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Aza-bicyclodiene based photoswitches for molecular solar thermal energy storage†

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Harnessing and storage of solar radiations employing molecular photoswitches are certainly of intense research interest *en route* to alleviate the increasing energy demand. The present report aims to scrutinize the effect of *N*-Substitution on the photoswitching behaviour of bicyclodienes with different bridge lengths for molecular solar thermal energy storage (MOST) application. The result reveals that the bicyclodiene attains stability with an increase in bridge length due to a decreasing ring strain, while the photoproduct acquires strain and becomes destabilized. Consequently, as the bridge length increases, the storage energy is enhanced while the back reaction barrier decreases. The photoswitching properties can be greatly altered based on the position of N in aza-bicyclodiene. Aza-bicyclodiene photoswitches are isobaric with the parent systems and do not reduce the energy storage density, unlike the bulky electron releasing and withdrawing substituents. *N*-substitution at the bridgehead position enhances the thermal back reaction barrier without compromising the storage energy in long-bridged switches. Further, *N*-substitution is effective at shifting (bathochromic) the excitation wavelength to the longer wavelength region of the spectrum. Therefore, *N*-substitution in long-bridge bicyclodiene photoswitches could be beneficial to improve the thermochemical as well as photophysical properties for MOST application.

1. Introduction

Fossil fuels, like natural gas, crude oil, and coal—although they are exhaustible energy resources—are currently the chief contributors to meet the energy demand.^{1,2} The natural reserves of these energy resources, however, are rapidly exhausting, but nevertheless the requirement for energy is always perpetual.^{2,3} The worldwide need for energy is further likely to increase by at least two-fold in the future.^{2,4} Therefore, the search for an inexhaustible energy resource to sustainably meet the increasing energy crises is an ongoing and focussed area of research.^{1,2,5}

The solar radiations emitted by the Sun are the fundamental, inexhaustible and ultimate energy resource responsible for the existence of life on the Earth.^{3,6} Living organisms containing chlorophyll pigments are capable of harvesting the solar energy and convert it into chemical energy *via* photosynthesis.^{6,7}

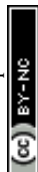
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† Electronic supplementary information (ESI) available: The calculated storage energies, energy storage densities, and thermal back reaction barriers of all the studied systems, optical absorption spectra of the reactants and photoproducts of the considered photoswitching couples, spectral data including the molar absorption coefficient, first important absorption wavelength (surpassing 0.01) and corresponding oscillatory strength for the bicyclodiene and photoisomer. See DOI: <https://doi.org/10.1039/d3ya00455d>

This biological phenomenon has inspired researchers to develop modern technologies, like solar cells, photocatalytic devices, energy dense fuels, molecular solar thermal energy storage devices, *etc.*, that can utilize energy from solar radiation.^{5,8–13} The intermittent and uneven geographical distribution of solar radiation has triggered the development of technological devices that not only aid the harnessing but also facilitate the long-term storage of solar energy.^{2,5,14}

A light-responsive molecule that can undergo photoinduced excitation to produce a metastable isomer and revert back to the parent isomer when triggered is known as a molecular photoswitch.¹⁵ Photoswitching couples have a potential to mimic this biological phenomenon and possess the ability to harness solar energy and store it in the chemical bonds as a metastable photoisomer.^{5,16–20} This stored chemical energy can be converted back into the thermal energy *via* activation of the metastable photoproduct when desired.^{5,21} The photoswitching molecules can serve as a means to harvest, store, and release energy, and thus promise to meet the energy crisis in a sustainable manner.^{5,21} The devices that employ photoswitches for the harvesting and storage of solar energy are called molecular solar thermal energy storage (MOST) systems or solar thermal fuels (STF).^{5,16–19,22,23}

The pioneering work on abiotic light harvesting molecular photoswitching systems were reported by Yoshida (1985) and Bren *et al.* (1991), and previously summarized by Dubonosov *et al.* (2002).^{24–26} Thereafter, the field was thoroughly investigated



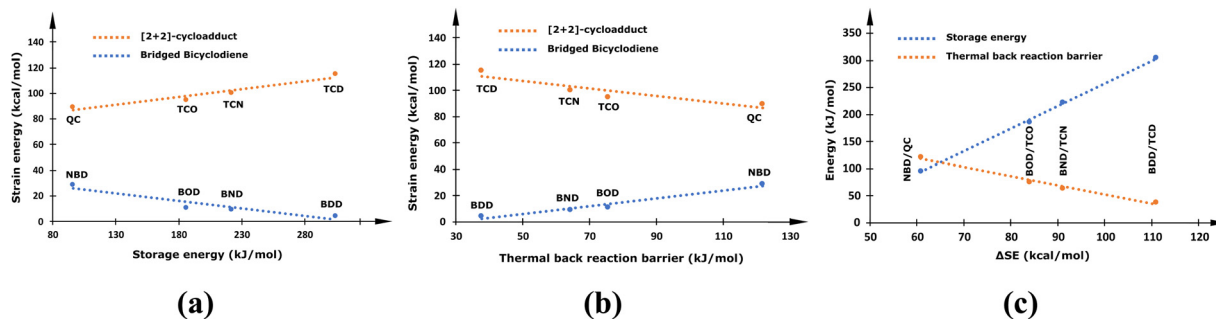


Fig. 1 Variation in thermochemical properties with molecular ring strain. (a) Variation in storage energy with the ring strain energy of the bridged bicyclodiene and photoproduct, (b) variation in the thermal back reaction with the ring strain energy of the bridged bicyclodiene and photoproduct, and (c) variation in thermochemical properties with the difference in ring strain energy between the bridged bicyclodiene and photoproduct (Δ SE).

the thermochemical properties with the ring SEs were analysed and the resulting data is systematically presented in Fig. 1. The calculated energy values are provided in S1 of the ESI† (Table S1).

The calculated ring strain energy decreases from 28.95 to 4.28 kcal mol⁻¹ with the progressive increase of -CH₂- units in the bridge (NBD to BDD) and the resulting bicyclic diene attains a high stability. However, the ring SE in the metastable [2+2]-cycloadduct obtained upon photoconversion increases from 89.75 to 115.19 kcal mol⁻¹ with bridge length (QC to TCD), thereby drastically increasing the instability of the photoproduct. Consequently, the difference in SE between the parent bicyclodiene and the corresponding cycloadduct (Δ SE) becomes larger (60.79 to 110.91 kcal mol⁻¹) as the bridge length increases. Therefore, the storage energy is remarkably improved from the NBD/QC (96.06 kJ mol⁻¹) to the BDD/TCD (304.39 kJ mol⁻¹) photoswitching system. The enhanced instability induced due to ring strain in the metastable photoisomer upsurges its propensity to revert back to the parent molecule. Therefore, the barrier to a thermal back reaction decreases from 121.77 to 37.63 kJ mol⁻¹ with the increase in -CH₂- bridging units (QC to TCD). Overall, the ring strain energy of the photoisomers is crucial to modulate the thermochemical properties of the MOST applications, as can be clearly seen in Fig. 1. The increase in bridge length, although it enhances the storage energy, remarkably affects the storage time due to the enhanced ring strain in the metastable photoisomer. Therefore, a larger Δ SE between two photoisomers can improve the thermochemical properties, provided that the ring strain in the metastable product does not increase significantly.

