C1 and C2 prior to the ring-closure induced either thermally or by light (Scheme 2). The ring-closure depends strongly on both solvent polarity and the presence of electron-donating and electron-withdrawing substituent groups.[14−16]

Scheme 1



It has been argued that many of the observations regarding solvent and substituent effects can be accounted for by a charge transfer state or a highly polar transition state between DHA and VHF.[17] Riedle and co-workers investigated the light-

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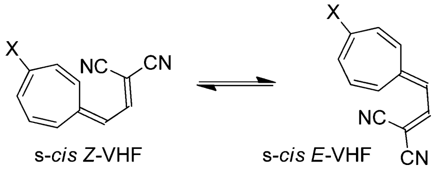
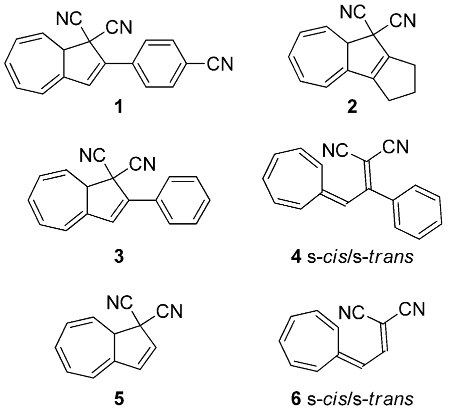
Scheme 2



induced ring-opening of a DHA incorporating a *p*-cyanophenyl substituent at position 2 (2-(4-cyanophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile, CN-DHA, **1** (see Chart 1)) in the

Chart 1



condensed phase and have mapped out the dynamics.[18,19] They found that the ring-opening takes place between 0.35 ps in acetonitrile and 1.2 ps in methanol, forming *s-cis*-CN-VHF in the excited state, which relaxes to the ground state within 10 ps whereupon the *s-trans* form appears on a microsecond−millisecond time scale. Although the quantum yield for the ring-opening was found to be 60% in acetonitrile,[14] quantum yields of 100% could be found in other species such as 1,2,3,8a,9-pentahydrocyclopent[*a*]azulene-9,9-dicarbonitrile (CP-DHA, **2**).[19] In the ring-closure reaction only the *s-cis* form is reactive.[18,19] This conformation was observed in three-pulse experiments on CN-DHA where the *s-cis*-VHF was excited 25 ps after initiating the DHA ring-opening.[19] These findings are supported by a careful computational study by Robb and co-workers.[20] However, our recent results indicate that a competing isomerization channel involving the exocyclic [1,2] double bond can be turned on and off, depending on the choice of solvent and substitution pattern on the seven-membered ring (see Scheme 2).[17] This suggests that there remain missing pieces in the full description of the light-induced processes in DHA and its substituted derivatives. Here we focus on the absence of a light-induced ring-closure reaction in VHF and on the previously observed substantial solvent and substituent effects on the isomerization and ring-closure reactions.[17] We used time-resolved photoelectron spectroscopy (TRPES) to study the ring-opening reaction of DHA (section 3.4), transient absorption spectroscopy (TA) for the possible back-reaction of VHF (section 3.5), and a VHF derivative substituted at the seven-membered ring to access the ring-closure in the ground state (section 3.6). We employed various solvents to probe the polarity dependence of the VHF dynamics. As the subject of these experiments, we chose the known DHA/VHF system **3**/**4** incorporating a phenyl substituent at position 2 (2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile, Ph-DHA) in order to provide a substituent that is fairly neutral with respect to its donor−acceptor properties. Since this system is somewhat different from that of Robb and co-workers, as it is unconstrained with respect to the *s-cis* to *s-trans* isomerization,[20] we additionally carried out ab initio calculations on selected points of the potential energy surface (sections 3.1−3.3).

2. EXPERIMENTAL AND COMPUTATIONAL DETAILS

Ph-DHA **3** was synthesized according to the literature[17] and was photolyzed with 400 nm fs pulses (1 kHz, 10 μJ/pulse), resulting in full conversion to Ph-VHF **4** in less than a minute. DHA **7** (see Figure 6) was synthesized as described in the Supporting Information. For studies via UV−vis spectroscopy, photoswitching experiments were performed by using a 150-W xenon arc lamp equipped with a monochromator; the DHA absorption maximum (lowest energy absorption) for each individual species was chosen as the wavelength of irradiation (line width ±2.5 nm). The thermal back-reaction was performed by heating the sample (cuvette) by a Peltier unit in the UV−vis spectrophotometer. All NMR spectra were acquired on a 300 MHz instrument.

