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# Modulating the thermal isomerization barriers of quadricyclane to norbornadiene through cross-conjugative patterns

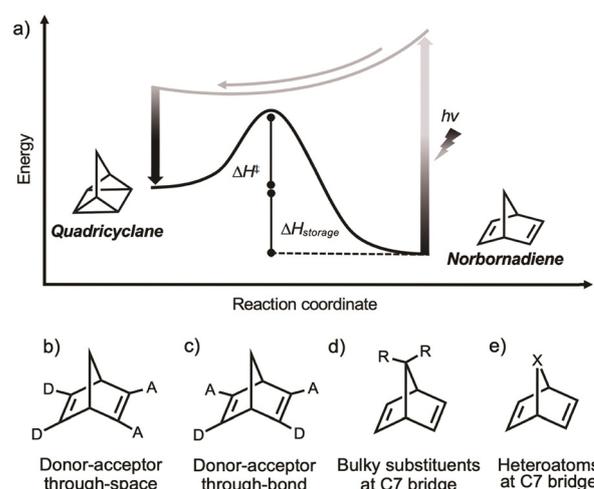
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**Computations show that thermal isomerizations of quadricyclane to norbornadiene can be modulated by heteroarene substitution. Heteroarenes that are non-cross-conjugated to the norbornadiene double bond increase delocalization of the transition state structure and lower the thermal activation enthalpy ( $\Delta H^\ddagger$ ), while cross-conjugated analogs increase  $\Delta H^\ddagger$  without significantly impacting the storage enthalpy ( $\Delta H_{\text{storage}}$ ).**

Molecular solar thermal energy storage (MOST) systems are photoswitchable molecules that store solar energy by converting light into chemical energy.<sup>1</sup> These systems typically exist as pairs of isomers that can reversibly convert through light-induced bond cleavage, bond rotation, or conformational changes. Common MOST frameworks include the *E/Z*-azobenzenes,<sup>2,3</sup> dihydroazulene–vinylheptafulvene,<sup>4–6</sup> dimetal fulvalene complexes,<sup>7,8</sup> and notably, the norbornadiene–quadricyclane (NBD–QC) pair.<sup>9,10</sup> A schematic illustration of the NBD–QC pair functioning as a MOST system is shown in Fig. 1a. Upon photoexcitation, NBD converts to the metastable QC. The energy difference of the two is the stored energy ( $\Delta H_{\text{storage}}$ ), which can then be released spontaneously or by external stimuli (*e.g.*, heat, light,<sup>2,3</sup> or electric potential<sup>11,12</sup>) through a thermal back reaction barrier ( $\Delta H^\ddagger$ ). Thermal relaxation of QC to NBD proceeds *via* a concerted, asynchronous, retro-[2+2] cycloaddition, and the transition state structure exhibits high diradical character.<sup>13–15</sup> Efficient MOST systems must meet several criteria: (I) absorption within the solar window; (II) a high photoisomerization quantum yield; (III) a high energy density; (IV) a high energy storage, and (V) a long thermal half-life for the metastable isomer (*i.e.*, a suitable thermal back reaction barrier,  $\Delta H^\ddagger$ ).<sup>9,16</sup> These features can be modified through structural designs of the MOST framework, but often, improving some criteria comes at the expense of others.

Norbornadiene stands out among common MOST systems for its low molecular weight and high energy density ( $0.97 \text{ MJ kg}^{-1}$ ),<sup>17</sup> but its absorption maximum lies outside of the solar window.<sup>18</sup>

Structural modifications of NBD–QC have been explored to improve performance, for example, by placing donor (D) and acceptor (A) pairs through-space,<sup>16</sup> (Fig. 1b) or through-bond<sup>19</sup> (Fig. 1c), placing bulky substituents at the C7 bridge, (Fig. 1d)<sup>20</sup> or by heteroatom substitution (Fig. 1e).<sup>21</sup> One way to red-shift the absorption maxima is by tethering conjugated units to NBD, but this increases the molecular weight and reduces the energy storage per unit mass.<sup>20</sup> It was found that bulky groups at the C7 bridge could introduce steric stress, improving the quantum yield and increasing the thermal life-time of QC, although storage energy decreases modestly.<sup>20</sup> Enhanced storage enthalpies,  $\Delta H_{\text{storage}}$ ,<sup>22</sup> and red-shifted absorptions<sup>17</sup> often correlate with reduced thermal isomerization barriers,  $\Delta H^\ddagger$ . Computational screening identified candidates with improved red-shift absorptions, storage capacity, and thermal half-lives.<sup>23,24</sup> Yet, strategies to maximize storage