3.2 Thermochemical properties

Storage energy (ΔG_{str}) and energy storage density. Initially, the storage energy (ΔG_{str}) was determined for the various bicyclodiene-based photoswitches with different bridge lengths. The calculated ΔG_{str} for the NBD/QC, BOD/TCO, BND/TCN, and BDD/TCD photoswitching couples is 96.06, 186.19, 222.00, and 304.39 kJ mol⁻¹ (Table S1). These values are obtained by computing the electronic energy with DLPNO-CCSD(T)/Def2TZVP and including the thermal correction at the M062X/6-311++G** level for the geometries optimized with the M062X/6-311++G** level of theory. In Table 1, the calculated storage energy and the first important excitation wavelength of the reactants and photoproducts are systematically compared with the previously reported data for bicyclic diene photoswitches. The calculated storage energy and the excitation wavelengths are in accordance with the previously reported values of 96.3 (NBD/QC), 192.8 (BOD/TCO), 223.0 (BND/TCN), and 305.8 (BDD/TCD) kJ mol⁻¹. Further, the experimentally determined enthalpy for the isomerization of quadricyclane to norbornadiene is 92.05 ± 1.18 kJ mol⁻¹ is also in agreement with the calculated data.⁶⁴ The norbornadiene shows the experimental absorption onset (log ϵ = 2) at ~267 nm in acetonitrile solvent, which is also closer to the excitation wavelength computed in the gaseous phase.⁶⁵ This ensures the reliability of the obtained outcomes.

En route to unravel the impact of *N*-substitution, ΔG_{str} was estimated for the various *N*-substituted systems of different bicyclodiene photoswitches. The variation in ΔG_{str} for different *N*-substitutions in the studied bicyclodiene systems with different bridge lengths is shown in Fig. 2. Herein, the ΔG_{str} of parent molecular photoswitching systems was considered as

Table 1 Comparison of the calculated storage energy and first important excitation wavelength with previously reported data

System	Storage energy (kJ mol ⁻¹)		$\lambda_{\text{reactant}}$ (nm)		λ_{product} (nm)	
	Calculated	Reported ¹⁶	Calculated	Reported ¹⁶	Calculated	Reported ¹⁶
NBD/QC	96.06	96.30	214.42	213.65	184.63	190.74
BND/TCN	222.00	223.00	206.69	206.67	199.61	208.46
ABND/ATCN	220.32	220.50	242.09	250.44	207.27	223.07
OBND/OTCN	213.25	213.70	213.22	216.45	193.35	204.87
BDD/TCD	304.39	305.80	207.52	207.66	202.19	210.97
ABDD/ATCD	299.99	302.60	223.66	239.98	208.76	219.63
OBDD/OTCD	290.76	292.40	204.14	211.98	198.98	209.74



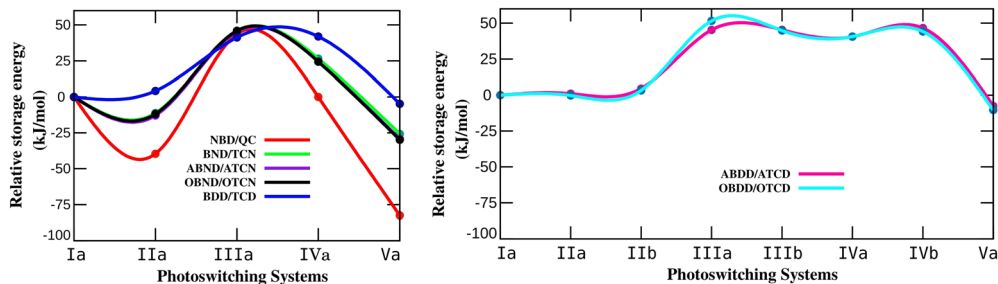


Fig. 2 Variation in the storage energy of *N*-substituted systems relative to their parent photoswitching system. The energy values were obtained by computing the electronic energy with the DLPNO-CCSD(T)/DefTZVP method and including the thermal correction at the M062X/6-311++G** level.

zero and the energies for different aza-substituted systems were accounted relative to their parent photoswitches. The calculated ΔG_{str} values are provided in S2 of the ESI† (Tables S2–S8).

It has been observed that the presence of N at the bridgehead position (IIa-NBD/QC) decreases the storage energy to $56.47 \text{ kJ mol}^{-1}$ when compared with that of the parent NBD/QC ($96.06 \text{ kJ mol}^{-1}$) (Table S2 of the ESI†). The calculated storage energy for IIa-NBD/QC is in accordance with the previously reported value of $53.81 \text{ kJ mol}^{-1}$ ($12.86 \text{ kcal mol}^{-1}$) for the same system calculated with the B3LYP/6-311++G* level.⁶⁶ The storage energy is significantly reduced to $13.48 \text{ kJ mol}^{-1}$ in the Va-NBD/QC photoswitch, where both the bridgehead C atoms are replaced by N. Notably, the substitution of N at the unsaturated C of a bicyclodiene (IIIa-NBD/QC) significantly increases the storage energy up to $139.77 \text{ kJ mol}^{-1}$. This value is also in agreement with the earlier reported value of $135.90 \text{ kJ mol}^{-1}$ ($32.48 \text{ kcal mol}^{-1}$) for *N*-substitution at the unsaturated position in the NBD.⁶⁶ The storage energy of IVa-NBD/QC is $96.02 \text{ kJ mol}^{-1}$ which is close to the parent NBD/QC system. This infers that the effect on ΔG_{str} is only marginal if the bridgehead and closest unsaturated C of bicyclodiene are replaced by N. The observed trend of variation in storage energy with position of N in bicyclodiene-based photoswitches with different bridge lengths resembles that of the NBD/QC system and the recently reported BOD/TCO system.⁵⁹ This indicates that the position of N is crucial for modulating the storage energy in bicyclodiene-based photoswitches with different bridge lengths. Notably, the presence of N in the unsaturated position improves the storage energy, whereas replacing the bridgehead C with N may degrade the energy storage properties in the studied bicyclodiene based photoswitches.