The transient absorption setup is based around a regeneratively amplified laser system (Spitfire, Spectra Physics) with pulse duration of 110 fs (fwhm) at a center wavelength of 800 nm and output energy of 1 mJ/pulse. The pulses were split 92:8; 92% were frequency doubled in a BBO crystal to generate the pump beam while the remaining 8% were used to generate a white light continuum in a sapphire plate for probing. Both pulses were collected and focused onto the fused silica sample cuvette (l = 1 mm, c = 0.36 mM in acetonitrile and hexane). For the focusing of the pump pulse a lens with 80 cm focal length was employed whereas the white light continuum was focused with a curved mirror (1 m focal length). The size of the pump beam was about three times larger than the size of the probe beam. Pump intensities were about 3×10^9 W/cm^2. The cuvette was continuously moved in order to ensure a homogeneous sampling of the solution. The time delay between the pump and the probe pulse was controlled with a mechanical stage. The pulses propagated through the sample in an angle of about 5%. Behind the sample, a monochromator was used to select the wavelengths which were detected by a photodiode. A mechanical chopper synchronized to the laser system blocked every second laser pump pulse to provide the change in optical density of the sample with and without excitation.

Time-resolved photoelectron spectroscopy (TRPES) experiments were performed by combining a femtosecond laser system with a supersonic molecular beam magnetic bottle time-of-flight photoelectron spectrometer. The setup has been described in detail elsewhere.[21] In brief, the femtosecond laser system consisted of a Ti:sapphire oscillator (Spectra Physics, Tsunami, 80 MHz, 800 nm, 80 fs) pumped by a Nd:YLF diode laser (Spectra Physics, Millenia) and a Ti:sapphire regenerative amplifier (Coherent, Legend) pumped by two Nd:YLF lasers (Positive Light, Evolution). Pump pulses of 350 nm wavelength were generated by the fourth harmonic of the output of an optical parametric amplifier (TOPAS, Light Conversion). For the probe step the second harmonic (400 nm) of the laser output was used. Pulse energies of the 350 and 400 nm pulses were 1.0 and 14 μJ, respectively. The pulses were focused mildly into the interaction region by an f/100 concave Al mirror. The temporal cross correlation between the pump and probe pulse was (145 ± 10) fs estimated by using the [2 + 1] ionization of 1,3-butadiene. The time delay was computer controlled by a motorized linear translation stage and the pump−probe signal was determined from the total signal by subtracting the background signal due to electrons generated by the pump and probe pulses alone.

In the interaction region, a supersonic molecular beam propagated perpendicular to the incoming laser pulses. The beam was generated by a 1 kHz Even−Lavie valve with a 200 μm diameter conical nozzle. Helium was used as carrier gas with a backing pressure of 3 kTorr. The solid sample was introduced into the body of the valve and heated to 110−120 °C. To prevent condensation of solid sample in the valve opening, the front of the valve was heated by a separate heater to keep its temperature approximately 20 °C higher than the temperature of the body, but still below the decomposition temperature of the compound. The photoelectron kinetic energies were calibrated by using the known photoelectron spectrum of NO.[22,23]

Ab initio calculations were conducted with the GAUSSIAN03,[24] GAMESS,[25] and MOLPRO[26] suites of programs. DHA **5** was employed instead of Ph-DHA to reduce the computational cost. All geometry calculations of ground state species were carried out at the B3LYP/6-31G(d) level. Excited state properties were calculated with the TD-B3LYP, TD-CAMB3LYP (GAUSSIAN), and CCSD(T) (GAMESS) methods with basis sets as specified in the text. Solvent properties of the excited states were investigated with the PCM model in Gaussian. To provide relative energies within chemical accuracy (4 kcal mol^{-1}) the G3MP2 method was employed for all ground state equilibrium species and for all ground state transition states.[27] State-averaged complete active space self-consistent-field (SA-CASSCF) calculations were performed to locate stationary points on the S$_1$ potential energy surfaces as well as conical intersections (CoIns) between S$_1$ and S$_0$. All calculations were performed without restricting the symmetry of the wave function. In the calculations performed on the full model compound containing the cyano groups, a (14,14) active space was employed, while for the compound without the cyano groups, we used a (10,10) full π valence active space. The basis set was 6-31G(d) in all cases. Frequency calculations used the same method as the corresponding geometry optimization to verify the nature of the stationary points as transition states (one imaginary frequency) or local minima (zero imaginary frequencies).

