Photoswitchable Molecular Rings for Solar-Thermal Energy Storage

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Ⓢ *Supporting Information*

ABSTRACT: Solar-thermal fuels reversibly store solar energy in the chemical bonds of molecules by photoconversion, and can release this stored energy in the form of heat upon activation. Many conventional photoswichable molecules could be considered as solar thermal fuels, although they suffer from low energy density or short lifetime in the photoinduced high-energy metastable state, rendering their practical use unfeasible. We present a new approach to the design of chemistries for solar thermal fuel applications, wherein well-known photoswitchable molecules are connected by different linker agents to form molecular rings. This approach allows for a significant increase in both the amount of stored energy per molecule and the stability of the fuels. Our results suggest a range of possibilities for tuning the energy density and thermal stability as a function of the type of the photoswitchable molecule, the ring size, or the type of linkers.
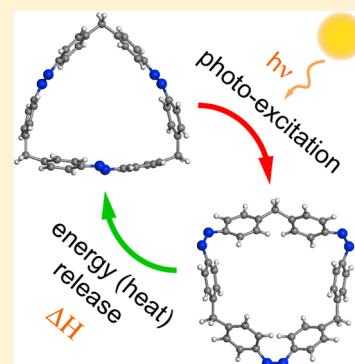
SECTION: Energy Conversion and Storage; Energy and Charge Transport

Efficient utilization of the sun as a renewable and clean energy source is one of the greatest goals and challenges of this century due to the increasing demand for energy and its environmental impact. Numerous strategies exist to convert sunlight into useful forms of energy, including photocatalytic processes, artificial photosynthesis,[1,2] photothermal power plants,[3] and photovoltaic applications.[4] An alternative strategy to these is to convert and store the sun's energy directly in the chemical bonds of metastable photoisomers of suitable molecular systems. The stored energy can then be released as heat on demand by an external trigger. Ideally both the photisomerization and heat release reactions reversibly occur in a closed-cycle without changing the chemical composition.[5] The clear advantage of such an approach is that the same material both converts and stores the sun's energy, providing a rechargeable fuel that can be safely transported and used on-demand; the materials used could, in principle, be cheap, nontoxic and abundant, and the cycle can be repeated thousands of times without any emission or waste.

The idea of storing solar energy in chemical bonds was first introduced with the photoisomerization reactions of organic molecules (such as norbornadiene⇌quadricyclane[6,7] and the trans⇌cis isomers of azobenzene[8]), although the concept was generally dismissed as unpractical[7] due to a number of reasons including degradation, instability of the photoinduced isomer (limited half-life or shelf life), low energy density, and cost. As such, the majority of recent experimental studies for such materials have focused on their photoswitchable properties,[9] as opposed to energy storage. The Ru-based organometallic complex (tetracarbonyl−diruthenium fulvalene)[10] has shown promise as a solar thermal fuel due to its high cyclability without degradation; however, substitutions for Ru must be found to reduce costs, and the volumetric energy density increased for practical applications.[11,12] Recently, a new strategy that combines photoswitchable molecules with nanoscale templates was shown to provide a promising platform for controlling both stability and energy density.[13] In such materials, the template serves as a means to rigidly pack and order the photoswitch molecules such that chemical interactions between the molecules can be tuned independently for the ground and excited states.

In this work, we suggest a different approach to design materials for solar thermal fuel applications, wherein once again well-known photoswitchable molecules are constrained in such a way as to allow for the tailoring of both the energy stored and stability in the charged state. However, unlike the case of templates which introduce new chemistries, here we approach the problem by using strain, imposed by the formation of molecular rings, to engineer the properties of the photoisomers. Using azobenzene and stilbene as examples, we employ first-principles calculations to predict the energy stored (ΔH) and heat release reaction barriers (E_a) for a variety of such tailored ring systems. Our calculations reveal that, as in the case of packing photoswitches on nanoscale templates, functionalized ring systems provide a template for tuning the key properties of photoswitchable molecules, transforming them into competitive

solar-thermal fuels. In particular, our calculations show that through a combination of the ring size and linker chemistry the strain in these systems can be exploited to engineer both the energy density and stability.