Although the trend in ΔG_{str} depends on the position of N, the extent of variation for the studied bicyclic dienes differs considerably with the bridge length. The reductions in ΔG_{str} for the bridgehead *N*-substituted IIa- and Va-NBD/QC systems are 39.59 and $82.58 \text{ kJ mol}^{-1}$, respectively. A recently reported BOD/TCO couple displayed a decrease in ΔG_{str} of 19.42 and $39.12 \text{ kJ mol}^{-1}$ for the same bridgehead *N*-substituted systems.⁵⁹ However, the reductions in ΔG_{str} in the BND/TCN, ABND/ATCN, and OBND/OTCN photoswitches are only 11.24 to $12.90 \text{ kJ mol}^{-1}$ for the IIa and 25.71 to $29.88 \text{ kJ mol}^{-1}$ for the Va systems. ΔG_{str} is decreased by only 0.23 kJ mol^{-1} for the IIa-OBDD/OTCD couple. Interestingly, the ΔG_{str} is even enhanced

by 1.09 to 4.62 kJ mol^{-1} in the IIa-BDD/TCD and IIa-ABDD/ATCD systems due to the presence of N at the bridgehead position. But, upon replacement of both bridgehead C atoms with N, 4.76 to $10.39 \text{ kJ mol}^{-1}$ decreases in ΔG_{str} of the Va-BDD/TCD, Va-ABDD/ATCD, Va-ABDD/ATCD systems are observed. The presence of a heteroatom (N or O) on the bridge has a comparatively minor effect on ΔG_{str} of the bridged bicyclodiene-based photoswitches. These observations led to the inference that the reduction in ΔG_{str} with *N*-substitution at the bridgehead position is more drastic for the NBD/QC system with short bridge lengths. Noteworthy, the decreasing effect in ΔG_{str} becomes less prominent after elongation of the bridge with $-\text{CH}_2-$ units. Therefore, the *N*-substitution at the bridgehead position provides better storage properties in bicyclodiene photoswitches with longer bridges.

It can be noted that the storage energy increases significantly when an unsaturated C is replaced with N in the studied bicyclodiene-based photoswitching systems. The enhancement in ΔG_{str} is almost constant and ranges from 41.26 to $51.59 \text{ kJ mol}^{-1}$ (Fig. 2) for the studied switches. This clearly suggest that, contrary to *N*-substitution at the bridgehead position, the increase in ΔG_{str} of the photoswitching system due to unsaturated N in the bicyclic diene does not depend on the bridge length. Therefore, *N*-substitution at the unsaturated position of the bicyclodiene would be beneficial to improve the storage energy of all the studied bridged bicyclic diene switches.

Furthermore, there is no significant variation in ΔG_{str} after replacement of the bridgehead and unsaturated C with N (IVa-NBD/QC) when compared with that of the parent NBD/QC system. According to a recent report, ΔG_{str} in the BOD/TCO couple increases by $14.34 \text{ kJ mol}^{-1}$ with N substitution at the bridgehead and unsaturated position. The increase in ΔG_{str} is 24.41 to $26.51 \text{ kJ mol}^{-1}$ for the IVa-BND/TCN, IVa-ABND/ATCN, and IVa-OBND/OTCN systems and 40.59 to $46.66 \text{ kJ mol}^{-1}$ for the IVa-BDD/TCD, IVa-IVb-ABDD/ATCD, and IVa-IVb-OBDD/OTCD systems. This clearly indicates that substituting the bridgehead and unsaturated C with N tends to increase ΔG_{str} with increasing bridge length of the bicyclodiene-based photoswitches. Therefore, the photoswitching systems with longer bridge lengths are better for improving storage energy due to *N*-substitution at the bridgehead and unsaturated position.

Since molecular photoswitching systems must have a low molecular weight, energy storage density is a more useful



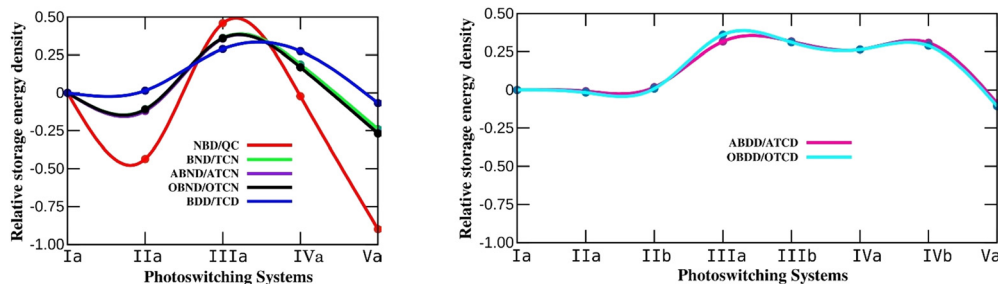


Fig. 3 Variation in the energy storage density of *N*-substituted systems relative to that of their parent photoswitching system. The energy values were obtained by computing the electronic energy with the DLPNO-CCSD(T)/Def2TZVP method and including thermal correction at the M062X/6-311++G** level.

quantity to predict the properties of MOST systems. Therefore, energy storage density is calculated for all the studied systems and the values are tabulated in S2 of the ESI† (Tables S2–S8). The variation in energy storage density of *N*-substituted chemical photoswitches relative to the parent systems is depicted in Fig. 3. It is apparent from the figure that the energy storage density in aza-bicyclodiene based photoswitches depends on the position of *N*. The trend observed for the variation in energy storage density for the different *N*-substituted systems is similar to that of storage energy. Since aza-bicyclodiene photoswitches are isobaric with their parent system, the energy density is not affected due to the mass of *N*. The properties of photoswitching systems are usually tuned by substituting electron donating and withdrawing groups, which reduces the energy storage density.⁵⁸ In aza-bicyclodiene switches, *N* may internally involve a push-pull mechanism and the properties can be tuned without reducing the energy storage density due to the mass of *N*, and thus is advantageous over bulky group substituents.⁵⁹

Thermal back reaction barrier (ΔE_{TBR}). A larger thermal back reaction barrier (ΔE_{TBR}) is essential to extend the lifespan of the metastable photoisomer and store solar energy as chemical energy for a longer period. Therefore, attention has also been devoted to estimating the energy required to convert the photoproduct to bicyclodiene in various *N*-substituted photoswitches. The calculated barrier height (ΔE_{TBR}) for the thermal back isomerization reaction of the studied photoswitching couples is provided in S2 of the ESI† (Tables S2–S8). The variation in ΔE_{TBR} for different aza-bicyclodiene photoswitching

systems relative to that of their parent systems is displayed in Fig. 4. Here, ΔE_{TBR} for the parent photoswitch was assumed to be zero and the energies for various aza-substituted photoswitches were calculated relative to that of the parent switch.

During the thermal back conversion of the photoproduct to bicyclodiene, dissociation of the two bonds occurs through an asynchronous mechanism.²² Initially, a bond is cleaved, leading to the formation of singlet biradicals in the transition state (TS).²² Owing to the multireference character of TS, the DFT functionals are inappropriate for predicting the TS and they overestimate the energy barrier.²² Multiconfigurational methods, like CASSCF, are rather more suitable for an accurate prediction of the energy barrier.²² As multiconfigurational calculations are computationally expensive, they cannot be routinely employed for simulations.^{16,22} A previous benchmark study demonstrated that the electronic energy calculated by CASSCF methods for TS geometries obtained using the PBE functional determine ΔE_{TBR} close to the experimental values at a cheaper computational cost.²² Therefore, in the present investigation, the geometry of transition states is obtained through climbing image nudged elastic band (CI-NEB) calculations using the PBE functional. Subsequently, the electronic energy of the transition states and photoproducts were computed with a single point energy calculation at the (8,8)-CASPT2/6-311++G** level of theory.