3. RESULTS AND DISCUSSION

3.1. The Ground State Potential Energy Surface.

Geometries and relative energies for minima and transition states on the ground state potential energy surface calculated at the G3MP2 level are shown in Figure 1. DHA **5** constitutes the global energy minimum. Thus, the ring-opening reaction to VHF **6** is endothermic and the most stable conformer is *s-trans*-VHF. This means that a thermal population of VHF does not have the terminal double bond lined up for ring-closure.

In the transition state between DHA and *s-cis*-VHF, the bond length of the cleaving C−C bond is 2.375 Å and the H-atom on the seven-membered ring at the one end of this bond and the C(CN)$_2$ moiety at the other have rotated in a conrotatorial manner. Inspection of the atomic polar tensor (APT) derived charges[28] in the transition state **TS: 5 → *s-cis*-6** shows that the C(CN)$_2$ moiety carries a significant negative charge whereas the carbon of the seven-membered ring is positively charged.

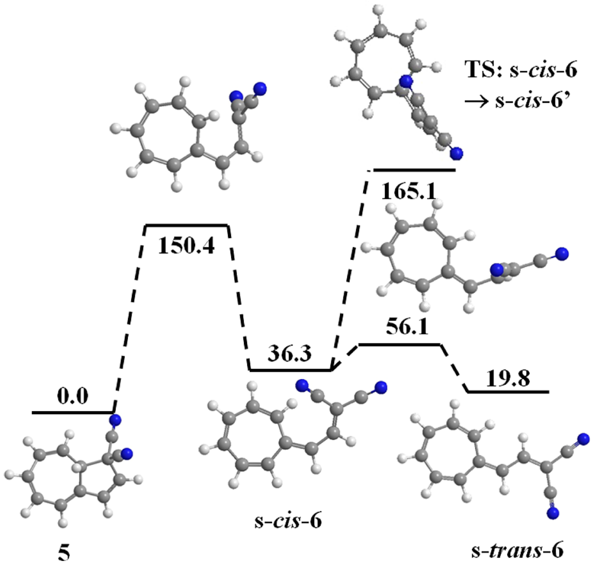


Figure 1. Energy scheme of the ground state reaction. Geometries and energies (kJ/mol) are calculated at the G3MP2/6-31G(d) level.

The dipole moment of the transition state is 10.6 D as compared to 5.6 D in the DHA ground state. The prediction of a polar transition state agrees well with the enhancement of the thermal ring-closure in polar solvents (rate constants of $k = 5.36 \times 10^{-5}$ s^{-1} versus $k = 4.95 \times 10^{-6}$ s^{-1} for Ph-DHA in acetonitrile and cyclohexane, respectively[17]). This charge transfer in the ring-opening process is valid also for the excited state manifold as was seen for fluorinated indolylfulgides in ref 10 where the authors claim that this characteristic is a prerequisite for a high quantum yield.

In the transition state between *s-cis*- and *s-trans*-VHF (**TS: *s-cis*-6 → *s-trans*-6**) the C(CN)$_2$ is perpendicular to the almost planar structure of the seven-membered ring. In this case, the APT charge distribution shows no significant polarization of the molecule and the energy barrier is as low as 19.8 kJ mol^{-1} as expected for rotation about a single C−C bond. In contrast, the **TS: *s-cis*-6 → *s-cis*-6′** has a barrier of 128.8 kJ mol^{-1} and exhibits a significant charge separation comparable to that of the ring-opening reaction.

