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Prospects of Improving Molecular Solar Energy Storage of the Norbornadiene/Quadricyclane System through Bridgehead Modifications†

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Abstract

We have investigated novel bicyclic diene molecular solar thermal energy storage systems that presently are the ones with the highest predicted energy density. Using a variety of different ab initio quantum chemical methods, we report storage energies, absorption spectra, and reaction barriers for the release of stored energy for a series of bicyclic dienes. The bicyclic dienes are all constructed by modifying the bridgehead of the well known norbornadiene/quadricyclane system. In conclusion, we find it promising that it is possible to significantly amplify the storage energy of the norbornadiene/quadricyclane system without seriously compromising other crucial properties by introducing simple modifications to the bridgehead.

Introduction

Molecular solar thermal energy storage (MOST) systems have become a popular area of research as efficient exploitation of solar energy can at least partially facilitate the transition to renewable energy sources. MOST systems rely on utilization of molecular photoswitches that can undergo reversible chemical transformations to a metastable photoproduct.1–14

The higher energy photoproduct stores energy in chemical bonds until a reaction back to the initial form takes place either through thermal, electrochemical, or catalytic activation during which the stored energy is released as heat. Several different molecular motifs have been studied as potential MOST candidates including anthracene,15 tetracarbonyl-fulvalenediruthenium,16,17 azobenzenes,18–20 the dihydroazulene/vinylheptafulvene photochromic couple,21–24 and the norbornadiene/quadricyclane (NBD/QC) system.25–29

In the past, the properties of the molecular systems mentioned above in MOST solutions have improved significantly. These improvements have mainly been facilitated by exploring different substitution patterns of the studied systems. The UV-Vis absorptions of e.g. azobenzene, NBD/QC, and DHA/VHF systems have been redshifted significantly by adding substituents that increase the conjugation length of the system or by introduction of
donor/acceptor functionalization.\textsuperscript{30–35} These efforts have provided great absorption overlaps with the solar spectrum. In addition to that, the thermal stabilities of the formed photoproducts have been engineered to feature storage times that range from a few seconds to years, which provides great tunability for specific applications.\textsuperscript{23,27,36–40} Yet, earlier studies that focused on the increase of the storage densities for the azobenzene, NBD/QC, and DHA/VHF systems have found that it is difficult to increase the storage energy without compromising the storage time.\textsuperscript{29,41–43} For a comprehensive review on MOST systems, we refer to the very recent review of Moth-Poulsen et. al.\textsuperscript{44} It is, however, clear that the development of MOST systems based on the above systems centers around discovering the perfect balance between different properties.

The applicability of the NBD/QC system relies upon the ability of the NBD as a bicyclic diene to undergo a photoinduced intramolecular [2,2]-cycloaddition (See Fig. 1) and it has been shown to be one the best performing motifs for MOST systems as it features a high storage energy density of 0.97 MJ/kg for the unsubstituted system\textsuperscript{29} due to its low molecular weight. Furthermore, the systems have relatively long thermal back reaction times. However, we have recently reported that the storage energy can be significantly increased by altering the bridging unit of the NBD/QC system, a line of thought which we will expand upon here.\textsuperscript{45,46}

In the current investigation, we report the theoretical prospects of modifying the bridging unit in the NBD/QC system in order to possibly improve on three crucial parameters of MOST systems: storage energy density, thermal back reaction barrier, and UV-Vis absorption properties. More specifically, we focus on scrutinizing the effects by elongating the bridging unit and on introducing hetero atoms. Our recent theoretical and experimental investigations have shown that elongating the bridge by a single carbon atom to obtain bicyclocloctadiene (BOD) resulted in a two- to threefold increase in the storage energy density of the system.\textsuperscript{45,46} This increase in storage energy is likely to be caused by increased strain in the ring systems of the tetracyclooctane (TCO) photoproduct for which the bridging unit,
contrary to the BOD, adopts a staggered conformation. The increased storage energy comes without compromising the linear optical properties, yet, the thermal back reaction barriers were significantly reduced relative to the NBD/QC analogs. Herein, we consider the systems shown in Fig. 1, where the bridging unit is either elongated by two or three carbon atoms or modified by introducing hetero atoms. We then go on to compare the MOST properties of these systems to those of the NBD/QC and BOD/TCO systems. Finally, we also present results for the side-substituted sub-NBD/sub-QC and sub-BOD/sub-TCO systems in Fig. 2. Thereby, we show that the introduction of substituents that have previously been used to redshift the absorption of NBD does not eliminate the gain in storage energy obtained through bridgehead modification.