It is apparent from the figure that the energy barrier for the thermal back conversion reaction significantly alters due to *N*-Substitution. Consistent with the storage energy, the observed

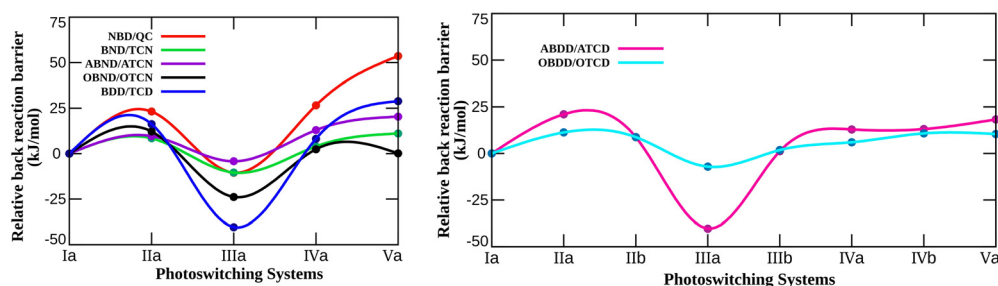


Fig. 4 Variation in the barrier for thermal back isomerization of the photoproduct to bicyclodiene in various *N*-substituted systems relative to that of their parent photoswitching system. The energy values were obtained by computing the electronic energy with the (8,8)-CASPT2/6-311++G** level of theory.



trend for the thermal back reaction barrier in the aza-substituted photoswitches depends solely on the position of the N atom. As can be seen from the figure, the barrier height increases by 23.17 kJ mol⁻¹ when N is substituted at the bridgehead position (IIa-NBD/QC) in the NBD/QC photoswitching pair. If both the bridgehead positions are replaced with N atoms (Va-NBD/QC), a substantial increment (53.62 kJ mol⁻¹) in the energy barrier is noticed. In contrast, if the unsaturated C is replaced with N (IIIa-NBD/QC), the ΔE_{TBR} decreases by 10.52 kJ mol⁻¹. Moreover, the barrier increases by 26.56 kJ mol⁻¹ when the bridgehead and nearest unsaturated C atoms are replaced with N (IVa-NBD/QC). This clearly indicates that the presence of N in the bridgehead position enhances the energy barrier for the thermal back conversion reaction. Further, substitution of N in the unsaturated position lowers the energy barrier relative to that of the parent photoswitching system. The trend observed for ΔE_{TBR} in various *N*-substituted NBD/QC systems is opposite to that of ΔG_{str} (Fig. 3 and 4). This simply means that when the thermal back reaction barrier for *N*-substitution in the short-bridged NBD/QC photoswitches is increased, then the storage energy is adversely affected and *vice versa*.

The variation in ΔE_{TBR} with *N*-substitution in the photoswitches of different bridge length relative to that of their parent system follows the same trend as that of the aza-NBD/QC pair. Therefore, ΔE_{TBR} also increases with the presence of N at the bridgehead position in the photoswitching systems with a longer bridge length. The calculated increase in the energy barriers of the thermal back reaction in the IIa-BDD/TCD and Va-BDD/TCD systems relative to that of their parent BDD/TCD pair are 16.28 and 28.88 kJ mol⁻¹, respectively. As mentioned earlier, the reducing effect of ΔG_{str} with bridgehead *N*-substitution becomes less prominent as the bridge length increases in bicyclodiene-based switches. Therefore, the *N*-substitution at the bridgehead position of the long-bridge photoswitching systems can uplift the barrier height (ΔE_{TBR}) without compromising the storage energy.

The overall analysis of thermochemical properties explicitly advocates that the presence of heteroatoms on the bridge have a minimal impact on the photoswitching properties, whereas replacement of the bridgehead or unsaturated C of bicyclodiene by N has a significant effect. Close analysis of the storage energy suggests that the substitution of N at one of the unsaturated C atoms in bicyclodiene remarkably improves the storage energy of the photoswitching system. The storage energy decreases when N is present at the bridgehead position in the short-bridge bicyclodiene photoswitch (NBD/QC pair). Interestingly, the decrease in storage energy becomes less prominent as the bridge length increases. Moreover, the barrier height for thermal back isomerization increases in bridgehead *N*-substituted systems. Thus, *N*-substitution at the bridgehead position of the long-bridge bicyclodiene photoswitch (aza-BDD/TCD) exhibits better thermochemical properties than those of the parent BDD/TCD pair. Therefore, it is interesting to mention that in the case of long-bridge photoswitches, the lifespan of the metastable photo-product can be enhanced without adversely affecting the amount of energy harnessed from solar radiation.

The short-bridged NBD/QC has the least storage energy (96.06 kJ mol⁻¹) and highest TBR barrier (121.76 kJ mol⁻¹). Contrarily, the long bridged BDD/TCD couple displays the largest storage energy (304.39 kJ mol⁻¹) with the least thermal barrier (37.63 kJ mol⁻¹). This clearly infers that an increase in bridge length enhances storage energy of the bicyclic diene photoswitches and compromises the TBR barrier, which is in accordance with the previous report.¹⁶ Owing to the large storage energy of the long bridged BDD/TCD couple, it could be considered as a better system to further investigate in the future, as it provides a large scope for tuning the photoswitching properties. Therefore, any structural modifications in the long bridged bicyclic dienes that enhance the thermal barrier for isomerization are desirable for engineering the MOST system.

Outcomes of this work reveal that the impact of *N*-substitution in these bicyclic dienes depends upon the position of N and size of the bridge. *N*-substitution at one of the unsaturated positions in diene (III) increases the storage energy by 41.94–51.60 kJ mol⁻¹ at the expense of the TBR barrier. The *N*-substitution at the bridgehead position (II and III) enhances the barrier for thermal isomerization at the cost of storage energy in the case of short bridged photoswitches. In contrast to this, *N*-substitution at the bridgehead position enhances the barrier for thermal isomerization without compromising the storage energy in the case of long bridged photoswitches.

Overall, the impact of *N*-substitution at bridgehead position in the long bridged Va-BDD/TCD couple is the enhancement of TBR by 28.88 kJ mol⁻¹ without significantly reducing the energy storage density relative to that of the Ia-BDD/TCD pair. Therefore, the *N*-substitution assists tuning the properties of the studied bridged bicyclic diene photoswitches and may guide the future designing of photoswitches for practical MOST applications. Despite the highest increment in TBR, the absolute TBR barrier of IIa- and Va-BDD/TCD systems remains lower than that desired for long-time energy storage devices due to the low intrinsic barrier in the Ia-BDD/TCD system. The results suggest that *N*-substitution at the bridgehead position could be one of the approaches that will considerably enhance the thermal barrier, while further substitutions must be carried out to make it relevant for practical MOST applications.