**Fig. 1** (a) Schematic illustration of the photoisomerization of norbornadiene (NBD) and quadricyclane (QC). NBD motifs with donor (D) and acceptor (A) groups (b) through-space or (c) through-bond, and with modified C7 bridges by (d) alkyl (R) groups or (e) heteroatom (X = O or NH) substitution.

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**Table 1** Computed activation enthalpies ( $\Delta H^\ddagger$ ), storage enthalpies ( $\Delta H_{\text{storage}}$ ), averaged absolute spin density values at the C3/C5 positions ( $|\delta_{\text{avg}}|$ ) of the TS structure, absorption maxima ( $\lambda_{\text{max}}$ , nm), and absorption intensity at  $\lambda_{\text{max}}$  ( $f$ ). All energies are in kcal mol<sup>-1</sup>

	$ \delta_{\text{avg}} $	$\Delta H^\ddagger$	$\Delta H_{\text{storage}}$	QC $\lambda_{\text{max}}$	NBD $\lambda_{\text{max}}$	NBD $f_{\text{max}}$
Parent	0.84	31.1	-20.9	185.7	246.5	0.000
<b>1NH'</b>	0.67	19.4	-28.7	248.8	333.5	0.272
<b>1O'</b>	0.65	19.2	-25.7	241.3	334.4	0.254
<b>1S'</b>	0.65	20.1 <sup>a</sup>	-25.0	253.1	337.5	0.245
<b>3NH'</b>	0.71	22.6	-26.8	236.2	321.3	0.144
<b>3O'</b>	0.70	22.8	-24.9	226.6	317.9	0.103
<b>3S'</b>	0.70	22.5 <sup>a</sup>	-24.6	238.4	325.2	0.151
<b>1NH</b>	0.52	9.7	-34.6	307.1	409.1	0.040
<b>1O</b>	0.49	7.1	-33.3	287.6	394.4	0.041
<b>1S</b>	0.50	8.2	-31.7	294.9	402.4	0.035
<b>2NH</b>	0.56	11.0	-35.8	292.9	386.3	0.042
<b>2O</b>	0.54	10.9	-32.3	283.5	381.8	0.040
<b>2S</b>	0.54	12.7	-30.9	272.6	385.6	0.031
<b>3NH</b>	0.60	14.0	-34.1	284.3	372.1	0.023
<b>3O</b>	0.59	14.7	-31.2	264.4	359.5	0.012
<b>3S</b>	0.58	14.9	-30.2	369.6	369.6	0.025
<b>4p</b>	0.68	22.4	-23.1	335.5	335.5	0.214
<b>4m</b>	0.70	23.3	-23.2	324.7	324.7	0.120
<b>5p</b>	0.67	22.3 <sup>a</sup>	-22.8	352.3	352.3	0.218
<b>5m</b>	0.70	23.2 <sup>a</sup>	-23.2	346.3	346.3	0.030
<b>6p</b>	0.70	23.0	-25.0	325.2	325.2	0.273
<b>6m</b>	0.70	23.4	-23.6	323.9	323.9	0.146
<b>7p</b>	0.69	22.3	-25.5	337.8	337.8	0.378
<b>7m</b>	0.70	23.2	-24.1	353.0	353.0	0.067
<b>8p</b>	0.68	22.2 <sup>a</sup>	-25.8	354.0	354.0	0.499
<b>8m</b>	0.70	23.5	-24.2	395.1	395.1	0.036
<b>9</b>	0.70	23.2 <sup>a</sup>	-23.9	241.7	317.3	0.171

<sup>a</sup> Experimental  $\Delta H^\ddagger$  values (in kcal mol<sup>-1</sup>) for **1S'** (22.8), **3S'** (25.8), **5p** (24.1), **5m** (28.0), **8p** (26.4), **9** (26.8) were derived from the Eyring equation, based on measurements at 25 °C in toluene.<sup>22,25</sup>