3.2. The Excited States of VHF.

While the absorption spectra of DHAs were already investigated in some detail,[29] less is known about the structure of the spectrum of VHFs. In Figure 2 (upper panel), we compare the absorption spectra of Ph-DHA **3** and Ph-VHF **4** in acetonitrile and cyclohexane.[17] For *s-trans*-Ph-VHF in acetonitrile, the first absorption maximum is seen at 472 nm, 36 nm on the red side of the absorption maximum of Ph-VHF in cyclohexane (see ref 17 and Figure S1 in the Supporting Information). As acetonitrile is a polar solvent, this shows that the excited state is more polar than the ground state. In contrast to DHA, our calculations reveal another electronically excited state below this one. For *s-trans*-VHF **6** this state results from excitation to an orbital that is localized on the seven-membered ring (see Figure 3) and has a significantly reduced permanent dipole moment (1.3 D vs 6.4 D in the ground state at EOM-CCSD/6-31G(d)) as well as a vanishing oscillator strength. The excitation energies were calculated to be 1.23, 0.87, and 0.55 eV by TD-CAM-B3LYP/6-311G(d,p), TD-B3LYP/6-311+G(d,p), and EOM-CCSD/6-31G(d), respectively. The second excited state (S$_2$) is bright, with an excitation energy of 2.69 eV for the DFT methods

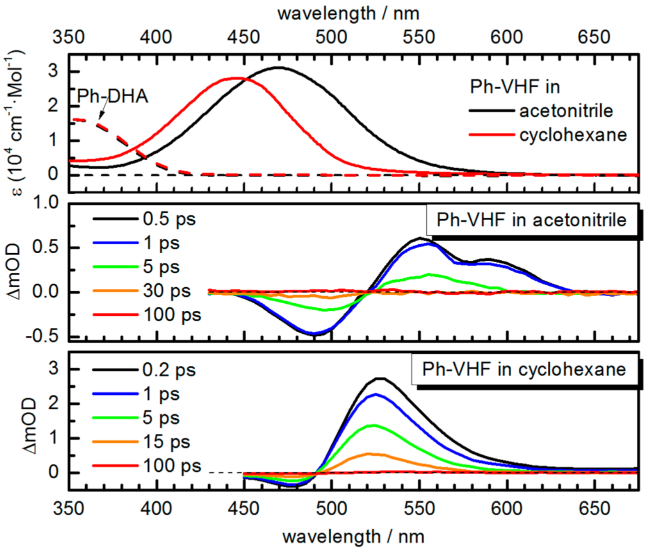


Figure 2. Absorption spectra of Ph-VHF **4** and Ph-DHA **3** in acetonitrile (black) and cyclohexane (red, upper panel, adopted from ref 17). Transient data of *s-trans*-Ph-VHF in acetonitrile and cyclohexane measured after excitation at 400 nm at selected delay times are shown in the lower panels.

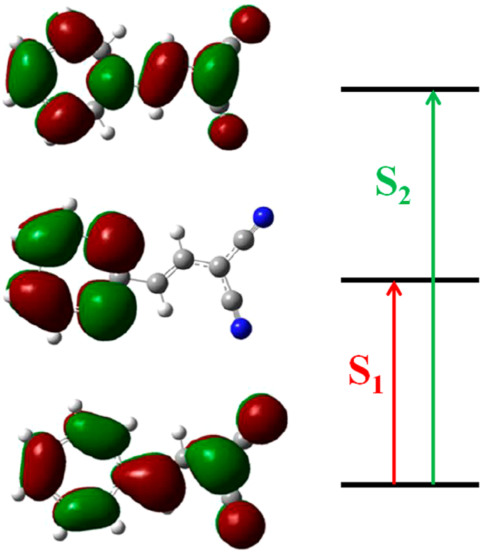


Figure 3. Orbitals involved in the excited states of VHF as calculated at the TD-B3LYP/6-31G(d) level (left). On the right side the minimum energy structure of the S_1 state is shown at the CASSCF(14,14)/6-31G(d) level.

(1.79 for EOM-CCSD) and a permanent dipole moment of 4.0 D. The next higher lying state (S_3) lies at 4.41 eV (TD-CAM-B3LYP) and has negligible oscillator strength.