The azobenzene molecule (AB)[14] can be photoisomerized reversibly from the more stable trans- to the cis-isomer. Because the process is fast (picoseconds) and has a high quantum yield,[15] AB has been considered for applications in opto-mechanical devices,[16,17] biochemical applications,[18] and photo-addressable storage media.[19] The cis isomer is roughly 0.6 eV higher in energy than the trans form. (See Figure 1.) As an
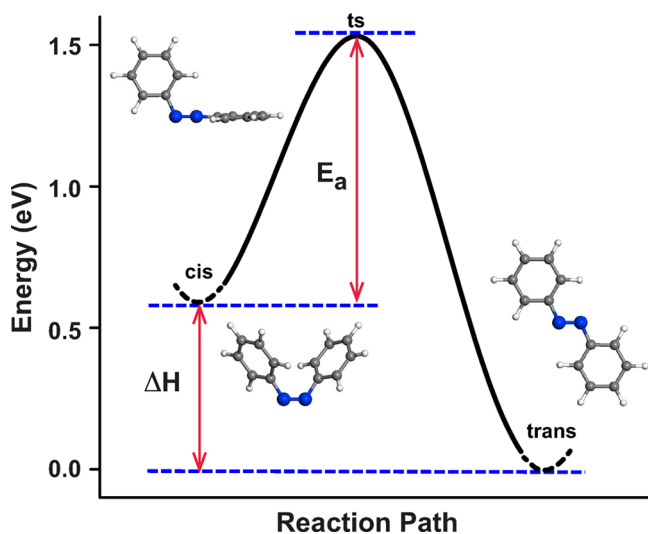
Figure 1. Back reaction (cis→trans) of a single azobenzene molecule in the gas phase. The cis, trans, and transition-state (ts) structures are shown where nitrogen, carbon, and hydrogen atoms are indicated by blue, gray, and white spheres, respectively.

energy storage medium[20,8] this leads to a rather poor energy density, and, more importantly, the activation energy barrier of the cis→trans back reaction is low (<1 eV), corresponding to a half life of only a few hours for the metastable state.[20] No substitution pattern is known that significantly increases the activation barrier or the stored energy above that of unsubstituted AB,[21] making it unpractical in its isolated state for solar thermal fuel applications.

Before considering ring systems, we first calculate ΔH and E_a for isolated AB (Figure 1). The cis isomer is found to be 0.58 eV higher in energy than the trans isomer, in good agreement with experimentally reported values.[20,22] For the cis→trans thermal back reaction,[23–25] we considered the inversion mechanism where one of the N atoms is inverted together with a perpendicular orientation of the N-phenyl ring, as shown in Figure 1. Our computed E_a is 0.93 eV, which is also consistent with experimental data.[20,26]

For molecular azobenzene rings, or azobenzenophanes [n − (s_1,...,s_n), where n is the number of AB units and s represents the cis (c) or trans (t) states], we first consider methylene (CH$_2$=α) linkers and n = 2−6. Azobenzenophanes with α linkers have been experimentally synthesized,[27] and the effect of steric distortion on photoisomerization as well as the thermal stability have been studied for the case of AB dimers.[28–30] Our results for the variation of ΔH with n (for n = 2−6) and structures for the 2-(t,t), 2-(c,c), 3-(t,t,t), 3-(c,c,c), 4-(t,t,t,t), and 4-(c,c,c,c) systems are shown in Figure 2a. For the dimer 2-(t,t) the induced strain is so large that the trans units deform

from their ideal planar geometry, resulting in a reversal of the trans/cis energy ordering for this smallest "ring" case. Recently, Norikane et al.[30] synthesized stable 2-(c,c) and showed that the trans case exhibited thermal isomerization to the cis state as well as reversible photochemical isomerization, in agreement with our calculations.

