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Excited State Topology Modifications of the Dihydroazulene Photoswitch Through Aromaticity

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Abstract

Gain and loss of aromaticity plays a key role in organic chemistry and in the prediction of rate-determining steps. Here, we explore the concept of aromaticity in photoisomerization reactions. Benzannulated derivatives of the dihydroazulene-vinylheptafulvene (DHA-VHF) photoswitch were investigated using transient absorption spectroscopy and time-dependent density functional theory to elucidate the effect of built-in aromaticity on the switching properties. We found that benzannulation hampered the switching ability by enhancing an already existing barrier on the excited state surface. This enhancement was found to arise from a significant loss of aromaticity in the DHA-to-VHF transition state on the excited state potential energy surface. The VHF was found to be highly aromatic on the excited state surface, showing a reversal of aromaticity compared to the ground state. The barrier was found to be dependent on the position of benzannulation, since one derivative was found to switch as fast as the non-benzannulated molecule although with lower efficiency, whereas another derivative completely lost the ability to undergo reversible photoswitching. The findings herein provide novel principles for the design of molecular photoswitches, shedding new light on excited state aromaticity, as previous discussions have mainly considered excited state aromaticity to be beneficial to switching. Our findings show that this view must be reconsidered.

Introduction

Organic photochromic switches (photoswitches) are molecular systems consisting of two or more molecules that are capable of interconverting through a photochemical isomerization. Photoswitches find applications in molecular electronics, intelligent optical devices, and molecular solar-thermal (MOST) energy storage systems. For efficient storage of heat in photochromic switches, the photoisomer produced must be considerably less stable than the original isomer. Furthermore, the barrier for thermal conversion back into the original isomer...
must be sufficiently high to prevent instantaneous release of energy. The dihydroazulene-vinylheptafulvene (DHA-VHF, 1a-1b, see Fig. 1) system, first published by Daub et al., has previously been proposed as a candidate for solar heat storage in the metastable VHF. One advantage of the system is the ease with which the molecules can be functionalized with high tunability of energy storage and release as a consequence. The energy stored in the metastable VHF ($\Delta G = 0.11 \text{ MJ kg}^{-1}$) is significantly lower than competing systems such as the norbornadiene-quadricyclane system ($\Delta G = 0.7 \text{ MJ kg}^{-1}$, estimated using DFT calculations), and it must be further optimized in order to find use as a solar heat battery. A way to increase the energy storage in the metastable isomer could be through building in an 'aromatization switch', in which the stable isomer has an aromatic moiety, which is broken upon photoswitching to the metastable isomer. This mechanism has been attempted for several photoswitches, which also proposes the introduction of anti-aromaticity in the benzene-ring as the driving force on the excited state surface towards reaching a non-aromatic (metastable) ground state product, providing both higher energy capacity and conversion efficiency. However, in the case of the DHA-VHF photoswitch, benzannulation at various positions was observed to dramatically change the photochromic behavior. As we have previously reported, the aromatization of DHA resulted in the onset of fluorescence, and photoswitching was assumed to be so fast that no VHF could be observed even at very low temperatures (-100 °C). Some photochromic behavior of 2a, shown in Fig. 1, was observed, however, as the regioisomer, 3a, was detected in the sample by NMR spectroscopy after prolonged irradiation of 2a (see Fig. 1). This led us to conclude that switching was taking place on an ultrafast timescale. In this work, we aim to shed light on the effect on the switching behavior induced by the benzannulation in order to discuss the role of excited state aromaticity on photoisomerizations.
Figure 1: The DHA-VHF system (1a-1b) can be interconverted through irradiation and heating, respectively. Upon irradiation of the benzannulated DHA 2a, the isomer 3a is formed. No VHFs corresponding to 2b and 3b were observed using stationary UV-Vis measurements, but have earlier been reported as possible intermediates in the isomerization.\cite{16}

**Results**

First, transient absorption (TA) spectroscopy was employed to elucidate the excited state dynamics of 2a and 3a upon excitation at their S$_1$ maxima (360 nm). The recorded TA data using ethanol (EtOH) as solvent are shown in Figs. 2 and 3 for 2a and 3a, respectively. TA data for 2a in EtOH and acetonitrile (MeCN) show similar spectra, however, with notably slower kinetics in EtOH due to hydrogen bonding and higher general viscosity (see Table 1). The spectrum of 2a shows ground state bleach (GSB) below 400 nm, excited state absorption (ESA) at 400 nm, stimulated emission at 450 nm and what seems to be three separate ESA bands at 570 nm, 700 nm, and 850 nm. The ESA bands at 400 nm, 570 nm, and 850 nm are all delayed relative to the 700 nm band, implying multiple species in the spectrum. The fluorescence seems short-lived and may hold important information on the kinetics of the compound, so fluorescence lifetimes (FLT) of both 2a and 3a were measured. FLT of 2a in EtOH shows the presence of three components, $\tau_{F1-3}$, one of which is indeed in the ps-
timescale with $\tau_{F1} = 50 \pm 1$ ps, while the remaining two components are on the ns-timescale. The third time constant, $\tau_{F3}$, has a very low amplitude, and is similar to the fluorescence lifetime of 3a, which is known to be formed by 2a through irradiation. We therefore assign $\tau_{F3}$ to a small amount of 3a formed during the measurement. The FLT time-constants are shown in Table 1, together with the TA time-constants discussed below. The presence of two distinct components of fluorescence with $\tau_{F1} = 50 \pm 1$ ps and $\tau_{F2} = 1.3 \pm 0.02$ ns imply a dual pathway, in which two distinct fluoroescing species are formed, which cannot interconvert. These species are formed in a ratio of approximately 93% and 7% between $\tau_{F1}$ and $\tau_{F2}$, respectively, with slightly higher percentages of $\tau_{F1}$ at higher wavelengths (See SI). FLT was also measured for 2a in cyclohexane (Cyh), which yielded a significantly longer lifetime for the short component, whereas the longer component becomes shorter-lived. The opposite change in fluorescence lifetime of $\tau_{F1}$ to $\tau_{F2}$ with solvent polarity implies a much higher dipole moment of the species fluorescing with $\tau_{F1}$ than $\tau_{F2}$, as the change can be related to a hypsochromic shift with decreasing solvent polarity. The shortened lifetime of $\tau_{F2}$ may be due to a bathochromic shift, or may be just a compensation of the fitting model to the longer lifetime of the major component. The knowledge of the existence of two distinct fluorescing species, which cannot interconvert allows us to refine the combined kinetic model. A purely parallel fitting scheme for 2a needed 5 exponential decays to be described satisfactorily. The parallel model suggests one pathway with two consecutive sequential steps in the model based on negative amplitudes for two of the components. The model shown in Fig. 2(b) was therefore used for fitting the TA data of 2a.