Furthermore, the substitution of N at the bridgehead and closest unsaturated position (IV) increases the TBR barrier and storage energy. Therefore, the molecules with these *N*-substitutions display the best photoswitching properties among the studied switches for MOST applications. The intrinsic TBR barrier of the short-bridged NBD/QC system is larger, and *N*-substitutions enhance the TBR barrier to 148.33 kJ mol⁻¹ without compromising the storage energy. Thus, among the studied photochromic couples, IVa-NBD/QC could be considered as the best system for energy storage applications.

3.3 Photophysical properties

Absorption of solar radiation by the molecule is one of the prerequisites to serve as a photoswitching system for MOST applications. Therefore, critical analysis of the photophysical



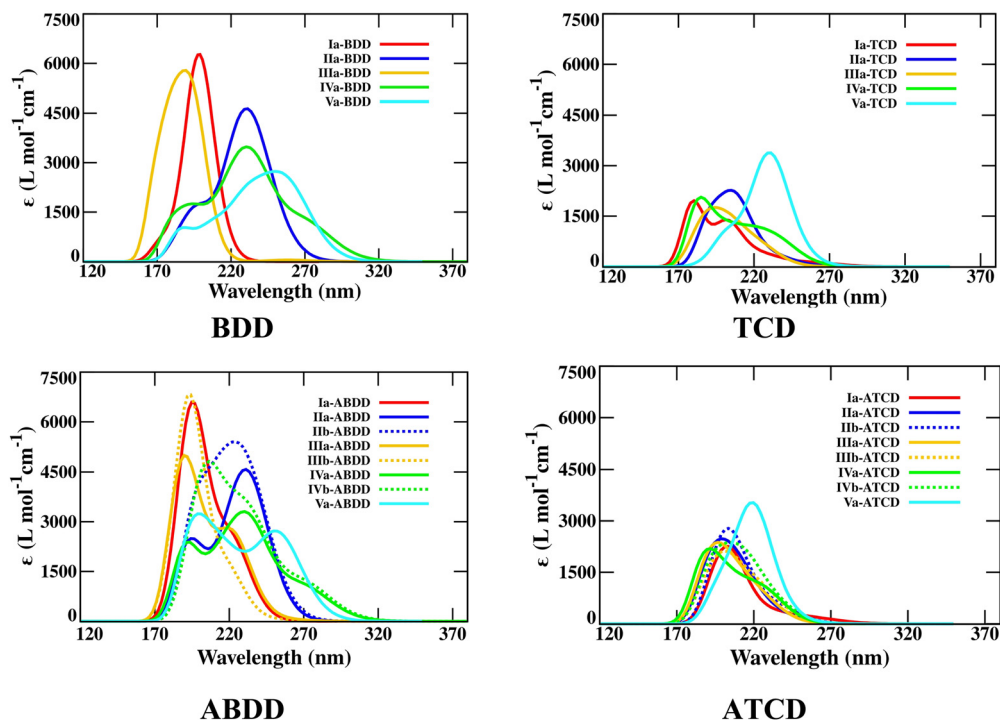


Fig. 5 Optical absorption spectra of the parent and *N*-substituted BDD/TCD and ABDD/ATCD photoswitching systems.

properties of the photoswitching couple is important. The photophysical properties of the studied photochromic couples were calculated and the optical absorption spectra of the parent BDD/TCD, ABDD/ATCD, their various *N*-substituted bicyclobienes and corresponding photoproducts are depicted in Fig. 5. The optical spectra of other studied systems are provided in S3 of the ESI† (Fig. S1). The spectral data, including the molar absorption coefficient, first important excitation wavelength and oscillatory strength (surpassing 0.01), are tabulated in S3 of ESI† (Tables S9–S15).

The calculated first excitation wavelengths for NBD, BND, and BDD are 214.42, 206.69, and 207.52 nm, respectively, which is in close agreement with the recently reported values of 213.65, 206.67, and 207.66 nm.¹⁶ The photophysical properties are greatly influenced by the substitution of *N* in these bicyclobienes. Further, the optical absorption spectra (optical properties) vary with the position of *N* in bicyclobiene molecules similar to that of thermochemical properties. It is noteworthy that the presence of *N* at the bridgehead position considerably red-shifts the first important excitation wavelength of bicyclobienes. The red-shift in the excitation wavelength becomes more prominent when both bridgehead C atoms are replaced with *N*. It has been noticed that the replacement of unsaturated C with *N* in bicyclobienes shows a slight hypsochromic shift in the first important excitation wavelength. This demonstrates that the position of *N* plays a crucial role in modulating the photophysical properties of bicyclobiene-based photoswitching systems, analogous with the thermochemical properties.

Upon substitution of both the bridgehead C atoms with *N*, bathochromic shifts of 58.67 and 51.63 nm are noticed in the

first excitation wavelengths of Va-BND and Va-BDD, respectively, when compared with those of their parent molecules. The first optical excitation wavelength of Va-BDD is 271.66 nm which is longer than the first excitation wavelength of the most studied NBD (213.65 nm), recently reported bicyclooctadiene (196.44 nm), and unsubstituted bicyclobiene molecules with different bridge lengths.¹⁶

En route to probe the delocalization of electrons in aza-bicyclobiene based photoswitches, natural bond orbital (NBO) analyses have been performed for the bicyclic diene and photoproducts. It has been observed that the lone pair of bridgehead *N* (N_{lp}) involves the delocalization with π^* -bonding orbitals in the bicyclic diene. The stabilization energy for the $N_{lp} \rightarrow \pi^*$ charge transfer is 1.21, 3.25, and 15.13 kcal mol⁻¹ in the IIa-NBD, IIa-BND, and IIa-BDD molecules, respectively. This infers that the extent of stabilization achieved due to $N_{lp} \rightarrow \pi^*$ electron delocalization increases with the length of the bridge. Likewise, the extent of stabilization achieved due to the $N_{lp} \rightarrow \sigma^*$ charge transfer in the photoproduct increases from 4.88 kcal mol⁻¹ in IIa-QC to 14.33 kcal mol⁻¹ in IIa-TCD. This suggests that the lone pair on *N* may involve an internal push-pull mechanism and assist to modulate the properties of the photoswitches. The stabilization achieved due to the delocalization of N_{lp} to π^* -bonding orbitals in bridgehead *N*-substituted (II) bicyclic diene photoswitches of different bridge lengths is shown in Fig. 6. In contrast to the bridgehead *N*, the lone pair on unsaturated *N* does not facilitate delocalization with the π^* -bonding orbitals.

The relationship of the molecular structure, particularly the position of *N* with the thermochemical and photophysical properties is systematically summarized in a concise manner



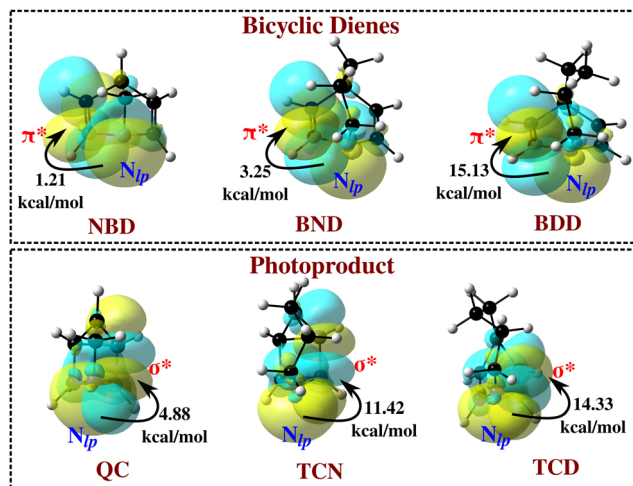


Fig. 6 The stabilization achieved due to delocalization of N_{lp} in bridgehead N -substituted bicyclic diene photoswitches with different bridge lengths.