As can be seen in Figure 2a, the case of the ring dimer is an exception, and for larger sizes all trans configurations are more stable than their cis counterparts.[27] Whereas our computed ΔH for 3-AB is 0.57 eV/AB (nearly identical to the isolated AB case), the energy stored per azobenzene molecule increases to 0.97 eV/AB for the four-member ring case, representing a 65% increase over that of the isolated AB molecule. This result demonstrates the potential for engineering properties of solar thermal fuels via curvature-induced strain. For this choice of photoswitch molecule and linker, the four-member ring induces more strain in the cis states compared with the trans states, leading to a substantial gain in energy storage. For larger rings, ΔH decreases as a function of size, gradually approaching the infinite ring limit of 0.61 eV/AB, where the trans and cis units approach their isolated geometry.[31]

To understand further the trends of ΔH shown in Figure 2a, we calculated separately the energy variation of a single AB molecule with respect to five different structural degrees of freedom, including torsion angles (∠2112 and ∠1123), bending angles (∠112 and ∠124), and linker bond angles (∠454), as shown in Figure 3a. (The change in bond lengths is also taken into account, although they are found to be negligible.) Each of these energy components can be expressed as a function of the change in angle with respect to isolated AB, and by calculating these energy components using the corresponding angles in the ring geometry the total energy of the AB unit in the ring systems can be estimated. As shown in Figure 3a, the variation in ΔH obtained with this method follows the same trend computed by ab initio calculations and indicates that the change in ΔH for the rings originates mainly from steric effects with respect to the isolated AB molecule imposed by α linkers and the ring framework. Both the cis and trans units (and the corresponding transition states) are destabilized with respect to their isolate counterparts by an amount of energy proportional to the induced strain. When this effect is larger for cis units than trans units, ΔH increases depending on the deviation from ideal geometry (Figure 3b), with a maximum when the strain of cis units is the largest while that of the trans units is the smallest. This type of simple fitting also allows us to predict the energy change in a wide range of possible ring geometries and sizes without carrying out further DFT calculations, but rather considering only the change in the five angles discussed above with respect to isolated AB. For example one can estimate the maximum ΔH by calculating the maximum strain[32–34] for which isolated cis-AB still remains stable, separately for all of the fitted structural degrees of freedom (Figure 3), and then using the corresponding angles in the model. Assuming a plausible ring geometry[35] where all trans units are very close to their isolated counterpart but all cis units are under the calculated maximum strain, we predict that ΔH for such a hypothetical case could be as high as 2.5 eV/AB.