The fitted time constants are shown together with the FLT data in Table 1. A comparison with 5 independent exponential decays is shown in the SI. In the evolution associated difference spectra (EADS) of the kinetic model in Fig. 2(b), the first time constant ($\tau = 1/k$) is very short, with $\tau_1 = 1.1 \pm 0.2$ ps, and is associated with GSB and stimulated emission below 500 nm, and a single peak at 700 nm. A variable splitting factor, $\alpha$, was introduced to optimize the flow of population into the two pathways independent of the fast decay times.
laying in the range of measurement artifacts. Optimization yielded $\alpha = 0.99$, corresponding to a 99\% branching into the B*-branch of the model, with the remaining 1\% forming C*. The splitting factor is quite high compared to the experimentally found 93\% splitting by FLT, but since $\tau_{F1}$ is competing with non-radiative processes (vide infra), the true splitting ratio is certainly higher than 93\%. The second time-constant, $\tau_2 = 1.3 \pm 0.1$ ns, is a broad, low-amplitude ESA peak centered at 700 nm, equal to that of $\tau_{F2}$, and therefore likely describes the same process. The third time constant, $\tau_3 = 10 \pm 1$ ps shows decay of a band peaking at 700 nm and some stimulated emission at 430 nm. This process is responsible for forming the 850 nm delayed band. The fourth time constant, $\tau_4 = 57 \pm 5$ ps, is a parallel process as described in the kinetics scheme, containing the decays from both of the states represented by the 700 nm and the 850 nm bands, respectively, thereby showing two distinct ESA peaks. The value fits the first fluorescence lifetime, $\tau_{F1}$, showing that the fast fluorescence component is related to this channel. The final component with a lifetime $\tau_5 >5$ ns shows a remaining GSB below 400 nm, and ESA at 570 nm. The formation of the state is coupled to the removal of ground state 2a, but is disappearing before the next (unpumped) probe pulse 1 ms later, and may therefore be a metastable photoproduct. These results are illustrated in Fig. 2.

For 3a, the main bands of the TA look rather similar to that of 2a, which is expected for structurally related molecules. Interpretation of the data, however, must be cautious in this case, since the 3a sample is prepared by irradiation of 2a. Even for a dilute sample irradiated over long times, some 2a may still be left. Therefore, traces of other species are likely present in the sample, and conclusions must be made with caution. The kinetics we observe in 3a are, however, significantly different from those of 2a.

To avoid the influence of artifacts at early times, the analysis was carried out from 0.5 ps to 5 ns. The spectrum is dominated by the features of ESA at 700 nm, stimulated emission at 480 nm and an emerging ESA band at 450 nm, suggesting at least 2 chemically distinct species. The delayed species observed at 570 nm and 850 nm in the TA-spectrum of 2a are...
Figure 2: (a) Transient absorption spectra of 2a in EtOH at various time delays. (b) The kinetics of traces at 400, 450, 570, 700, and 850 nm, with fits shown as lines. The inset shows the kinetic model chosen. (c) EADS of 2a in EtOH fitted to five exponentials according to the kinetics scheme shown in (b).

not observed here, suggesting significantly different dynamics. FLT measurements of 3a in EtOH show two ns-timescale components in the fluorescence of $\tau_{F1} = 1.24 \pm 0.01$ ns and $\tau_{F2} = 2.26 \pm 0.05$ ns, suggesting again different dynamics than those of 2a, with only a single fluorescence channel. Due to possible contamination of the sample we decided to use a purely parallel fitting scheme for the TA-data. Global analysis from 0.5 ps to 5 ns can be satisfactorily carried out with 5 exponential functions, in which a single component, $\tau_4$, stands out as the most intense by far. After $\tau_4$, $\tau_5$ and $\tau_3$ have the largest amplitudes, while the two fastest components ($\tau_1$ and $\tau_2$) have fairly low amplitudes. Interestingly, the 700 nm
ESA band seems to continue to grow until \( \sim 10 \) ps after excitation, suggesting a continual bleeding into the states making up the band, from other states. All components except \( \tau_5 \) have the largest amplitude at this band, and are associated with growth, narrowing, or shifting of the peak. The first component, \( \tau_1 = 0.53 \pm 0.2 \) ps, is mainly associated with a narrowing of the 700 nm peak, while the second component, \( \tau_2 = 14 \pm 2 \) ps, is associated with growth and a slight blueshift of the same peak, and is in the time-range of vibrational relaxation dynamics with the solvent. The third component, \( \tau_3 = 0.2 \pm 0.02 \) ns, is associated with a growth of the 700 nm peak and decay of a band at 500 nm, which seems hidden by the 475 nm fluorescence band in the raw spectrum. The fourth component, \( \tau_4 = 1.5 \pm 0.2 \) ns, is the major component and represents the decay of the 700 nm peak, and is kinetically coupled to the 475 nm stimulated emission band and corresponds well with the observed fluorescence lifetime. Finally, the last component, \( \tau_5 > 5 \) ns is associated mainly with the build-up of the band at 450 nm, which is metastable on the timescales of the current experiment.