Invoking a PCM model, we find that the transition to the first excited state shows a significant blue shift upon solvation, as expected for a decreasing permanent dipole moment (1.23 eV (gas phase) → 1.47 eV (cyclohexane) → 1.95 eV (acetonitrile) in CAM-B3LYP/6-311G(d,p)) while only a minor shift is predicted for the second excited state (2.69 eV (gas phase) → 2.51 eV (cyclohexane) → 2.73 eV (acetonitrile)). The above findings imply the involvement of two excited states in the course of the photodynamics and a strong solvent dependence due to the varying dipole moments.

Finally, we found that adding the phenyl group to the gas-phase structure of *s-trans*-VHF has a significant effect on the S_1 state which rises to 2.35 eV at TD-B3LYP/6-311G(d,p) while the bright S_2 state rises to 2.99 eV.

For *s-cis*-VHF in the gas phase, the picture is quantitatively different. At B3LYP/6-311G(d,p), the dark and the bright state are close together at 2.94 and 3.20 eV, respectively, while at EOM-CCSD/6-31G(d), the order is reversed (3.96 vs 3.75 eV) and the dipole moments of ground, bright, and dark state are 2.4, 5.0, and 2.0 D, respectively.

Vertical ionization potentials (IPs) of DHA **5** were calculated in MP2/G3MP2large. At this level, the value is 9.75 eV. IPs of *cis*- and *trans*-VHF species were calculated to be 10.37 and 10.08 eV with respect to the DHA ground state and 9.93 and 9.75 eV with respect to the ground state of the respective isomer. Therefore, the energetic thresholds in TRPES are likely not much different. The one-color ionization spectra of Ph-DHA do not show any clear onset of an ionization band.

3.3. Calculated Geometries in the S_1 State. Characterizations of the excited state potential energy surface leading from DHA to VHF were done on **3**/**4** without the cyano groups on a CASSCF(10,10)/6-31G(d) level. On the S_1 surface, DHA has a minimum energy geometry; however, we were unable to locate a minimum for VHF. Two CoIns were found: one with *s-cis*-like structure and one with *s-trans*-like structure (see Figure 4). One striking distinction between these two geometries is their differing dipole moments. While the *s-cis*-like CoIn is almost nonpolar, with a dipole moment of 1.3 D, the *s-trans*-like CoIn has a dipole moment of 9.5 D. Moreover, in the *s-trans*-CoIn geometry, the vinyl group is rotated by an angle of approximately 45° around the exocyclic $C_1{=}C_2$ double bond. When considering a planar ground state geometry, this indicates that the dynamics impart a momentum for a consecutive *cis*–*trans* isomerization about the $C_1{=}C_2$ double bond in the ground state. The presence of this CoIn is, therefore, a first indication as to why light excitation of the *s-trans*-VHF molecules does not lead to ring-closure: the *cis*–*trans* isomerization about the exocyclic double bond might be more efficient than a possible ring-closing path (see discussion below). Attempts to reoptimize the structures at a CAS-(14,14)/6-31G(d) level following addition of the CN groups led to a DHA minimum structure that was close to the structure calculated for the molecule without the cyano groups, while the CoIns of the VHF structures failed to converge.

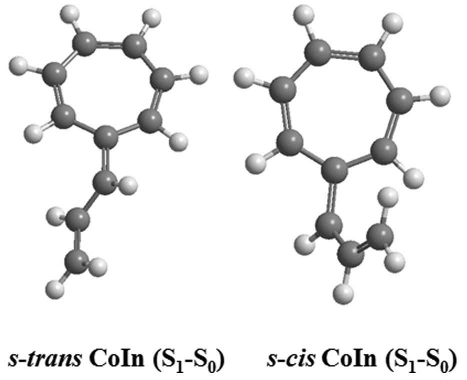


Figure 4. The structures at the two conical intersections (CoIns) between the S_1 and S_0 potential energy surfaces of VHF.