In addition to the size of the ring, this kind of asymmetric strain engineering can also be controlled by the choice of linker chemistry. As an example, N$_2$ (β) can also be used to connect the phenyl rings of isolated AB. For the case of 3-AB, we compared the structures and ΔH trends of the rings formed with one, two, or all of the α linkers replaced by β linkers [3-
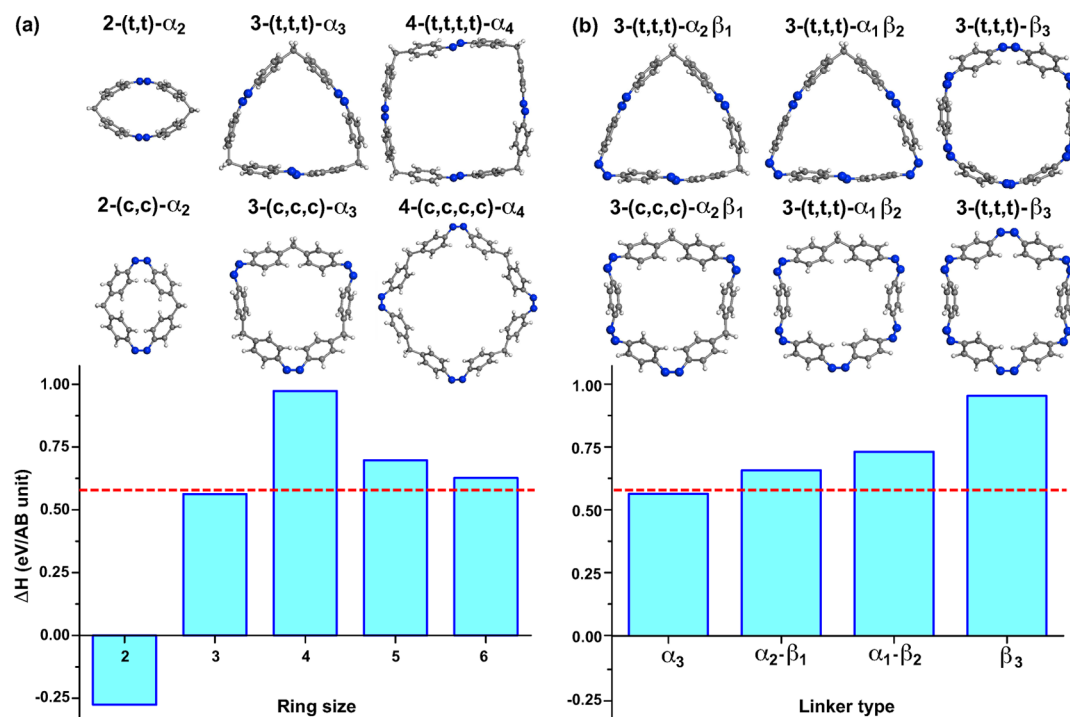
Figure 2. (a) Structure of 2-(t,t)-α_2, 2-(c,c)-α_2, 3-(t,t,t)-α_3, 3-(c,c,c)-α_3, 4-(t,t,t,t)-α_4, and 4-(c,c,c,c)-α_4 and the variation of ΔH with number of AB units. (b) Structure of 3-(t,t,t)-$\alpha_2\beta_1$, 3-(c,c,c)-$\alpha_2\beta_1$, 3-(t,t,t)-$\alpha_1\beta_2$, 3-(c,c,c)-$\alpha_1\beta_2$, and 3-(t,t,t)-β_3, 3-(c,c,c)-β_3 and the variation of ΔH with type of linker. The nitrogen, carbon, and hydrogen atoms are indicated by blue, gray, and white spheres, respectively.
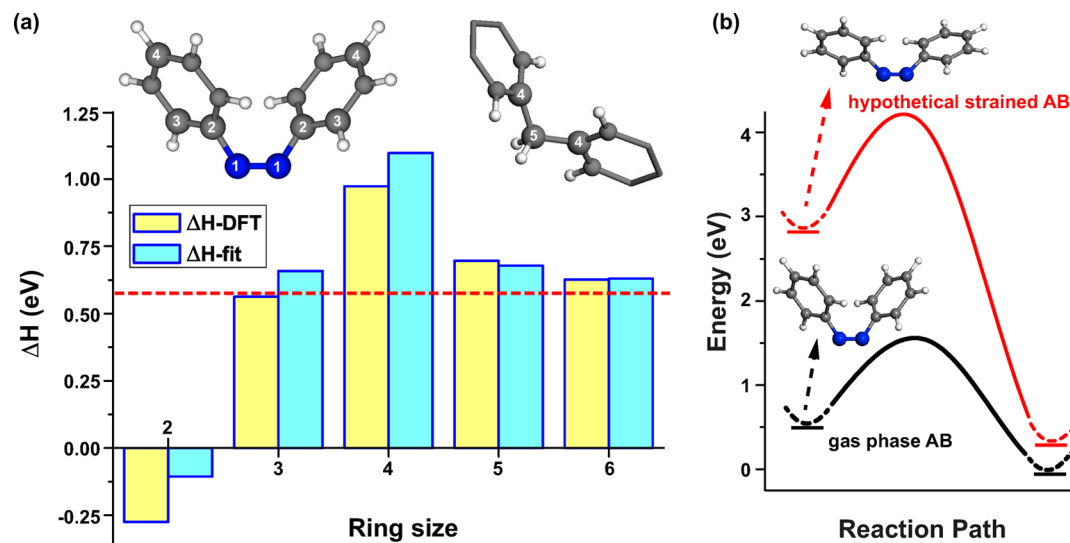
Figure 3. (a) Comparison of ΔH computed by DFT calculations and calculated by an energy decomposition methods. (See the text.) The atoms are labeled in order to define the five energy components including torsion, bending, and linker angles. (See the text.) ΔH for an isolated AB molecule is indicated by the red dashed line. (b) Energy variation of cis, trans, and transition states with and without strain is shown by black and red lines, respectively.