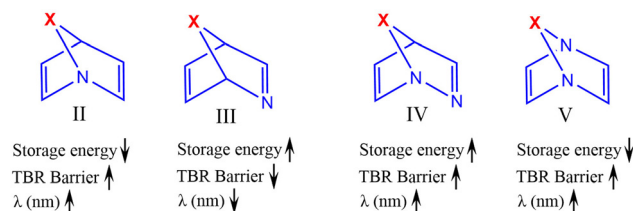


Fig. 7 Systematic summary of the relationships of the molecular structure, particularly the position of N with the thermochemical and photophysical properties.

in Fig. 7. The results reveal that the substitution of N at the bridgehead position (II) increases the TBR barrier and the first important wavelength of excitation at the cost of the storage energy. The effect is found to be more pronounced if both the bridgehead positions are substituted with N (V). In contrast, the presence of N at the unsaturated position (III) improves the storage energy while the TBR barrier and wavelength of absorption is observed to decrease. Further, the substitution of N at the bridgehead and the closest unsaturated position (IV) mostly increases all three parameters in the studied bridged bicyclic diene photoswitches.

4. Conclusion

The decreasing ring strain energy (28.95 to 4.28 kcal mol⁻¹) stabilizes the bicyclodiene, whereas increasing ring SE (89.75 to 115.19 kcal mol⁻¹) destabilizes the metastable photoproduct with progressive increase in bridge length of the bicyclodiene-based photoswitches. Therefore, the storage energy is improved while the barrier for the thermal back reaction is reduced with an increase in $-CH_2-$ units in the bridge. The photoswitching properties of the bridged bicyclodiene-based photoswitches can be significantly altered with the N -substitution and are

governed by the position of N. The thermochemical properties elucidate that the replacement of unsaturated C in bicyclodiene with N increases the storage energy but decreases the thermal back reaction barrier. The presence of N at the bridgehead position in the NBD/QC increases the barrier for thermal isomerization at the cost of storage energy. The decrease in storage energy due to N -substitution at the bridgehead position becomes less prominent with an increase in bridge length. Therefore, it is worth mentioning that the thermal back reaction barrier of the bridgehead N -substituted BDD/TCD photo-switch can be uplifted by 28.88 kJ mol⁻¹ without compromising storage energy. Furthermore, the replacement of bridgehead C with N remarkably red-shifts the first important excitation wavelength. Therefore, N -substitution significantly improves the thermochemical and photophysical properties, particularly of the long-bridged bicyclic diene switches. Moreover, the substitution of N at the bridgehead and the closest unsaturated position improves the storage energy, TBR barrier and first excitation wavelength of the studied photoswitching pairs, making them more relevant for MOST applications. The outcomes exclusively emphasize that the N -substitution can greatly modulate the photoswitching properties and will, indeed, be beneficial for future designing of a novel photochromic couple for practical MOST applications.

Conflicts of interest

The authors declare there are no conflicts of interest.

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References

- P. J. Megía, A. J. Vizcaíno, J. A. Calles and A. Carrero, Hydrogen Production Technologies: From Fossil Fuels toward Renewable Sources. A Mini Review, *Energy Fuels*, 2021, **35**, 16403–16415.
- N. S. Lewis and D. G. Nocera, Powering the planet: Chemical challenges in solar energy utilization, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15729–15735.
- C. Ngô and J. B. Natowitz, *Our Energy Future*, John Wiley & Sons, Ltd, 2016, pp. 1–25.
- M. Grätzel, Powering the planet, *Nature*, 2000, **403**, 363.
- J. Orrego-Hernández, A. Dreos and K. Moth-Poulsen, Engineering of Norbornadiene/Quadricyclane Photoswitches for