3.4. Ultrafast Ring-Opening and Gas-Phase Pump–Probe Experiments on DHA.

The time-resolved photoelectron spectrum of Ph-DHA pumped at 350 nm and probed with three photons of 400 nm (resulting in a total energy of 12.8 eV) is shown in Figure 5. It is spectrally broad and featureless, as can be the case for a multiphoton probe in complex molecules because of a dense manifold of intermediate states.[30,31] Moreover, a typical fitting routine based on a set of exponential functions as described in ref 32 fails to describe the data. Representative slices along the time axis of the time-resolved photoelectron spectrum are shown in Figure 5. By using a fitting routine, it is possible to describe the data by two single exponential decays (τ_1 = (320 ± 50) fs and τ_2 = (340 ± 50) fs, respectively), where the second component is shifted by (190 ± 40) fs, as well as a component rising to a constant level. We illustrate the different contributions for the energy slice at 0.3 eV kinetic electron energy in Figure 5; the complete decay associated spectra (DAS) are shown in the Supporting Information, Figure S2. A similar fitting procedure has been reported before in a TRPES study of cyclohexene.[33]

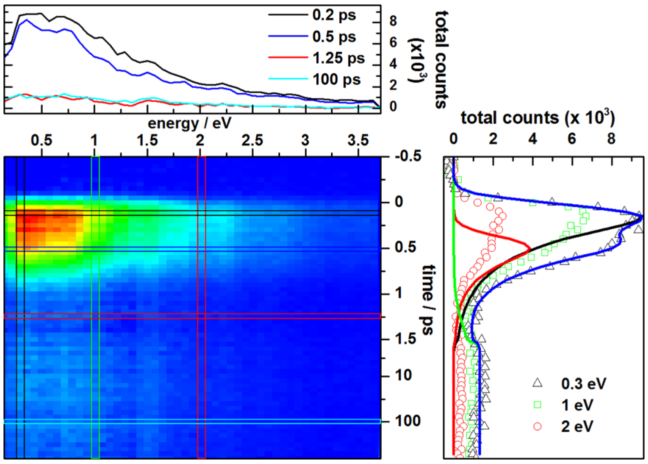


Figure 5. Photoelectron spectrum of Ph-DHA **3** after excitation at 350 nm and probing with two photons of 400 nm. On the right graph, we added a slice of the global fitting (blue line) and its components (black, red, and green, see text for detail).

These data are consistent with the following picture. Upon excitation of DHA, ring-opening occurs within τ_1. We cannot, however, exclude a second reaction channel leading back to the ground state which was discussed previously for similar systems.[29] The ring-opening is supposed to be a ballistic process and not a statistical decay as seen in the dynamics of cyclohexene;[33] hence, the second process appears delayed in time. Due to a dense manifold of intermediate states and as the molecule still resides in S_1, the ionization cross section of both intermediates are actually not much different. Additionally, the ionization potentials of both molecules are similar with respect to the DHA ground state (see section 3.2), which is reflected in the similarities of the DAS (Figure S2).

After the ring-opening process, the molecule passes through the CoIn to the *s-cis* ground state. The time-resolved photoelectron spectrum shows a minimum at a decay time of about 1 ps before rising to its long time value. This dip is probably caused by the *s-cis*/*s-trans* isomerization. It has been shown earlier that the spectrum of *s-cis*-CN-VHF is red-shifted with respect to *s-trans*-CN-VHF.[29] This causes a reduced absorption cross section at 400 nm and, hence, multiphoton ionization is supposed to be less likely since absorption of the first photon now is a nonresonant process. A similar dip in the photoelectron spectrum of a photoswitch, a spiropyran, has been observed before[34] which, opposite to the present study, was assigned to an intermediate structure in the excited state in the more complex spyropyran dynamics.

The ground state *s-cis*/*s-trans* isomerization of Ph-VHF takes place on a picosecond time scale, as opposed to the liquid phase where the reaction requires microseconds due to solvent effects. The main reason for this is the steric hindrance of the large phenyl group, whereas the effect of the ~20 kJ/mol energy barrier can be considered negligible since the excited molecule possesses a high excess internal energy. Such acceleration of a rotational motion by several orders of magnitude was previously reported in the excited state intramolecular proton transfer dynamics of salicylidene derivatives.[35,36]