Table 1: The results of the global analysis of the transient absorption data (TA) measured in EtOH and MeCN, compared with the measured fluorescence lifetimes (FLT) in EtOH and Cyh using a global fit over 4 emission wavelengths.

<table>
<thead>
<tr>
<th></th>
<th>( \tau_1 )</th>
<th>( \tau_2 )</th>
<th>( \tau_3 )</th>
<th>( \tau_4 )</th>
<th>( \tau_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2a</strong>&lt;sup&gt;(EtOH)&lt;/sup&gt;</td>
<td>1.1 ( \pm ) 0.2 ps</td>
<td>1.3 ( \pm ) 0.1 ns</td>
<td>10 ( \pm ) 1 ps</td>
<td>57 ( \pm ) 5 ps</td>
<td>( &gt; 5 ) ns</td>
</tr>
<tr>
<td><strong>2a</strong>&lt;sup&gt;(MeCN)&lt;/sup&gt;</td>
<td>0.8 ( \pm ) 0.2 ps</td>
<td>1.7 ( \pm ) 0.1 ns</td>
<td>4.5 ( \pm ) 0.5 ps</td>
<td>47 ( \pm ) 5 ps</td>
<td>( &gt; 5 ) ns</td>
</tr>
<tr>
<td><strong>FLT</strong>&lt;sup&gt;(EtOH)&lt;/sup&gt;</td>
<td>50 ( \pm ) 1 ps</td>
<td>1.3 ( \pm ) 0.02 ns</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>FLT</strong>&lt;sup&gt;(Cyh)&lt;/sup&gt;</td>
<td>170 ( \pm ) 1 ps</td>
<td>0.9 ( \pm ) 0.04 ns</td>
<td>-</td>
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<td>-</td>
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<table>
<thead>
<tr>
<th></th>
<th>( \tau_1 )</th>
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<th>( \tau_3 )</th>
<th>( \tau_4 )</th>
<th>( \tau_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>3a</strong>&lt;sup&gt;(EtOH)&lt;/sup&gt;</td>
<td>0.53 ( \pm ) 0.2 ps</td>
<td>14 ( \pm ) 2 ps</td>
<td>0.2 ( \pm ) 0.02 ns</td>
<td>1.5 ( \pm ) 0.2 ns</td>
<td>( &gt; 5 ) ns</td>
</tr>
<tr>
<td><strong>FLT</strong></td>
<td>1.24 ( \pm ) 0.01 ns</td>
<td>2.26 ( \pm ) 0.05 ns</td>
<td>-</td>
<td>-</td>
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</table>

Next, we turned to calculations, where the excited state reaction path of the DHA structures, \( 2a^* \) and \( 3a^* \), towards the VHF structures, \( 2b^* \) and \( 3b^* \), was successfully obtained through IRC calculations following the transition vector of the \( S_1 \) transition state for the electrocyclic ring-opening reaction (see Fig. 4). The results showed somehow similar trends for the two systems in the \( S_1 \) state with the TS forming an excited state barrier for the reaction from the DHA to the VHF. Furthermore, the VHF is more stable than DHA on
Figure 3: (a) Transient absorption spectra of 3a in EtOH at various time delays. (b) The kinetics of traces at 430, 450, 650, 700, and 850 nm, with fits shown as lines. (c) Decay associated spectrum of 3a in EtOH fitted to five time constants with a parallel fitting scheme. The inset shows the normalized DAS using the same method.

the excited state surface, and the barrier was found to be roughly equal for the two systems ($\Delta^\ddagger G_{S_1} = 0.33$ eV for $3a^*\rightarrow 3b^*$ and $\Delta^\ddagger G_{S_1} = 0.31$ eV for $2a^*\rightarrow 2b^*$). However, the energy difference between $3a^*$ and $3b^*$ ($\Delta G_{S_1} = -0.52$ eV from the relaxed S$_1$ minima) was smaller compared to $2a^*$ and $2b^*$ ($\Delta G_{S_1} = -0.64$ eV from the relaxed S$_1$ minima). Once the VHF structures were found, we managed to connect the two systems through a relaxed dihedral scan following the S$_1$ PES from $2b^*$ to $3b^*$. The potential turned out to be very flat, although $2b^*$ tends to be more stable than $3b^*$ on the S$_1$ PES.

Furthermore, we calculated the accessible kinetic energy of the S$_1$ DHA as the energy
difference between the vertical excitation energy of the ground state DHA, hence the energy of the Franck-Condon (FC) state, and the energy of the $S_1$ DHA minimum. The results showed that $2a^*$ has slightly more kinetic energy available to surmount the excited state barrier than $3a^*$ ($\Delta E_{FC,S_1\text{min}}^{2a} = 0.80$ eV and $\Delta E_{FC,S_1\text{min}}^{3a} = 0.62$ eV). We note that the IRCs correspond to the minimum energy path on the $S_1$ PES, which is different from earlier mappings in which ground state IRCs were vertically projected onto the excited states.$^{22,23}$ Therefore, the PES will look qualitatively different, and, as seen in Fig. 4, no avoided crossing region is observed. The necessity of the avoided crossing region in the model will be discussed below.
Figure 4: (a) IRC of the 3a-3b system following the S₁ PES (b) Dihedral scan connecting 3b* and 2b*. (c) IRC of the 2a-2b system following the S₁ PES. Note, that the structures shown in the three plots are S₁ geometries, and all S₀ PES are formed from projections of the S₁ geometries onto the S₀ surface. All energy scales are set relative to that of GS 2a.
Discussion