AB-α_3, 3-AB-$\alpha_2\beta_1$, 3-AB-$\alpha_1\beta_2$ and 3-AB-β_3] (Figure 2b). Interestingly ΔH increases for each additional β and reaches up to 0.95 eV/AB for 3-AB-β_3, as shown in Figure 2b, considerably larger than the 0.57 eV/AB for the 3-AB-(α_3) case. For the β-linker, which forms the same nitrogen double bond as in AB, ΔH increase because of the new bond formation and the linker bonding angle (between the linker and phenyl rings). Similar to isolated AB when the linker bonding angle (thus, the geometry) is close to the $\angle 112$ of *trans*-AB, the system becomes energetically more favorable. When all AB units are connected with β linkers, AB molecules become indistinguishable, and the system turns into a ring of phenyl rings connected by N_2. For this case, the ground-state configuration is obtained when 3-(t,t,t)-β_3 is in a circular shape, as illustrated in Figure 2b, which is unique to 3-(t,t,t)-β_3, where there are no more α linkers attempting to preserve the tetrahedral angle between C−C−C (4−5−4) bonds, thus inducing strain on the system.

When the ring size is larger than 3-AB, β linkers start to destabilize the *cis*-AB units they are connecting by converting them into *trans*-AB upon geometry relaxation according to our

calculations. As an example, for 4-AB-$\alpha_3\beta_1$ ΔH, where all AB units are still in the cis form, ΔH increases to 0.65 eV/AB compared with the isolated case, but it decreases upon additional β linkers as cis-AB units start to transform into the trans form. Finally, when all α linkers are replaced by β, all cis-AB units are converted into trans-AB, making 4-(c,c,c,c)-β_4 unstable. (See the Supporting Information.) Similar to 3-(t,t,t)-β_3, 4-(t,t,t,t)-β_4 also has a circular shape, and even if the initial configuration is 4-(c,c,c,c)-β_4 the circular geometry with all trans units is the final structure after optimization.

In addition to ring size and linker chemistry, another degree of freedom for modifying the energy storage can be introduced by adding hydrogen bonds that vary in number between the cis and trans states, similar to what was recently demonstrated in templated chromophore systems.[13] Toward this end, we consider a redesigned ring structure with a single AB with two OH groups, as shown in Figure 4. The addition of hydroxyl
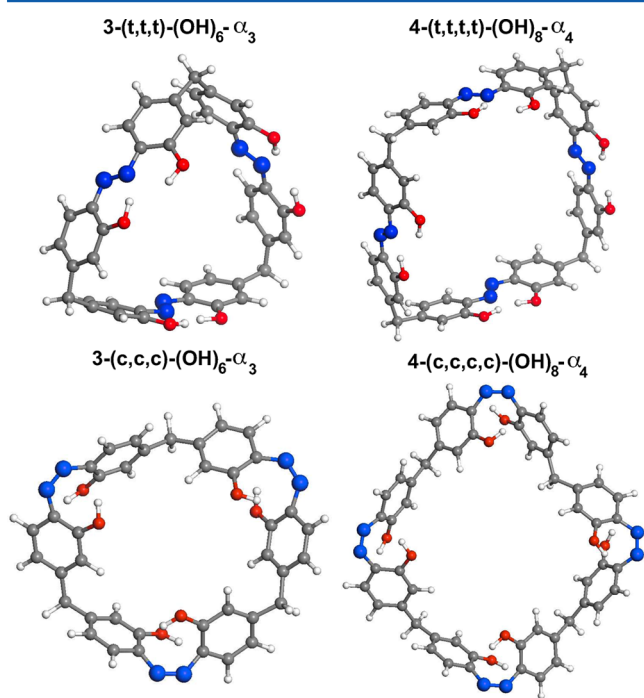
Figure 4. Structures of OH-substituted 3-(c,c,c), 3-(t,t,t), 4-(c,c,c,c), and 4-(t,t,t,t) structures.

groups in this way leads to an increases in ΔH to 0.99 eV/AB and 1.20 eV/AB for 3-AB and 4-AB, respectively, corresponding to a 68 and 103% increase when compared with isolated AB. Whereas strain induced by the ring framework destabilizes the two isomers (vide supra), the new H-bond formation stabilizes them with different amounts of energy. Our results indicate that these two mechanisms can be combined and the relative difference in the stabilizing and destabilizing energy of cis and trans units can provide even larger values of ΔH.

Considering the ring structure as a torus and assuming maximum packing efficiency, the maximum volumetric and gravimetric energy densities of our calculated azobenzenophanes would be 1.2 MJ/L and 0.60 MJ/kg, which are significantly larger than solid azobenzene (~0.32 MJ/L, ~0.32 MJ/kg). These values could be even larger considering the predicted hypothetical ΔH value from our strain analysis model.