- Molecular Solar Thermal Energy Storage Applications, *Acc. Chem. Res.*, 2020, **53**, 1478–1487.
- 6 J. S. Amthor, From sunlight to phytomass: on the potential efficiency of converting solar radiation to phyto-energy, *New Phytol.*, 2010, **188**, 939–959.
 - 7 E. Collini, Light-Harvesting: The Never-Ending Lesson of Nature, *ACS Cent. Sci.*, 2022, **8**, 306–308.
 - 8 G. D. Scholes, G. R. Fleming, A. Olaya-Castro and R. van Grondelle, Lessons from nature about solar light harvesting, *Nat. Chem.*, 2011, **3**, 763–774.
 - 9 J. Su and L. Vayssieres, A Place in the Sun for Artificial Photosynthesis?, *ACS Energy Lett.*, 2016, **1**, 121–135.
 - 10 D. K. Dogutan and D. G. Nocera, Artificial Photosynthesis at Efficiencies Greatly Exceeding That of Natural Photosynthesis, *Acc. Chem. Res.*, 2019, **52**, 3143–3148.
 - 11 Y. Gao, K. Huang, C. Long, Y. Ding, J. Chang, D. Zhang, L. Etgar, M. Liu, J. Zhang and J. Yang, Flexible Perovskite Solar Cells: From Materials and Device Architectures to Applications, *ACS Energy Lett.*, 2022, **7**, 1412–1445.
 - 12 M. Melchionna and P. Fornasiero, Updates on the Roadmap for Photocatalysis, *ACS Catal.*, 2020, **10**, 5493–5501.
 - 13 V. Romano, G. D'Angelo, S. Perathoner and G. Centi, Current density in solar fuel technologies, *Energy Environ. Sci.*, 2021, **14**, 5760–5787.
 - 14 Z. Wang, H. Hölzel and K. Moth-Poulsen, Status and challenges for molecular solar thermal energy storage system based devices, *Chem. Soc. Rev.*, 2022, **51**, 7313–7326.
 - 15 M.-M. Russew and S. Hecht, Photoswitches: From Molecules to Materials, *Adv. Mater.*, 2010, **22**, 3348–3360.
 - 16 A. E. Hillers-Bendtsen, P. G. Iuel Lunøe Dünweber, L. H. Olsen and K. V. Mikkelsen, Prospects of Improving Molecular Solar Energy Storage of the Norbornadiene/Quadricyclane System through Bridgehead Modifications, *J. Phys. Chem. A*, 2022, **126**, 2670–2676.
 - 17 A. E. Hillers-Bendtsen, M. Quant, K. Moth-Poulsen and K. V. Mikkelsen, Investigation of the Structural and Thermochemical Properties of [2.2.2]-Bicyclooctadiene Photoswitches, *J. Phys. Chem. A*, 2021, **125**, 10330–10339.
 - 18 M. Quant, A. E. Hillers-Bendtsen, S. Ghasemi, M. Erdelyi, Z. Wang, L. M. Muhammad, N. Kann, K. V. Mikkelsen and K. Moth-Poulsen, Synthesis, characterization and computational evaluation of bicyclooctadienes towards molecular solar thermal energy storage, *Chem. Sci.*, 2022, **13**, 834–841.
 - 19 A. Lennartson, A. Roffey and K. Moth-Poulsen, Designing photoswitches for molecular solar thermal energy storage, *Tetrahedron Lett.*, 2015, **56**, 1457–1465.
 - 20 M. Morikawa, Y. Yamanaka and N. Kimizuka, Liquid Bisazobenzenes as Molecular Solar Thermal Fuel with Enhanced Energy Density, *Chem. Lett.*, 2022, **51**, 402–406.
 - 21 Z. Wang, P. Erhart, T. Li, Z.-Y. Zhang, D. Sampedro, Z. Hu, H. A. Wegner, O. Brummel, J. Libuda, M. B. Nielsen and K. Moth-Poulsen, Storing energy with molecular photoisomers, *Joule*, 2021, **5**, 3116–3136.
 - 22 M. J. Kuisma, A. M. Lundin, K. Moth-Poulsen, P. Hyldgaard and P. Erhart, Comparative Ab-Initio Study of Substituted Norbornadiene-Quadricyclane Compounds for Solar Thermal Storage, *J. Phys. Chem. C*, 2016, **120**, 3635–3645.
 - 23 E. N. Cho, D. Zhitomirsky, G. G. D. Han, Y. Liu and J. C. Grossman, Molecularly Engineered Azobenzene Derivatives for High Energy Density Solid-State Solar Thermal Fuels, *ACS Appl. Mater. Interfaces*, 2017, **9**, 8679–8687.
 - 24 Z. Yoshida, New molecular energy storage systems, *J. Photochem.*, 1985, **29**, 27–40.
 - 25 V. A. Bren', A. D. Dubonosov, V. I. Minkin and V. A. Chernovyanov, Norbornadiene–quadricyclane—an effective molecular system for the storage of solar energy, *Russ. Chem. Rev.*, 1991, **60**, 451.
 - 26 A. D. Dubonosov, V. A. Bren and V. A. Chernovyanov, Norbornadiene–quadricyclane as an abiotic system for the storage of solar energy, *Russ. Chem. Rev.*, 2002, **71**, 917.
 - 27 M. Bertram, F. Waidhas, M. Jevric, L. Fromm, C. Schuschke, M. Kastenmeier, A. Görling, K. Moth-Poulsen, O. Brummel and J. Libuda, Norbornadiene photoswitches anchored to well-defined oxide surfaces: From ultrahigh vacuum into the liquid and the electrochemical environment, *J. Chem. Phys.*, 2020, **152**, 044708.
 - 28 K. Börjesson, A. Lennartson and K. Moth-Poulsen, Efficiency Limit of Molecular Solar Thermal Energy Collecting Devices, *ACS Sustainable Chem. Eng.*, 2013, **1**, 585–590.
 - 29 K. Börjesson, A. Lennartson and K. Moth-Poulsen, Fluorinated fulvalene ruthenium compound for molecular solar thermal applications, *J. Fluorine Chem.*, 2014, **161**, 24–28.
 - 30 U. Jacovella, E. Carrascosa, J. T. Buntine, N. Ree, K. V. Mikkelsen, M. Jevric, K. Moth-Poulsen and E. J. Bieske, Photo- and Collision-Induced Isomerization of a Charge-Tagged Norbornadiene–Quadricyclane System, *J. Phys. Chem. Lett.*, 2020, **11**, 6045–6050.
 - 31 F. Waidhas, M. Jevric, M. Bosch, T. Yang, E. Franz, Z. Liu, J. Bachmann, K. Moth-Poulsen, O. Brummel and J. Libuda, Electrochemically controlled energy release from a norbornadiene-based solar thermal fuel: increasing the reversibility to 99.8% using HOPG as the electrode material, *J. Mater. Chem. A*, 2020, **8**, 15658–15664.
 - 32 Z. Wang, H. Hölzel and K. Moth-Poulsen, Status and challenges for molecular solar thermal energy storage system based devices, *Chem. Soc. Rev.*, 2022, **51**, 7313–7326.
 - 33 Z. Wang, H. Moïse, M. Cacciarini, M. B. Nielsen, M. Morikawa, N. Kimizuka and K. Moth-Poulsen, Liquid-Based Multijunction Molecular Solar Thermal Energy Collection Device, *Adv. Sci.*, 2021, **8**, 2103060.
 - 34 Z. Wang, Z. Wu, Z. Hu, J. Orrego-Hernández, E. Mu, Z.-Y. Zhang, M. Jevric, Y. Liu, X. Fu, F. Wang, T. Li and K. Moth-Poulsen, Chip-scale solar thermal electrical power generation, *Cell Rep. Phys. Sci.*, 2022, **3**, 100789.
 - 35 A. Kjaersgaard, H. Hölzel, K. Moth-Poulsen and M. B. Nielsen, Photolytic Studies of Norbornadiene Derivatives under High-Intensity Light Conditions, *J. Phys. Chem. A*, 2022, **126**, 6849–6857.
 - 36 A. E. Hillers-Bendtsen, M. H. Hansen and K. V. Mikkelsen, The influence of nanoparticles on the excitation energies of