Spectral assignments

The EADS of the first component of $2a$ can be assigned to represent the dynamics of $S_1$ $2a$ from the Franck-Condon geometry, while vibrationally excited. The position of the main band at 700 nm is virtually identical to that assigned to the $S_1$ minimum found in previous TA studies of non-benzannulated DHA derivatives, in which bands centered at 695 nm and 690 nm were observed. The position of the $S_1$ minimum of $2a$ is expected to be similar to that of non-benzannulated DHAs, based on stationary UV-Vis measurements of $1a$, $2a$, and $3a$, in which the positions of the peaks are almost unchanged, and only the extinction coefficients vary. The vibrationally excited $2a^*$ gives rise to two different states, denoted $B^*$ and $C^*$, respectively, both of which are initially represented by the 700 nm band. $B^*$ can be assigned to excited state VHF, $2b^*$, due to the prior knowledge that $2a$ is photochromic, and that the channel responsible for the short-lived fluorescence component, $\tau_{F1}$, has the larger dipole moment, and has a large hypsochromic shift with lower solvent polarity, which is known for VHF. $C^*$ can therefore be assigned to vibrationally cold DHA, $2a^*$, which is separated from $2b^*$ by the barrier shown above. A barrier of 0.3 eV is likely prohibitive to vibrationally cold molecules on the ps-to-ns timescale, thus explaining the lack of competition between the two fluorescence channels. When VHF $2b^*$ is formed after crossing the barrier it likely reaches a crossing-area, in which the energetic difference between $S_1$ and $S_0$ is smaller, as shown in Fig. 4(b), and where the higher number of degrees of freedom available to the VHF leads to an increase in the competing non-radiative decay rate. This explains the much lower lifetime of fluorescence from this state, $\tau_{F1}$, as it is competing with non-radiative processes. Fluorescence from $2b^*$ likely occurs alongside relaxation dynamics on the tens of picoseconds timescale. The relaxation dynamics consists of vibrational cooling of the molecule, but solvent relaxation may also play a role, due to the significantly larger dipole moment of $2b^*$ than $2a^*$ (vide infra). The process seen in the EADS of $\tau_3$ is likely relaxation.
dynamics of $2b^*$, and is seen in the parallel model to be coupled to the formation of the 850 nm band. The 850 nm band may therefore represent the relaxed $2b^*$ state, shown in the kinetics scheme as $B^*_{\text{relax}}$. Both $B^*$ and $B^*_{\text{relax}}$ decay to $B$, which can be assigned to the ground state VHF $2b$, and does not decay on the timescale of the experiment. The time component $\tau_2$ can then be assigned to the decay of $2a^*$ through fluorescence, as observed in the FLT measurements.

Figure 5: Comparison of the TA spectra of $2a$ and $3a$ at long time-delays shows the formation of different photoproducts, assigned to $2b$ and $4a$ (tentative assignment).

For $3a$, dynamics can be boiled down to mainly the pathways leading to the state(s) represented by the 700 nm band, and the pathways leading away from it. The first time component, $\tau_1$, probably shows the decay of what can be assumed to be the FC geometry into the $S_1$ minimum, based on their opposite signs and the narrowing of the peak due to less vibrational energy available. The $S_1$ minimum, represented by the 700 nm peak, is observed at the same position as in the $2a$ spectrum. In the DAS of the next time constant, $\tau_2$, the dynamics observed is likely solvent relaxation, leading to a blueshift of the absorption peak. The third component, $\tau_3$, is interesting and may be real or an artifact from contamination. It is associated with a band at 500 nm and the 700 nm band, and could show the relaxation dynamics of the band at 500 nm, which is later found blueshifted to 450 nm in $\tau_5$. The fourth component, $\tau_4$, shows the decay of the $S_1$ minimum with fluorescence, which matches the time constants measured for fluorescence in $3a$, and as such we may assume that any
population left undergoing photophysics after $\tau_4$ is not $S_1 \ 3a^*$. The time constants $\tau_3$ and $\tau_5$ both describe the dynamics of the bands found at 450-500 nm, and likely describe the formation/relaxation and decay of the state, respectively. The state is metastable on the timescale of the experiment, and could represent either a photoproduct or another excited state than the $S_1$ state of $3a$. We cannot conclusively assign the band to a VHF based on its significant blueshift contrary to that expected for a benzannulated VHF (*vide infra*) and the fact that no switching has previously been observed from $3a$. The state may be a triplet state, since very stable triplets have previously been observed in crystals of DHA at low temperatures.\textsuperscript{23} A sufficiently high barrier to VHF formation may induce similar dynamics, if there is no competition with photoisomerization to remove population from the $S_1$ minimum state.

**Kinetic Model**

The fits of the TA data and the discussion above allow for invoking the model shown in Fig. 6. Excitation of $2a$ leads to the formation of a FC state decaying to either the $S_1$ minimum geometry, or directly to the excited state VHF, $2b^*$. A large fraction of the population crosses the barrier within $\tau_1 = 1.1 \pm 0.2$ ps, while a fraction stays in the minimum. The population that managed to cross the barrier undergoes solvent relaxation with $\tau_3$, and/or decays through fluorescence competing with non-radiative decay routes in the coupling region with $\tau_4 = 57 \pm 5$ ps and forms a ground state photoproduct represented by the band at 570 nm, which we assign to the VHF ($2b$). Branching ratios for the bifurcation can be given by the amplitudes in the fluorescence lifetime measurements; 93\% of fluorescence occurs with this time-constant. As fluorescence from $2b^*$ is competing with non-radiative processes, the total percentage of the population crossing the excited state barrier is higher than 93\%. Therefore, we estimate the lifetime of $2a^*$ to be similar to $\tau_1$.

For $3a$, the picture is much different; initial decay into the $S_1$ minimum occurs with $\tau_1 = 0.53 \pm 0.2$ ps, followed by relaxation with $\tau_2 = 14 \pm 2$ ps. From here fluorescence is observed
with $\tau_4 = 1.5 \pm 0.2$ ns, which is likely the main decay route from the $S_1$ state. A metastable state, tentatively assigned to a triplet, is formed and relaxes with $\tau_3 = 0.2 \pm 0.02$ ns, and decay with $\tau_5 = >5$ ns.