3.5. Condensed-Phase Pump–Probe Experiments on VHF: No Photoinduced Cyclization.

Transient spectra from Ph-VHF in cyclohexane upon excitation at 400 nm are shown in Figure 2. The data can be fitted by a biexponential decay, using a global fitting routine with time constants of $\tau_{1,\mathrm{CHX}}$ = (2 ± 0.5) ps and $\tau_{2,\mathrm{CHX}}$ = (12 ± 2) ps. At the blue end of the transient spectrum (450–470 nm), only ground state bleach (GSB) is seen, which recovers monoexponentially with $\tau_{2,\mathrm{CHX}}$. Since no residuals are observed, the molecules return exclusively to the *s-trans*-Ph-VHF ground state. The short time constant is associated only with excited state absorption components, with the decay associated difference spectrum (DADS) peaking around 540 nm and stretching well beyond 630 nm. In agreement with our ab initio calculations, we assign this time constant to the internal conversion between the $S_2(\pi\pi^*)$ state and the dark S_1 state in Ph-VHF.

The GSB component of the transient spectrum of VHF in acetonitrile is shifted to the red by about 30 nm relative to the spectrum in cyclohexane, due to the shift in the absorption spectrum (Figure 2). Besides this shift, the DADS are fairly similar, with time constants of $\tau_{1,\mathrm{ACN}}$ = (1.0 ± 0.5) ps and $\tau_{2,\mathrm{ACN}}$ = (11 ± 3) ps. This means that, while the return to the ground state (within $\tau_{2,\mathrm{CHX}}$ or $\tau_{2,\mathrm{ACN}}$) seems to take place on the same time scale in both solvents, the first crossing is significantly faster in the polar solvent acetonitrile as compared to the nonpolar cyclohexane.

There are several reasons for this behavior. First, acetonitrile is a smaller molecule with a viscosity of 0.35 m·Pa·s as compared to 0.89 m·Pa·s at 298 K in the case of cyclohexane.[37] We anticipate that internal conversion is determined by a motion involving the large phenyl group, which brings the molecule toward a CoIn between the two excited states. Moreover, the S_1 state of *s-trans*-Ph-VHF is less polar than the S_2 state, which means that a polar solvent destabilizes the transition which is opposite to reactions with an increased dipole moment in the excited state (see e.g. ref 38). Finally, we note that dielectric relaxation of the solvent cannot be considered to be the rate determining factor, as dielectric relaxation of acetonitrile is faster than the measured time constant $\tau_{1,\mathrm{ACN}}$.[39]

3.6. The Thermal Back Reaction to Ph-DHA.

The solvent dependence of the thermally induced back transformation was studied with a substituted Ph-DHA system 7 (see Figure 6; experimental details are given in the Supporting Information). In cyclohexane, the ring-opening and the consecutive ring-closure was observed without any noticeable side reactions. In acetonitrile, however, the thermal back

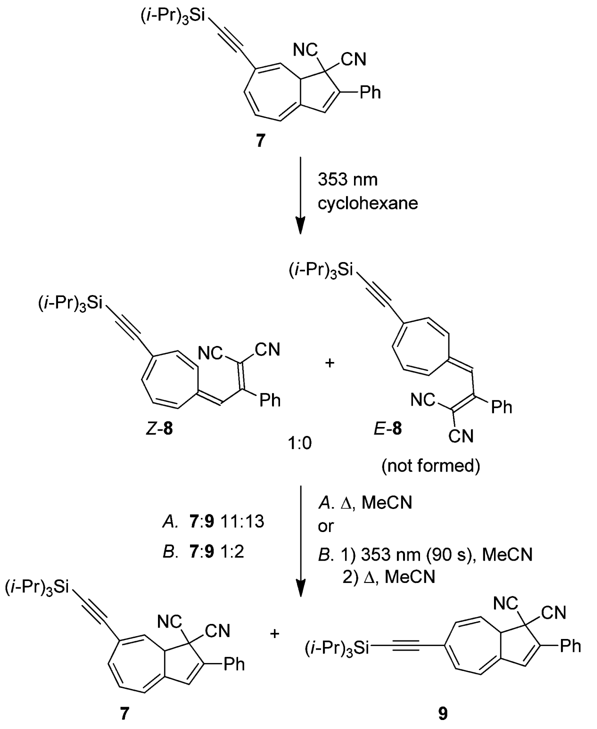


Figure 6. Ring-closing studies of a DHA derivative with a substituent on the seven-membered ring.