Direct comparisons of pairs of cross-conjugated *vs.* non-cross-conjugated species show that  $\pi$ -conjugation patterns can largely affect electron delocalization of the QC  $\rightarrow$  NBD TS structure (Table 1). Consistent with the schematic illustration shown in Fig. 2b,  $|\delta_{\text{avg}}|$  values for the non-cross-conjugated TS structures, **1NH'** (0.67), **1O'** (0.65), **1S'** (0.65), are smaller than those of the cross-conjugated isomers, **3NH'** (0.71), **3O'** (0.70), **3S'** (0.70), indicating increased delocalization in **1NH'**, **1O'**, **1S'**. At the TS structure, non-cross-conjugated species exhibit more delocalization (*i.e.*, less spin at C3 and C5, *cf.* Fig. 2b, top, in purple), while cross-conjugated species display less delocalization (*i.e.*, more spin at C3 and C5, *cf.* Fig. 2b, bottom, in orange). Accordingly, computed  $\Delta H^\ddagger$  barriers for the non-cross-conjugated, **1NH'** (19.4 kcal mol<sup>-1</sup>), **1O'** (19.2), **1S'** (20.1), are lower compared to those of their cross-conjugated isomers, **3NH'** (22.6), **3O'** (22.8), **3S'** (22.5). Increased thermal stability of QC (*i.e.*, a larger  $\Delta H^\ddagger$ ) correlates with a decreased storage enthalpy (*i.e.*, a less negative  $\Delta H_{\text{storage}}$ ).<sup>20,28,29</sup> Thus, the computed  $\Delta H_{\text{storage}}$  values for **1NH'** (-28.7 kcal mol<sup>-1</sup>), **1O'** (-25.7), and **1S'** (-25.0), are more exothermic than that of **3NH'** (-26.8), **3O'** (-24.9), and **3S'** (-24.6). Nevertheless, we note that a meaningful increase in  $\Delta\Delta H^\ddagger$  (3.2, 3.6, 2.4 kcal mol<sup>-1</sup>, respectively, for **1NH'** *vs.* **3NH'**, **1O'** *vs.* **3O'**, and **1S'** *vs.* **3S'**) only is accompanied by a comparably small change in  $\Delta\Delta H_{\text{storage}}$  (1.9, 0.8, 0.4 kcal mol<sup>-1</sup>, respectively, for **1NH'** *vs.* **3NH'**, **1O'** *vs.* **3O'**, and **1S'** *vs.* **3S'**). These results suggest that it is possible to modulate  $\Delta H^\ddagger$  without significantly compromising  $\Delta H_{\text{storage}}$ .<sup>20</sup>

NBD frameworks containing two sets of through-bond donor-acceptor pairs (**1**, **2**, and **3**, X = NH, O, S) display even more pronounced spin delocalization and barrier lowering effects. Isomers with two non-cross-conjugated heteroarenes tethered to the double bonds of NBD, **1** (X = NH, O, S), have largely delocalized unpaired electrons at the TS structure. This is followed by isomers with a mixed conjugative pattern, **2** (X = NH, O, S). Isomers with two cross-conjugated heteroarenes tethered to the double bonds of NBD, **3** (X = NH, O, S), display the least delocalized unpaired electrons at the TS structure. Indeed, computed  $|\delta_{\text{avg}}|$  values for the non-cross-conjugated: **1NH** (0.52), **1O** (0.49), **1S** (0.50), are smaller than those computed for isomers of the mixed set: **2NH** (0.56), **2O** (0.54), **2S** (0.54), while values for the cross-conjugated isomers: **3NH** (0.60), **3O** (0.59), **3S** (0.58) are the highest, indicating decreased delocalization of the unpaired electrons (Table 1). Notably, computed  $\Delta H^\ddagger$  barriers for **1NH** (9.7 kcal mol<sup>-1</sup>), **1O** (7.1), **1S** (8.2) are lower than that computed for the mixed set: **2NH** (11.0), **2O** (10.9), **2S** (12.7), while the cross-conjugated isomers, **3NH** (14.0), **3O** (14.7), **3S** (14.9), display the highest  $\Delta H^\ddagger$  barriers. By comparing examples from the two extreme cases, **1** *vs.* **3**, we note again that a meaningful increase in  $\Delta\Delta H^\ddagger$  (4.3, 7.6, and 6.7 kcal mol<sup>-1</sup>, respectively, for **1NH** *vs.* **3NH**, **1O** *vs.* **3O**, and **1S** *vs.* **3S**) only is accompanied by a small decrease in  $\Delta\Delta H_{\text{storage}}$  (0.5, 2.1, 1.5 kcal mol<sup>-1</sup>, respectively, for **1NH** *vs.* **3NH**, **1O** *vs.* **3O**, and **1S** *vs.* **3S**).