Figure 6: Graphical representation of the dynamics of 2a (top) and 3a (bottom) upon excitation based on calculated surfaces, transient absorption measurements, and fluorescence lifetimes.

The lifetime of 3a$^*$ is longer than that of non-benzannulated DHA molecules by 3 orders of magnitude, while 2a$^*$ seems to have a similar lifetime to that of 1a$^*$, when not counting the vibrationally cold 2a$^*$, which is long-lived. In total, three DHA derivatives have previously been studied by fs-spectroscopy, all of which are non-benzannulated.$^{24,25,29,30}$ In solution, the time constants for complete deexcitation are in the range of 0.6 ps$^{24}$ (acetone) to 1.2 ps$^{25}$ (methanol), matching that of 2a$^*$, while in the gas-phase, deexcitation occurs within 0.34 ps.$^{30}$ In the work by Schalk et al.$^{30}$ the metastable VHF isomer was measured through TA, showing ESA peaks at 550 nm and 580 nm with lifetimes of 11-12 ps depending on
the solvent. These peaks were assigned to the S$_2$ and S$_1$ states of VHF, respectively. The longer lifetime of VHF indicates either a barrier before the conical intersection, which can be reached faster by the DHA, or a coupling region on the VHF side, which is only accessible after internal vibrational redistribution (IVR). These same bands were observed by De Waele et al.$^{25}$ as an intermediate to VHF formation. Since we observe only a single peak at 570 nm, one may assume the spectrum to be of the S$_1$ VHF (2b$^+$). However, given the fluorescence from the intermediate state with $\tau_{F1}$, we can safely assume that the observed band stems from absorption from the ground state of 2b. Combined with the increased amount of degrees of freedom available to the VHF, we would expect a lifetime of $\tau > 5$ ns to be highly unlikely. The more likely assumption is that the S$_0$ absorption band has been redshifted by the benzannulation. Calculations of the UV-Vis spectrum (TD-M06-2X/6-311+G(d,p)) of 2b compared to 1b support this argument, since the $\lambda_{\text{max}}$ is estimated to be redshifted by 50 nm (see SI). A redshift from the known experimental $\lambda_{\text{max}} = 471$ nm for 1b in EtOH to $\lambda_{\text{max}} = 570$ nm may then be justified.

We conclude that VHF formation does take place upon irradiation of 2a, whereas a similar conversion does not occur for 3a. This means that benzannulation can indeed be used to form metastable isomers that store more energy than the non-benzannulated molecules. We find that the energy storage capacity in vacuum has been increased from 0.11 MJ kg$^{-1}$ in the 1a-1b system to 0.32 MJ kg$^{-1}$ in the 2a-2b system. The energy storage capacity reduces to 0.21 MJ kg$^{-1}$ upon inclusion of the ester and phenyl substituents, however, due

Table 2: Energetic barriers on the S$_1$ surface calculated using TD-DFT at the M06-2X/6-311+G(d) level of theory in EtOH compared to the energetic difference between the vertically excited ground state (FC) geometry and the S$_1$ minimum energy geometry, and to the smallest time constant, $\tau$, corresponding to decay of the S$_1$ population.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta E_{\text{FC-S}_1\text{min}}$</th>
<th>$\Delta^2 G_{S_1}$</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a ($p$-CN)</td>
<td>0.84 eV</td>
<td>0.17 eV</td>
<td>1.2 ps$^a$</td>
</tr>
<tr>
<td>2a</td>
<td>0.80 eV</td>
<td>0.31 eV</td>
<td>1.1 $\pm$ 0.2 ps</td>
</tr>
<tr>
<td>3a</td>
<td>0.62 eV</td>
<td>0.33 eV</td>
<td>1.5 $\pm$ 0.2 ns</td>
</tr>
</tbody>
</table>

$^a$ From de Waele et al.$^{25}$
to increased molecular weight. In conclusion, benzannulation has provided a doubling of the energy storage capacity of 1a, but with the drawback of lower quantum yield and a decreased back-reaction barrier.

**Potential Energy Surface Mapping**

Several other works have aimed to describe the potential energy surfaces connecting DHA and VHF on the excited state. Boggio-Pasqua et al. described the surface for model systems with no nitrile groups on the C1-position, showing a conical intersection sloping on the DHA side. Other groups have estimated the surfaces, but a full description of the excited state surfaces for a non-model system has yet to be completed. The surfaces presented in Fig. 4 cannot be considered a full mapping, and the choice of TD-DFT for accurate description of the excited state surfaces does not allow for quantitative analysis. However, given the size of the molecules 2a and 3a, any multireference wavefunction methods were considered unfeasible. The surfaces do allow for qualitative analysis, and from this we find that the energy difference between the FC geometry and the S1 minimum geometry (giving a measure of the kinetic energy available to the molecule upon reaching the S1 minimum) is smaller for 3a* than for 2a*, and the excited state barrier is roughly equal (see Table 2). Furthermore, the relative energy across the barriers, i.e. ΔG for the excited state reaction, is less exergonic for 3a*, and the surface is significantly more flat in topology. Since both values of excess kinetic energy for 2a* and 3a* are higher than the respective barriers, and since the kinetic energy may still be dissipated through IVR and transferred to the solvent, the difference in photochemistry between 2a and 3a may not derive exclusively from the barriers. The energetic difference between the barrier in 1a-1b and the benzannulated systems is, however, significant and shows the benzannulation to have introduced a higher barrier than before. The barrier was also shown to be present by Boggio-Pasqua et al. and it was estimated to be 11 kcal mol\(^{-1}\) (~0.46 eV), and the kinetic energy from the FC-S1 relaxation to be more than twice the barrier. Our value for the barrier on the S1 surface of 1a* is 2 times lower, at
\( \Delta G^\dagger = 0.17 \) eV, and is possibly inaccurate due to the deficiency of the TD-DFT methodology in calculating precise energies. However, when compared with the barrier heights found for \( 2a^* \) and \( 3a^* \) (see Table 2), the observed lack of propensity for photoisomerization seems to correlate to the barrier height. Previous experimental work with determining fluorescence quantum yields of DHA derivatives\(^{32} \) showed a significant increase in \( \Phi_f \) upon cooling down, supporting the presence of an excited state barrier. As mentioned above, the calculated PESs do not show the presence of conical intersections due to the choice of reaction coordinate mapped. We do not presume that our mapping proves the absence of conical intersections in the present systems, and they could probably still be located by mapping other coordinates. However, the presence of fluorescence from the bifurcated state assigned to \( 2b^* \) (see Fig. 6) with a lifetime of \( 57 \pm 5 \) ps shows the conical intersection to be difficult to access after traversing the barrier. As such, we believe our choice of coordinate space to be sufficient to describe the photochemistry observed.