Figure 1: The structures and relevant reactions schemes for a MOST application of the studied bicyclic diene systems including the NBD/QC system and derivatives thereof in which the bridging unit has been modified.
Figure 2: The structures and relevant reaction schemes for the sub-NBD/sub-QC and sub-BOD/sub-TCO systems.

**Thermochemical properties**

The storage energies of the different MOST systems are determined from molecular structures that are initially optimized using density functional theory (DFT) at the M06-2X/6-311++G(d,p) level of theory. This methodology is chosen as earlier studies have shown good performance for both NBD/QC and BOD/TCO systems. Subsequently, we refine the electronic energy of the determined structures using the newly developed cluster perturbation theory CPS(D-4) model, which provides energies of CCSD quality at a low cost, while we utilize the vibrational and entropic energy contributions of the DFT calculations. The resulting storage energies are given in Table 1. It is clearly evident that the theoretically predicted storage energies are increased quite significantly for all of the studied motifs compared to the NBD/QC system. Yet, only the systems that feature a bridge length of four atoms display potential storage energies that are larger than those observed for the BOD/TCO system. Meanwhile, the introduction of an oxygen or nitrogen atom in the bridging units only has minor effects on the predicted storage energies of both the BND/TCN and BDD/TCD motifs, where small decreases are seen. Thereby, the results indicate that the storage energy of the NBD/QC system can possibly be dramatically increased by engineering
the bridging unit of the system. Lastly, we note that the introduction of side substituents does not alter the energy difference between the NBD and QC or between the BOD and TCO molecules. However, given that the sub-NBD/sub-QC and sub-BOD/sub-TCO systems have a higher molecular weight, the storage densities of the systems are significantly lower. Nevertheless, we still see that the sub-BOD/sub-TCO system has a significantly higher storage density than that of the sub-NBD/sub-QC system thus indicating that the increased storage energy obtained through the bridgehead modification is not lost as substituents are introduced. Yet, the above observations are of little value if the barrier for the thermal back reaction decreases to the same extent that the storage energy increases.

Table 1: Thermochemical data for all of the studied systems. Reaction barriers are extracted from the (8,8)-CASPT2/6-311++G(d,p) calculations on the structures from the NEB reactions paths, where the vibrational and entropic energy contributions from M06-2X/6-311++G(d,p) are added. All numbers are determined at 298.15 K.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta G_{\text{Storage}}$ [kJ/mol]</th>
<th>$\Delta G_{SD}$ [MJ/kg]</th>
<th>$\Delta G_{TBR}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBD/QC</td>
<td>96.3</td>
<td>1.05</td>
<td>124.1</td>
</tr>
<tr>
<td>BOD/TCO</td>
<td>192.8</td>
<td>1.82</td>
<td>118.1</td>
</tr>
<tr>
<td>BND/TCN</td>
<td>223.0</td>
<td>1.86</td>
<td>87.9</td>
</tr>
<tr>
<td>ABND/ATCN</td>
<td>220.5</td>
<td>1.84</td>
<td>91.71</td>
</tr>
<tr>
<td>OBND/OTCN</td>
<td>213.7</td>
<td>1.78</td>
<td>89.59</td>
</tr>
<tr>
<td>BDD/TCD</td>
<td>305.8</td>
<td>2.50</td>
<td>119.9</td>
</tr>
<tr>
<td>ABDD/ATCD</td>
<td>302.6</td>
<td>2.46</td>
<td>120.85</td>
</tr>
<tr>
<td>OBDD/OTCD</td>
<td>292.4</td>
<td>2.35</td>
<td>57.82</td>
</tr>
<tr>
<td>sub-NBD/sub-QC</td>
<td>101.6</td>
<td>0.48</td>
<td>208.06</td>
</tr>
<tr>
<td>sub-BOD/sub-TCO</td>
<td>185.2</td>
<td>0.82</td>
<td>180.55</td>
</tr>
</tbody>
</table>