As discussed, concomitant with higher storage densities, the ability to control the stability of a solar thermal fuel in its charged state is of paramount importance to its practical use. Toward this end, we have computed the back reaction barrier (E_a) and possible reaction paths for all cis-azobenzenophanes. For example, for the case of 4-AB, we consider three different reaction paths: I: (c,c,c,c)→(t,c,c,c)→(t,t,c,c)→(t,t,t,c)→(t,t,t,t), II: (c,c,c,c)→(t,t,c,c)→(t,t,t,c)→(t,t,t,t), and III: (c,c,c,c)→(t,t,t,t). E_a is calculated as 1.16, 2.71, and 3.17 eV for paths I, II, and III, respectively, which suggests that the heat release reaction for such ring systems will be stepwise as opposed to concerted (see Figure 5) in agreement with
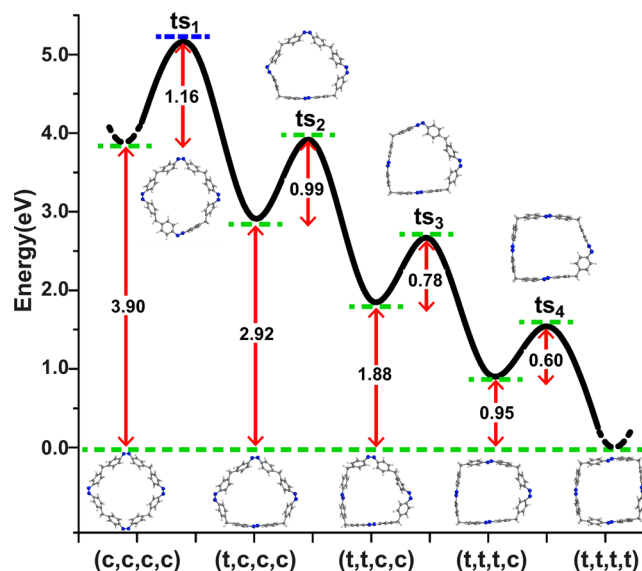
Figure 5. Computed stepwise back reaction path from the 4-(c,c,c,c)-α_4 to 4-(t,t,t,t)-α_4 isomer of azobenzenophane. E_a and ΔH values and corresponding structures for each step are shown.

experimental data.[27] For path I, E_a is largest for the first step and decreases for subsequent steps, indicating that the stability of 4-(c,c,c,c) is mainly determined by the first cis→trans barrier. We carried out similar sets of nudged-elastic band calculations (see Supporting Information) to predict E_a for the 3-AB, 5-AB, and 6-AB ring systems as well as for 3-AB with β linkers, summarized in Table 1. When compared with isolated AB, the ring geometry shows an increase in E_a and follows the same qualitative trend as ΔH with ring size. The energy decomposition model discussed above is also able to capture both the magnitude and mechanism of the variation of E_a computed by ab initio calculations. As an example, an examination of the structural degrees of freedom in the model reveals that during the back reaction of 4-(c,c,c,c), when one cis unit transforms into the transition state (ts$_1$) as shown in Figure 5, the ring framework not only induces strain on the converted unit but also induces additional strain on the other three cis units, which results in an increase in the total energy of ts$_1$ and thus in E_a. For the second E_a (ts$_2$), because one cis-unit is already converted to the trans-state, the additional strain reduces and E_a decreases, and so on. Accordingly, we can conclude that the induced strain not only increases the total energy of all-cis-AB configurations but also stabilizes the photoinduced high-energy metastable state. From the computed E_a values, the half life of the cis states can be predicted,[36] and considering an average increase of 20% for E_a compared

Table 1. Variation of First Activation Energy (E_a) with ring size ($n = 2–6$) and Type of Linkers for 3-AB[a]

ring size (n)	1	3				4	5	6
linker type		α_3	$\alpha_2\beta_1$	$\alpha_1\beta_2$	β_3	α_4	α_5	α_6
E_a (eV)	0.93	0.98	1.13	1.35	1.25	1.16	1.11	1.03

[a]Our computed E_a for isolated AB is shown for comparison.

with isolated AB, the metastable *cis*-azobenzenophanes would have a half-life of greater than 1 year.[37] For the system under maximum strain discussed above, although it is challenging to determine the exact corresponding reaction path, we computed E_a for a number of different possible transition states and found a range of 0.9 to 1.1 eV, indicating that the activation energy for this hypothetical, extreme case would lie in the same range as our reported values for the other ring systems. A similar trend and mechanism are observed for 3-AB rings with β linkers, where the addition of each β-linker uniformly increases E_a of the first step, except for 3-AB-β_3, in which case all AB units become indistinguishable, as discussed above.