**Ground- and Excited State Aromaticity Evaluation**

Since the only difference between \( 2a \) and \( 3a \) is the position of the benzannulation on the seven-membered ring, the basis of the difference in potential energy surfaces must be found here. The factors in play may be electronic, sterical or a combination of both. An electronic factor certainly in play is aromaticity, which may be affecting \( 2a \) and \( 3a \) to different degrees in the ground- and excited states. Aromaticity, whether in the ground- or excited state, may be described by several descriptors.\(^{18,34–36} \) We have chosen a subset of methods to probe the aromaticity changes on the excited state, namely the HOMA,\(^{37,38} \) PDI,\(^{39} \) FLU,\(^{40,41} \) MCI,\(^{42,43} \) and AV1245\(^{44} \) descriptors. In Table 3, the results of the aromaticity evaluations using the methods above for the various points of interest on the \( S_0 \) and \( S_1 \) surfaces are shown.

Using the AV1245 descriptor,\(^{44} \) which also works for rings larger than six atoms, the seven-membered rings were also probed for aromaticity changes. No difference in aromaticity was found between the \( 2a-2b \) and \( 3a-3b \) systems (see SI for details), showing that the
Table 3: HOMA, PDI, FLU, MCI and AV1245 values for the various geometries of the $S_0$ and $S_1$ surfaces calculated as indicators of change in aromaticity with benzene added as a reference for aromaticity and anti-aromaticity. Values considered to be aromatic by similarity to the benzene reference values are colored green (Aromatic) and red (Anti-aromatic), whereas nonsimilar values are kept black.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>HOMA</th>
<th>PDI</th>
<th>FLU</th>
<th>MCI</th>
<th>AV1245</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_0$</td>
<td>$S_1$</td>
<td>$S_0$</td>
<td>$S_1$</td>
<td>$S_0$</td>
</tr>
<tr>
<td>$2a$ minimum</td>
<td>0.94</td>
<td>0.61</td>
<td>0.090</td>
<td>0.057</td>
<td>0.0023</td>
</tr>
<tr>
<td>$2a$ TS</td>
<td>0.83</td>
<td>0.57</td>
<td>0.077</td>
<td>0.060</td>
<td>0.0060</td>
</tr>
<tr>
<td>$2b$ minimum</td>
<td>0.52</td>
<td>0.93</td>
<td>0.060</td>
<td>0.088</td>
<td>0.0197</td>
</tr>
<tr>
<td>$3a$ minimum</td>
<td>0.95</td>
<td>0.79</td>
<td>0.093</td>
<td>0.069</td>
<td>0.0014</td>
</tr>
<tr>
<td>$3a$ TS</td>
<td>0.83</td>
<td>0.66</td>
<td>0.075</td>
<td>0.061</td>
<td>0.0073</td>
</tr>
<tr>
<td>$3b$ minimum</td>
<td>0.52</td>
<td>0.93</td>
<td>0.060</td>
<td>0.089</td>
<td>0.0202</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.99</td>
<td>0.68</td>
<td>0.105</td>
<td>0.015</td>
<td>1.0E-6</td>
</tr>
</tbody>
</table>

The TSs on the excited state surface can be shown for all descriptors except PDI to lose the most aromaticity, and the activational barrier may be rewritten in terms of an "aromaticity-loss barrier", $\Delta A r^{\dagger} = A r_{TS, S_1} - A r_{DHA, S_1}$, where $A r$ denotes the value of a given aromaticity descriptor. This barrier is several times greater for $3a^*$ than for $2a^*$ in all descriptors, since the $\Delta A r^{\dagger}$ of $2a^*$ is quite low. This means that the aromaticity-loss contribution to the $2a^*$-excited state barrier is lower than for $3a^*$, and it may be the reason why photochemistry is still observed in $2a$. Furthermore, the aromaticity gained from the DHA $S_1$ minimum to the VHF side is smaller for $3a$ than for $2a$, as the $3a$ benzene ring seems less affected by excitation than that of $2a$, and the VHFs show similar aromaticity in all descriptors. This suggests that the TSs of the two pathways are significantly different, and that $2a$ copes better with the aromaticity loss along the reaction, making the reaction path from the FC state to the TS shorter. The difference in transition states may then lead to $3a^*$ taking another

\[ 19 \]
pathway, leading to a different excited state, or possibly a photoproduct. The descriptors for the ground state changes in aromaticity show what was expected in the initial work on these systems with an aromatic DHA, less aromatic TS and non-aromatic VHF.\textsuperscript{16} Thereby, the ground- and excited state surfaces show almost the opposite aromatic behavior except for the TSs for which excitation affects the aromaticity more than the DHAs (see Fig. 7 for a graphical representation of the aromaticity evaluation). The point that \(3a\) has a higher aromaticity loss barrier than \(2a\) is interesting, and a simple explanation could be that of conjugation; crystal structures of DHA derivatives\textsuperscript{5,10,12,16} show that the C7,C8-double bond is bent out of conjugation due to the sp\(^3\) carbon in the C8a-position, which is reproduced in our calculations for the S\(_1\) minimum geometries. Thus, no stabilization can be drawn upon from conjugation when aromaticity is lost in the excited state TS, meaning that losses will be felt more keenly.