Computed activation enthalpies ( $\Delta H^\ddagger$ ), storage enthalpies ( $\Delta H_{\text{storage}}$ ), and  $|\delta_{\text{avg}}|$  values for the 2-cyano-3-phenyl-NBD derivatives support that stabilizing the unpaired electrons at the *para*-positions of the phenyl group lower  $\Delta H^\ddagger$ . *Para*-substituted analogs enable more efficient delocalization from the NBD core to the phenyl ring, and therefore display consistently lower  $|\delta_{\text{avg}}|$  values than the parent **9** (0.70) and the *meta*-substituted analogs: **4p** (0.68) < **4m** (0.70), **5p** (0.67) < **5m** (0.70), **6p** (0.70)  $\approx$  **6m** (0.70), **7p** (0.69) < **7m** (0.70), and **8p** (0.68) < **8m** (0.70). Accordingly, the computed  $\Delta H^\ddagger$  barriers are lower for the *para*-isomers than for **9** (23.2 kcal mol<sup>-1</sup>) and the *meta*-isomers: **4p** (22.4) < **4m** (23.3), **5p** (22.3) < **5m** (23.2), **6p** (23.0) < **6m** (23.4), **7p** (22.3) < **7m** (23.2), and **8p** (22.2) < **8m** (23.5).

Finally, an effective MOST system also must absorb within the solar spectrum (*i.e.*, between 300 to 700 nm). However, strategies that red-shift the absorption of NBD often also red-shift that of QC, which compromises the efficiency of photoconversion. As shown in Table 1, all of the NBD derivatives have absorption maxima at regions above 300 nm, while those the QC derivatives absorb at regions near or below 300 nm. We note that the non-cross-conjugated species are modestly red-shifted compared to their cross-conjugated analogs, but the variations are small (less than 20 nm). This suggests that the choice of incorporating non-cross-conjugated *vs.* cross-conjugated motifs has a minor effect on the absorption wavelength of NBD-QC systems. Interestingly, computed UV spectra indicate that NBD species with non-cross-conjugated motifs generally exhibit stronger absorption intensities ( $f_{\text{max}}$ ) than those with cross-conjugated motifs. Similarly, within the 2-cyano-3-phenyl-NBD framework, *para*-substituted phenyl groups with  $\pi$ -donating or  $\pi$ -accepting substituents have higher absorption intensities compared to the *meta*-substituted



derivatives. Plots of  $\lambda_{\max}$  vs.  $\Delta H^\ddagger$  ( $R^2 = 0.691$ ) show some correlation between the maximum absorption wavelengths of the NBD structure and the activation enthalpies. Additional correlation plots are included to the SI Fig. S5.

An excellent correlation was found between computed  $|\delta_{\text{avg}}|$  values for the QC  $\rightarrow$  NBD TS structures vs. the thermal back reaction barriers ( $\Delta H^\ddagger$ ) for all investigated compounds ( $R^2 = 0.977$ , see data in SI). Yet, what do these calculations tell us about how to design effective MOST NBD–QC systems? The substituted NBD–QC systems investigated here meet several MOST criteria: they absorb within the solar window, exhibit high energy densities, and have meaningfully storage energies. A few structural features were identified as likely to prolong the thermal half-life of the QC  $\rightarrow$  NBD transformation, including heteroarenes with cross-conjugative relationships to the NBD double bond and *meta* substituted phenyl groups. These insights offer practical chemical handles for the design of NBD–QC-based MOST systems and may be extend to other MOST frameworks with thermal back reactions that proceed through transition states with pronounced diradicaloid character.

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## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5cc05209b>.

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