In addition to thermodynamic considerations, the effect of the ring geometry or induced strain on the absorption spectrum is another important issue. It is well known that the absorption spectrum of single *trans*-AB shows a weak band at 450 nm ($n–\pi^*$ excitation) and a strong one at 320 nm ($\pi–\pi^*$).[36] Norikane et al.[27] synthesized and studied the absorption spectra of similar ring structures (two- to four-member rings with methylene linkers) and reported that the absorption maxima of trans isomers slightly shifted when compared with AB (by a maximum 10 nm to shorter or longer wavelengths for different sizes) but still remained near 320 nm. According to our calculations, when compared with isolated *trans*-AB, the energy gap of *trans*-azobenzenophanes is slightly reduced due to the induced strain, resulting in a small shift of the absorption maxima toward longer wavelengths. Thus, large changes in the absorption spectra are not expected for the ring structures considered here, in good agreement with previous experimental measurements. Systems with different linkers or two-member rings that are under very high strain could certainly have bigger changes in their absorption features.[38,39]

We believe the trends observed for ring systems presented here are not just limited to azobenzene but rather applicable to a wide range of photoconvertible molecules. To test one additional case, we analyze the stilbene molecule (SB), which is a prototype molecule for investigating photoisomerization effects and applications and has been the subject of a substantial number of experimental and theoretical studies.[40] For isolated SB, our calculated ΔH is 0.22 eV, in agreement with experimental measurements that report a value of 0.20 eV in benzene solution.[41] Similar to the AB case, for 3-SB ΔH slightly decreases to 0.19 eV/SB but significantly increases to 0.65 eV for 4-SB, and using β-linkers instead of α also increases ΔH up to 0.68 eV for 4-SB. Isolated *cis*-SB is rather unstable, with an experimentally measured E_a for c→t isomerization of ∼0.05 eV,[42,43] and our computed E_a for isolated SB is 0.06 eV, consistent with the reported values. However, when in a ring form, just as for the azobenzenophanes, our calculations predict that for stilbenophanes E_a significantly increases up to 0.38 and 0.44 eV for 3-SB-(c,c,c)-α_3 and 3-SB-(c,c,c)-β_3, respectively.

In conclusion, we have shown that the molecular rings formed by connecting well-known photoswitchable molecules by suitable linker agents can simultaneously increase the stored energy and the reaction barrier of the back reaction of the photoswitch. These results indicate that the formation of rings

of photoswitches holds the potential to be a promising template concept for solar-thermal fuels, with a number of degrees of freedom including the ring size, type of linker, H-bonding, or type photoconvertible molecule.

■ METHODOLOGY

Our calculations were performed within density functional theory (DFT),[44] using PAW potentials[45] implemented in the VASP package.[46] The exchange-correlation potential was approximated within the generalized gradient approximation (GGA),[47] and to test the functional dependence of our results we also carried out calculations using the HSE06 hybrid functional.[48,49] The Brillouin zone integration was performed at the gamma point. We used a plane-wave basis set with a kinetic energy cutoff of 500 eV, which was checked to be sufficient to obtain fully converged results. All structures were considered as isolated molecules in a vacuum and were relaxed using the Kosugi algorithm (special Davidson block iteration scheme) with simultaneous minimization of the total energy and interatomic forces. The convergence on the total energy was set to 10^{-5} eV, and the maximum residual force allowed on each atom was fixed at 10^{-2} eV/Å. For each ring system, a number of simulations was carried out from multiple different initial configurations and relaxed without any constraints to obtain ground-state structures. Minimum energy path calculations were performed using the nudged-elastic band approach.[50]

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Variation of ΔH with different types of linkers for 4-AB and computed stepwise back reaction path from the 3-(c,c,c)-α_3 to 3-(t,t,t)-α_3. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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