APT-charges were also calculated for the points of interest (see SI) with focus on the benzannulated seven-membered ring system, and it was found that the DHAs \(2a\) and \(3a\) in both their S\(_0\) and S\(_1\) minimum energy geometries are largely uncharged on the annulated ring-system. The ground state geometries of both VHF\(_s\) and TS\(_s\) were found to be significantly
more charged than their S\textsubscript{1} counterparts. Of special interest, however, is the distribution of charges across the annulated ring-system in both S\textsubscript{0} and S\textsubscript{1}. The S\textsubscript{1} TSs develop larger charges compared to the S\textsubscript{1} DHAs, which, interestingly, are reversed compared to the ground state. The S\textsubscript{1} VHF systems develop charges, which are also reversed compared to those of the ground state, and are now reminiscent of that seen in aromatic benzotropylium (see SI). The charge distribution of the TSs is opposite to that of benzotropylium, showing a dipole moment going in the opposite direction. The above analysis is approximate as the C1 nitriles on the exocyclic bond induce a large polarization in the ringsystem, perturbing the distribution from their ideal values. Previous studies\textsuperscript{34,47,48} have likewise shown that ground state aromatic fulvenes reverse their charge distribution upon excitation and become anti-aromatic, and vice versa for the ground state anti-aromatic fulvenes. The behaviors of the VHFs and TSs match this picture as being excited state aromatic and anti-aromatic, respectively, whereas the DHAs do not behave this way. However, the change in charge distribution for 2b* and its TS is far less pronounced than that of 3b* and its TS, showing that the TSs for the two pathways have different character. The observations of charge and aromaticity changes along the reaction coordinate further show that the DHAs are somehow shielded from the worst of the aromaticity-loss, whereas the excited state TS of 3a*, and to a smaller degree the TS of 2a*, takes the full brunt of the loss.

The results above show that the desired aromaticity effect that should provide a lower barrier due to anti-aromaticity in the S\textsubscript{1} state of DHA instead affects mainly the excited state TS. Hence, it induces a higher barrier with severely hampered switching as a result, contrary to the conclusions on the effect of excited state aromaticity in other photoswitches.\textsuperscript{21}

Based on the discussion above, we may comment on the hope for using excited state aromaticity on photoswitches to provide higher quantum yields and faster switching expressed by recent reviews and comments.\textsuperscript{17–19,34} In the DHA-VHF photoswitch, aromaticity has been built into three variants of the system,\textsuperscript{12,16} and for all three systems, switching has been hampered rather than facilitated. The lifetimes in the ”reactive” S\textsubscript{1} minimum energy
geometries are progressively longer and deexcitation due to fluorescence rather than photochemistry starts to dominate due to increasing barrier-heights on the S\textsubscript{1} surface. Hence, we must reconsider the idea of excited state aromaticity as a driver for higher photoswitching yields in solar energy storage or molecular electronics as suggested, at least for the present system.

Conclusions

Using TA and computational methods, we have investigated the excited state dynamics of two benzannulated dihydroazulene systems, 2\textsubscript{a} and 3\textsubscript{a}, which were previously concluded to have either lower switching capabilities or to be capable of switching on a timescale too fast to be resolved without pulsed lasers. The measurements, combined with excited state potential energy surfaces calculated using TD-DFT, showed the switching of both isomers to be severely hampered by the benzannulation. Measurements of the excited state dynamics showed the excited state lifetime of the S\textsubscript{1} state of 2\textsubscript{a} to be roughly the same as the parent system 1\textsubscript{a}-1\textsubscript{b}, although with lower conversion efficiency due to fluorescence, while the S\textsubscript{1} lifetime of 3\textsubscript{a} was roughly 1000 times longer, such that for 3\textsubscript{a} virtually all deexcitation occurred through fluorescence. For 2\textsubscript{a}, a large part of the population was observed to cross an excited state barrier to form electronically excited VHF, 2\textsubscript{b*}, which upon relaxation to the ground state may form 3\textsubscript{b} through rotation around the exocyclic bond. A fraction of the excited state population, however, was still found to deexcite through fluorescence. The calculated S\textsubscript{1} surfaces show a significant barrier on both systems' pathway to the crossing regions, which could explain the higher lifetimes of the excited states. The barrier and the topology on both sides of the barrier could be explained through changes in aromaticity on the excited state, in which the transition state is significantly less aromatic than the DHA, while the excited state VHF was found to become highly aromatic as expected. We thus conclude that whereas the introduction of aromaticity into photochromic switches may
increase the energy stored in the metastable isomer, the aromaticity will not necessarily be beneficial to the switching dynamics in the excited state as it is currently believed to be.