reaction from Z-VHF **8** leads to an almost 1:1 ratio between 6-DHA **9** and 7-DHA **7**. This behavior is explained by the polar TS between the two VHF isomers (see section 3.1 and Figure 1): In acetonitrile, this TS energy will drop significantly as compared to the TS between *cis*-VHF and DHA and be energetically close such that isomerization can occur before ring-closure. When irradiating the VHF species before thermal ring-closure can take place, more 6-DHA is observed. This implies two things: (i) the substituent on the seven-membered ring influences the stability of the ring system such that *E*-VHF is favored and (ii) there must be a light-induced *cis*–*trans* isomerization about the [1,2] double bond. While the experiment does not allow any conclusions on the quantum yield of the photoinduced isomerization, as was already inferred from our ab initio calculations, this channel can be considered to be a consequence of the dark S_1 state in the reaction pathway.

3.7. Reaction Scheme of the Ph-DHA/Ph-VHF Photoswitch. A proposed reaction scheme for the Ph-DHA/Ph-VHF system is depicted in Figure 7. Excitation of DHA leads to the well-known ring-opening reaction[13,14,18−20,40,41] and consecutive isomerization as confirmed by our TRPES data (red arrows in Figure 7). The ring-closing reaction starting with a thermalized sample does not occur via a photoinduced process (green arrows). This can be explained by our experimental and computational data: calculations show that the *s-trans* conformation is more stable than the *s-cis* conformation and a thermalized sample predominantly contains the *s-trans* conformer. For the ring-closure to occur via a photoinduced process, an *s-trans*/*s-cis* isomerization has to take place first. This isomerization, although having a small barrier in the ground state, cannot happen in the excited state for several reasons: (i) In a simple picture, the bond length of single and double bonds changes upon excitation. This increases the *s-trans*/*s-cis* isomerization barrier. Rather, Figure 6 evinces rotation about the exocyclic 1,2-bond (supra vide). (ii) Access to the "dark" S_1 state within 1−2 ps upon excitation fixes the molecules in the *s-trans* conformation. This state is the lowest lying excited state in *s-trans*-Ph-VHF, but its energy becomes closer to that of the bright state in *s-cis*-Ph-VHF (see the computational section). Therefore, the excited molecules have only a very short period to overcome the barrier separating the *s-cis* and the *s-trans* conformation. This behavior is similar to the ring-closure mechanism of fluorinated indolylfulgide[10] and photomerocyanine, which also does not exhibit photoinduced ring-closure, since it is effectively quenched via an intermediate dark state.[4,6]

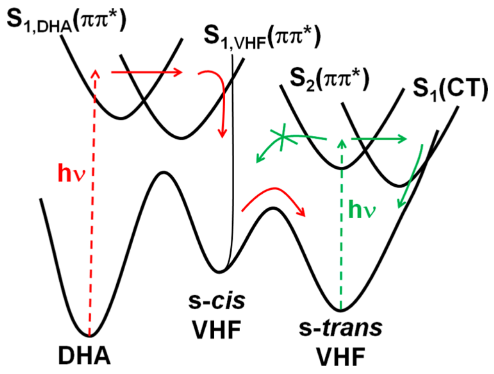


Figure 7. Scheme of the excited state dynamics of the DHA/VHF photoswitch.

4. CONCLUSIONS AND OUTLOOK

In conclusion, we have investigated several aspects of the photoswitching cycle of 2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (Ph-DHA) which reacts to the corresponding vinylheptafulvalene (Ph-VHF). In the gas phase, the most stable *s-trans*-Ph-VHF is formed within 1.5 ps upon photoexcitation, consecutive ring-opening, return to the ground state, and isomerization. The ring-closure of *s-trans*-Ph-VHF back to Ph-DHA cannot occur photochemically, as was evinced by a combination of transient absorption experiments and ab initio calculations. We have shown that fast internal conversion to a dark state within a few picoseconds hinders isomerization between the *s-trans* and the *s-cis* form, which would have to precede the ring-closing reaction. Future work may consider the influence of specific modifications such as substitutions on the seven-membered ring which so far have not been investigated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cartesian coordinates for all structures discussed in this article, synthesis of the used molecules, and the full absorption spectrum of Ph-DHA and Ph-VHF in both cyclohexane and acetonitrile. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: theis@kiku.dk.

Notes

The authors declare no competing financial interest.

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