We thus explored the minimum energy reaction path of the thermal back reaction of the different systems based on the strategy outlined in a previous study by Kuisma et al. on NBD/QC systems.\textsuperscript{41} The strategy involves utilizing the climbing image Nudged Elastic Band (NEB) method\textsuperscript{52} as implemented in the atomic simulation environment\textsuperscript{53} using DFT-PBE with a finite Fermi temperature as implemented in GPAW\textsuperscript{54} to obtain forces. Due to the large multi-reference character of the biradical transitions states of NBD/QC systems we utilized the (8,8)-CASPT2\textsuperscript{55–57} method in combination with the 6-311++G(d,p) basis set as
implemented in the Molpro program\textsuperscript{58–60} for calculating the electronic energy of each NEB image. In the SI, we have also given the similar minimum energy reaction paths for all of the systems using the DFT-PBE method with which the NEB path was determined (See Fig. S1). Those calculations all result in much larger thermal back reaction barriers than those obtained utilizing multireference methods which highlights that the biradical character of the NBD/QC transition state is also present for the modified systems. The minimum energy reaction paths obtained using CASPT2 are displayed in Fig. 3 along with the relative bond length of the two bonds that are broken during the reactions. In Table 1, we have also given the thermal back reaction barriers that are extracted from the CASPT2 minimum energy reaction path with the thermal and entropic contributions from M06-2X/6-311++G(d,p) added.

From the results displayed in Fig. 3 and Table 1, we observe that especially the trajectories obtained for the thermal back reaction barriers are in general lower for the compounds with a modified bridging unit than that of NBD/QC. Especially the BND/TCN, ABND/ATCN, and OBDD/OTCD compounds, for which the predicted storage energy was rather large, have very low barriers. These correspond to half lives in the range of seconds to a few minutes at room temperature, using the Eyring equation. On the other hand, the utilized methodology also predicts that the BOD/TCO, BDD/TCD, and ABDD/ATCD compounds have similar thermal back reaction barriers compared to NBD/QC. Combining this with their significantly larger predicted storage energies clearly shows that they could be new systems for MOST applications given that they can be synthesized with suitable substituents. The sub-NBD/sub-QC and sub-BOD/sub-TCO systems both show significantly larger thermal back reaction barriers than those of the unsubstituted analogous. Moreover, both the the sub-NBD/sub-QC and sub-BOD/sub-TCO systems show significant asymmetry in the breaking of the two bonds which is most likely a result of the substituents. We note that the OBDD/OTCD system likewise shows a significant asymmetry in the bond breaking, though without the increase in thermal back reaction barrier. Overall, the calculated back
Figure 3: Top-left: Minimum energy reactions paths for the thermal back reaction of the studied compounds obtained from (8,8)-CASPT2/6-311++G(d,p) calculations on the NEB trajectory given by the points. A spline function has been utilized for connecting the points. Top-right: A zoom in on the TS area of the minimum energy reaction paths. Bottom-left: The relative bond length of the two bonds that are broken during the reactions. Bottom-right: The relative bond length of the two bonds that are broken during the reactions excluding OBDD/OTCD, BND/TCN and the two substituted systems.
reaction barriers suggests that one can significantly improve the MOST properties of the NBD/QC motif by engineering the bridging unit, since the storage energies are much larger than those of NBD/QC while the back reaction barriers are still large enough for some of the studied systems. Also, the introduction of substituents increases the back reaction barrier for the sub-BOD/sub-TCO system and this shows once more that bridgehead modifications do not seem to degrade other MOST properties as the storage energy is increased.

Optical properties

Finally, we computed the absorption spectra of all the systems utilizing the resolution-of-identity-CC2 model\textsuperscript{61} as implemented in LSDalton\textsuperscript{62} in combination with the 6-311++G(d,p) basis set and the structures resulting from the DFT optimizations. The spectra were simulated by convoluting the 15 lowest vertical excitation energies and associated oscillator strengths to Lorentzians using a full width half maximum of 0.4 eV. It is critical for the

![Figure 4: Simulated UV-Vis spectra of the studied unsubstituted MOST candidates.](image-url)
application of MOST systems that the utilized systems absorb sunlight, which has been one of the main challenges concerning the NBD/QC system. If we inspect the resulting UV-Vis spectra for the unsubstituted compounds in Fig. 4 and the first important excitation energies in Table 2 for the reactant form of the investigated MOST systems, then it is clear that the modification of the bridging unit does not lead to redshifts of the NBD absorption into the solar spectrum. Yet, it is noteworthy that the absorption cross section is significantly increased for the BND, BDD, ABDD, and OBDD systems compared to that of NBD and BOD. Furthermore, we note that significant redshifts occur when comparing first absorption maximum of the studied systems to those of NBD and BOD. The most significant redshifts occur for the ABND and ABDD systems where an amine has been introduced in the bridging unit. Combining these observations with the success with which the NBD absorption has been redshifted in earlier studies and as seen in Fig. 5 for the substituted systems, it is very likely that the studied systems can also be tuned to absorb sunlight. Furthermore, we have depicted the absorption of the photoproducts in Fig. 4 and given data on the first excitation energy with an oscillator strength above 0.01 in Table 2 given that the absorption of the reactants and photoproducts should overlap as little as possible to ensure efficient conversion. In general, the spectra in Fig. 4 show similar trends with respect to bridge modifications as those in Fig. 4. Comparison of the spectra and inspection of Table 2 does, however, reveal that the spectral overlaps of the modified systems are not entirely minimized compared to the NBD/QC and BOD/TCO photochromic couples although especially the BDD/TCD system has absorption with decent separation. Therebe, one would risk reaching a photostationary state rather than achieving full conversion if the photoproduct is reactive following excitation. Although the spectral overlap does not seem promising, it is still important to point out that this issue has been overcome for the NBD/QC systems and that the experiences gained from the study of these systems will most likely be convenient for the tuning of systems with modified bridging units. This point is also evident is we inspect Fig. 5 and the data for the substituted systems in Table 2, where it is evident that side
substitution can significantly redshift and increase the absorption of not only NBD but also BOD. Furthermore, the same redshift is not observed for the QC and TCO forms relative to the NBD and BOD forms, meaning that lower spectral overlap is achieved simultaneously. We therefore find strong indications that side substitution can be used to tune the MOST properties of the systems with a modified bridgehead without seriously compromising either the storage energy, the thermal back reaction barrier, or the optical properties.