Methodology

Spectroscopic Methods

The benzannulated DHA 2a was synthesized as previously reported,\textsuperscript{16} and purity was confirmed by $^1$H-NMR spectroscopy. DHA 3a was formed by irradiation of a solution of 2a in ethanol (EtOH) with a 365 nm UV-lamp for 1.5 hrs. Transient absorption spectra of 2a and 3a were recorded after excitation using 360 nm, using the setup at Lund University, previously described by Chabera \textit{et al.}\textsuperscript{49} A flow-cell driven by a peristaltic pump was used to ensure that no accumulation of photodegraded products had taken place. The femtosecond laser setup is based on a MaiTai seeded Spitfire Pro XP (Spectra Physics) with central output wavelength of 796 nm and 1 kHz repetition rate, delivering $\sim$80 fs pulses. The beam was split into two parts: one for pumping a collinear optical parametric amplifier (TOPAS-C, Light Conversion) to generate the pump beam, and the second one was focused onto a 2-mm sapphire plate to generate a white light continuum. The acquired probe beam was then led through a computer-controlled delay line (Aerotech), and subsequently the probe pulse was split into two parts: The former overlapping with the pump pulse in the sample volume and the latter serving as a reference. The probe and the reference beams were then brought to the entrance slit of a spectrograph and dispersed onto a double photodiode array, each with 512 elements (Pascher Instruments). The intensity of excitation pulses was kept below $\sim$ 1014 photons per pulse per cm$^2$. Mutual polarization between pump and probe beams was set to the magic angle (54.7 $^\circ$) by placing a Berek compensator in the pump beam. Time-resolution of the setup after dispersion correction is $\leq$150 fs. Fluorescence lifetimes were measured with a FluoroTime 300 system (PicoQuant, Berlin, Germany). The emission signal was measured using a PMT detector in a spectral range of 300-700 nm. The
compounds 2a and 3a were both excited at 350 nm by using a solid-state laser excitation source. The instrument-response function was recorded at the excitation wavelength by using a dilute solution of Ludox\textsuperscript{T M}. The fluorescence decays were analyzed by using the Fluo-Fit software package version 4.2.1 using a global fitting algorithm. The fluorescence decay data was found to be triexponential for 2a and biexponential for 3a, and was fitted by an iterative reconvolution of the sum of exponentials shown below, where IRF is the (gaussian) experimentally obtained instrumental response function of (50 ps), $\alpha$ is the amplitude and $\tau$ is the fluorescence lifetime.

$$I_f(t) = IRF(t) \otimes \sum_{i=1}^{n} \alpha_i \cdot e^{-\frac{t}{\tau_i}}$$

The data of transient absorption was corrected for potential chirp (wavelength dependent arrival time) and analyzed in the region after 300 fs to avoid the well known influence of solvent and instrumental artifacts like e.g. cross-phase modulation. The data was fitted globally from 300 fs to 3 ns, after which the signal-to-noise become too low to adequately fit. The data was initially fitted with 5 independent exponential decays each convoluted with the an IRF of 86 ps. Based on the knowledge of two independent fluorescent channels and their lifetimes the more detailed model discussed in detail above (see Fig. 3) was formed and globally optimised following Ruckebusch and Stokkum with an in-house developed code.\textsuperscript{50,51}

The routine is a guided principle component analysis (PCA) in which the extracted spectral and temporal components shown in Fig. 3 b and 3 c. For compound 3a a model of 5 parallel exponential decays, each convoluted with the IRF was employed, with the details discussed above.

**Computational Methods**

The molecular mechanisms behind the photochemical rearrangement of the benzannulated DHA-VHF system were investigated through intrinsic reaction coordinate (IRC) calculations.
on the potential energy surface (PES) of the first excited singlet state (S\textsubscript{1}) following the reaction coordinate of the electrocyclic ring-opening/closure. The phenyl and ester groups were omitted from the systems in our computational studies in order to reduce the computational requirements. This choice is justified by calculations (cf. SI) showing little conjugation between the core ring systems and the above-mentioned substituents. Furthermore, no significant alterations of the geometry of these core ring systems were observed when removing these substituents. All calculations were performed in Gaussian 16\textsuperscript{52} using density functional theory (DFT) and its time-dependent analogue (TD-DFT). We employed the hybrid meta-GGA functional M06-2X\textsuperscript{53,54} and the Pople style 6-311+G(d) basis set\textsuperscript{55–57} as deemed appropriate in previous benchmark studies\textsuperscript{11,58} and work on similar systems.\textsuperscript{22,59–61} Furthermore, the IEF-PCM continuum solvation model\textsuperscript{62,63} was used to describe polarization effects of a surrounding dielectric medium resembling EtOH through a static and an optical dielectric constant (\(\epsilon_{\text{st}} = 24.85\) and \(\epsilon_{\text{op}} = 1.853\), respectively). Structures resulting from geometry optimizations were confirmed as true energy minima or transition states (zeroth- or first-order saddle points, respectively) through harmonic frequency analyses (having zero or a single imaginary frequency, respectively). For the transition states (TSs) of the electrocyclic ring-opening/closure, the imaginary frequencies were confirmed to correspond to the C1-C8a bond-breaking/forming reaction coordinate (see atom numbering in Fig. 1). In the ground state, the TS reported is the energetically lowest of the two electrocyclic pathways.\textsuperscript{33} The Gibbs free energy calculations include the zero-point vibrational energy and thermal contributions evaluated at a temperature of 298.15 K and a pressure of 1.00 atm. The connection between the VHF structures of the two systems were found through a relaxed S\textsubscript{1} PES scan around the C8a-C3a-C3-C2 dihedral angle of 2b\textsuperscript{*} (-52.5°) towards the C4-C3a-C3-C2 dihedral angle of 3b\textsuperscript{*} (-116.3°), where * denotes the molecule to be in the S\textsubscript{1}-state.

The aromaticity of the benzannulated six-membered ring was evaluated by employing the Quantum Theory of Atoms in Molecules (QTAIM) partition introduced by Bader.\textsuperscript{64} QTAIM is a real space partition method that defines an atom in a molecule using the topology of the
electron density. Calculations of the atomic overlap matrices and computations of the aromaticity descriptors HOMA, PDI, FLU, MCI and AV1245 were performed using the AIMAll software package and the ESI-3D program, respectively. In brief, the HOMA and FLU descriptors are both deviation methods based on reference parameters of aromatic systems. HOMA describes the average bond length deviation from a "true" aromatic bond length (i.e. ground state benzene), and yields 1 for a perfectly aromatic ring. FLU gives the average fluctuation in electron density between neighboring atoms in a ring, and should be zero for a fully aromatic ring. PDI, MCI and AV1245 are all parameter-less descriptors and show delocalization between either para-related atoms (PDI), entire rings (MCI) or 1,2,4,5-related atoms in a ring (AV1245). For all of these descriptors, the higher the value, the more aromatic is the ring. HOMA uses only the geometry, whereas the other descriptors include the wavefunction, making them sensitive to the electronic configuration.

Conflicts of Interest

There are no conflicts of interest to declare.

Acknowledgements

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Graphical TOC Entry