- the photochromic dihydroazulene/vinylheptafulvene system, *Phys. Chem. Chem. Phys.*, 2019, **21**, 6689–6698.
- 37 A. E. Hillers-Bendtsen, M. B. Johansen and K. V. Mikkelsen, Promoting the thermal back reaction of vinylheptafulvene to dihydroazulene by physisorption on nanoparticles, *Phys. Chem. Chem. Phys.*, 2021, **23**, 12889–12899.
- 38 S. Helmy, F. A. Leibfarth, S. Oh, J. E. Poelma, C. J. Hawker and J. Read de Alaniz, Photoswitching Using Visible Light: A New Class of Organic Photochromic Molecules, *J. Am. Chem. Soc.*, 2014, **136**, 8169–8172.
- 39 S. Crespi, N. A. Simeth and B. König, Heteroaryl azo dyes as molecular photoswitches, *Nat. Rev. Chem.*, 2019, **3**, 133–146.
- 40 P. Bolle, C. Menet, M. Puget, H. Serier-Brault, S. Katao, V. Guerchais, F. Boucher, T. Kawai, J. Boixel and R. Dessapt, Enhanced reversible solid-state photoswitching of a cationic dithienylethene assembled with a polyoxometalate unit, *J. Mater. Chem. C*, 2021, **9**, 13072–13076.
- 41 R. Eschenbacher, T. Xu, E. Franz, R. Löw, T. Moje, L. Fromm, A. Görling, O. Brummel, R. Herges and J. Libuda, Triggering the energy release in molecular solar thermal systems: Norbornadiene-functionalized trioxatriangulen on Au(111), *Nano Energy*, 2022, **95**, 107007.
- 42 G. Li, L. Sun, L. Ji and H. Chao, Ruthenium(II) complexes with dppz: from molecular photoswitch to biological applications, *Dalton Trans.*, 2016, **45**, 13261–13276.
- 43 R. Boese, J. K. Cammack, A. J. Matzger, K. Pflug, W. B. Tolman, K. P. C. Vollhardt and T. W. Weidman, Photochemistry of (Fulvalene)tetracarbonyldiruthenium and Its Derivatives: Efficient Light Energy Storage Devices, *J. Am. Chem. Soc.*, 1997, **119**, 6757–6773.
- 44 A. A. Beharry and G. A. Woolley, Azobenzene photoswitches for biomolecules, *Chem. Soc. Rev.*, 2011, **40**, 4422–4437.
- 45 M. W. H. Hoorens, M. Medved', A. D. Laurent, M. Di Donato, S. Fanetti, L. Slappendel, M. Hilbers, B. L. Feringa, W. Jan Buma and W. Szymanski, Iminothioindoxyl as a molecular photoswitch with 100 nm band separation in the visible range, *Nat. Commun.*, 2019, **10**, 2390.
- 46 J. L. Greenfield, M. A. Gerkman, R. S. L. Gibson, G. G. D. Han and M. J. Fuchter, Efficient Electrocatalytic Switching of Azoheteroarenes in the Condensed Phases, *J. Am. Chem. Soc.*, 2021, **143**, 15250–15257.
- 47 R. Zhao, Y. Li, J. Bai, J. Mu, L. Chen, N. Zhang, J. Han, F. Liu and S. Yan, Preparation of flexible photo-responsive film based on novel photo-liquefiable azobenzene derivative for solar thermal fuel application, *Dyes Pigm.*, 2022, **202**, 110277.
- 48 M. Cacciarini, M. Jevric, J. Elm, A. U. Petersen, K. V. Mikkelsen and M. B. Nielsen, Fine-tuning the lifetimes and energy storage capacities of meta-stable vinylheptafulvenes via substitution at the vinyl position, *RSC Adv.*, 2016, **6**, 49003–49010.
- 49 M. D. Kilde, P. G. Arroyo, A. S. Gertsen, K. V. Mikkelsen and M. B. Nielsen, Molecular solar thermal systems – control of light harvesting and energy storage by protonation/deprotonation, *RSC Adv.*, 2018, **8**, 6356–6364.
- 50 A. Mengots, A. Erbs Hillers-Bendtsen, S. Doria, F. Ørsted Kjeldal, N. Machholdt Høyer, A. Ugleholdt Petersen, K. V. Mikkelsen, M. Di Donato, M. Cacciarini and M. Brøndsted Nielsen, Dihydroazulene-Azobenzene-Dihydroazulene Triad Photoswitches, *Chem. – Eur. J.*, 2021, **27**, 12437–12446.
- 51 M. H. Cardenuto, H. M. Cezar, K. V. Mikkelsen, S. P. A. Sauer, K. Coutinho and S. Canuto, A QM/MM study of the conformation stability and electronic structure of the photochromic switches derivatives of DHA/VHF in acetonitrile solution, *Spectrochim. Acta, Part A*, 2021, **251**, 119434.
- 52 R. Asato, C. J. Martin, T. Nakashima, J. P. Calupitan, G. Rapenne and T. Kawai, Energy Storage upon Photochromic 6- π Photocyclization and Efficient On-Demand Heat Release with Oxidation Stimuli, *J. Phys. Chem. Lett.*, 2021, **12**, 11391–11398.
- 53 G. Jones, T. E. Reinhardt and W. R. Bergmark, Photon energy storage in organic materials—The case of linked anthracenes, *Sol. Energy*, 1978, **20**, 241–248.
- 54 P. Lorenz, F. Wullschläger, A. Rüter, B. Meyer and A. Hirsch, Tunable Photoswitching in Norbornadiene (NBD)/Quadricyclane (QC) – Fullerene Hybrids, *Chem. – Eur. J.*, 2021, **27**, 14501–14507.
- 55 N. Ree and K. V. Mikkelsen, Benchmark study on the optical and thermochemical properties of the norbornadiene-quadricyclane photoswitch, *Chem. Phys. Lett.*, 2021, **779**, 138665.
- 56 A. E. Hillers-Bendtsen, F. Ø. Kjeldal, N. M. Høyer and K. V. Mikkelsen, Optimization of the thermochemical properties of the norbornadiene/quadricyclane photochromic couple for solar energy storage using nanoparticles, *Phys. Chem. Chem. Phys.*, 2022, **24**, 5506–5521.
- 57 R. Szabo, K. N. Le and T. Kowalczyk, Multifactor theoretical modeling of solar thermal fuels built on azobenzene and norbornadiene scaffolds, *Sustainable Energy Fuels*, 2021, **5**, 2335–2346.
- 58 A. E. Hillers-Bendtsen, J. L. Elholm, O. B. Obel, H. Hölzel, K. Moth-Poulsen and K. V. Mikkelsen, Searching the Chemical Space of Bicyclic Dienes for Molecular Solar Thermal Energy Storage Candidates, *Angew. Chem.*, 2023, e202309543.
- 59 A. A. Sangolkar, M. Faizan, K. R. Krishna and R. Pawar, Azabicyclooctadiene/tetracyclooctane couples as promising photoswitches for molecular solar thermal energy storage applications, *Mol. Syst. Des. Eng.*, 2023, **8**, 853–865.
- 60 P. R. Rablen, A Procedure for Computing Hydrocarbon Strain Energies Using Computational Group Equivalents, with Application to 66 Molecules, *Chemistry*, 2020, **2**, 347–360.
- 61 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai,



- T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16, Revision C.01*, 2016.
- 62 P. Giannozzi, O. Baseggio, P. Bonfà, D. Brunato, R. Car, I. Carnimeo, C. Cavazzoni, S. de Gironcoli, P. Delugas, F. Ferrari Ruffino, A. Ferretti, N. Marzari, I. Timrov, A. Urru and S. Baroni, Quantum ESPRESSO toward the exascale, *J. Chem. Phys.*, 2020, **152**, 154105.
- 63 F. Neese, Software update: the ORCA program system, version 4.0, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2018, **8**, e1327.
- 64 X. An and Y. Xie, Enthalpy of isomerization of quadricyclane to norbornadiene, *Thermochim. Acta*, 1993, **220**, 17–25.
- 65 V. Gray, A. Lennartson, P. Ratanalert, K. Börjesson and K. Moth-Poulsen, Diaryl-substituted norbornadienes with red-shifted absorption for molecular solar thermal energy storage, *Chem. Commun.*, 2014, **50**, 5330–5332.
- 66 E. Vessally, Maximizing the Solar Energy Storage of the Norbornadiene-Quadricyclane System: Mono-Heteroatom Effect by DFT Calculations, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2009, **184**, 2307–2313.