Table 2: The first excitation energy and associated oscillator strength of the studied compounds, where the oscillator strength surpasses 0.01.

<table>
<thead>
<tr>
<th>System</th>
<th>$\lambda_{\text{reactant}}$ [nm]</th>
<th>$f_{\text{reactant}}$</th>
<th>$\lambda_{\text{photoproduct}}$ [nm]</th>
<th>$f_{\text{photoproduct}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBD/QC</td>
<td>213.65</td>
<td>0.0166</td>
<td>190.74</td>
<td>0.0185</td>
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<tr>
<td>BOD/TCO</td>
<td>196.44</td>
<td>0.0408</td>
<td>204.92</td>
<td>0.0273</td>
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<tr>
<td>BND/TCN</td>
<td>206.67</td>
<td>0.0225</td>
<td>208.46</td>
<td>0.0249</td>
</tr>
<tr>
<td>ABND/ATCN</td>
<td>250.44</td>
<td>0.0243</td>
<td>223.07</td>
<td>0.0134</td>
</tr>
<tr>
<td>OBND/OTCN</td>
<td>216.45</td>
<td>0.0490</td>
<td>204.87</td>
<td>0.0171</td>
</tr>
<tr>
<td>BDD/TCD</td>
<td>207.66</td>
<td>0.0210</td>
<td>210.97</td>
<td>0.0341</td>
</tr>
<tr>
<td>ABDD/ATCD</td>
<td>239.98</td>
<td>0.0417</td>
<td>219.63</td>
<td>0.0185</td>
</tr>
<tr>
<td>OBDD/OTCD</td>
<td>211.98</td>
<td>0.0255</td>
<td>209.74</td>
<td>0.0228</td>
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<td>sub-NBD/sub-QC</td>
<td>271.17</td>
<td>0.2187</td>
<td>246.81</td>
<td>0.0234</td>
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<td>sub-BOD/sub-TCO</td>
<td>255.38</td>
<td>0.1140</td>
<td>245.55</td>
<td>0.0362</td>
</tr>
</tbody>
</table>

Conclusion

Overall, we have given a computational evaluation of the prospects of utilizing bicyclic dienes for MOST applications. The study is facilitated by a comparison to the well known and intensely studied NBD/QC system as well as the newly proposed BOD/TCO system. Our results and the two recent studies on BOD/TCO systems display the potential of significantly improving the MOST properties of the NBD/QC system by modifying the bridging unit of the system. Especially, the potential storage energy that can be significantly improved using the modified motifs given that a significant amount of ring strain can be introduced in the photoproduct. Our results indicate that this can be done with increased absorption and without seriously compromising the storage time. We also found that these trends hold
Figure 5: Simulated UV-Vis spectra of the substituted NBD/QC and BOD/TCO candidates.
for the BOD/TCO system when side substitution is introduced. Our results show that bridgehead modification of the NBD/QC motif potentially paves the way for the exploration of completely novel photoswitches that provide vastly improved MOST properties compared to existing candidates.

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Notes

The authors have no known financial or personal interest, which could have influenced this work, to declare.

Supporting Information Available

Geometry optimized structures using M06-2X/6-311++G(d,p) given in XYZ-coordinates, RI-CC2 excitation energies and associated oscillator strengths, and DFT-PBE nudged elastic band minimum energy reaction pathways.

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Better MOST Properties?