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Title: The Dewar isomer of 1,2-dihydro-1,2-azaborinines: Isolation, fragmentation, and energy storage

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The Dewar isomer of 1,2-dihydro-1,2-azaborinines: Isolation, fragmentation, and energy storage.

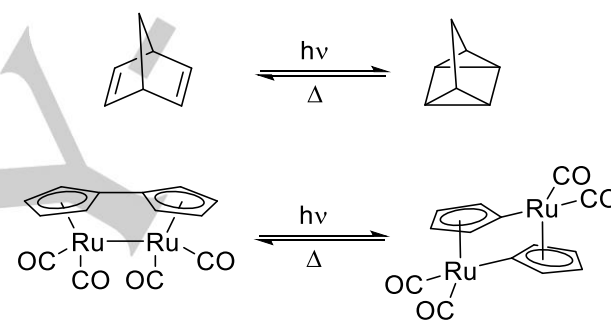
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Abstract: The photochemistry of 1,2-dihydro-1,2-azaborinine derivatives was studied under matrix isolation conditions and in solution. Photoisomerization occurs exclusively to the Dewar valence isomers upon irradiation with UV light (> 280 nm) with high quantum yield (46 %). Further photolysis with UV light (254 nm) results in the formation of cyclobutadiene and iminoborane. The thermal electrocyclic ring opening reaction of the Dewar valence isomer back to the 1,2-dihydro-1-*tert*-butyldimethylsilyl-2-mesityl-1,2-azaborinine has an activation barrier of 27.0 ± 1.2 kcal·mol⁻¹. In the presence of Wilkinson's catalyst, the ring opening occurs rapidly and exothermically ($\Delta H = -48 \pm 1$ kcal·mol⁻¹) at room temperature.

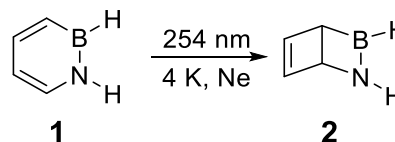
Solar energy as a renewable energy technology is an important part of the solution of the increasing world energy demand and limited fossil energy sources. The development of technologies for storing solar energy is however challenging. A promising technology is molecular solar thermal systems (MOST),^[1] where photons induce a photoisomerization to a high-energy species that has a sufficiently high activation barrier for the reversible reaction and releases thermal energy only on demand (e.g., in the presence of a catalyst). Beside E/Z isomerizations of CC or NN double bonds,^[2] and photodimerization of anthracene^[3] several valence isomer pairs like norbornadiene/quadracyclane,^[19-4] the fulvalene diruthenium system,^[5] and hexamethylbenzene (HMB) that undergoes a photoisomerization to hexamethyl Dewar benzene (HMDB) and hexamethylprismane,^[6] are considered as potential MOST systems (Scheme 1). Here we present a new valence isomer pair as a candidate for storing solar energy that is based on the photoisomerization of 1,2-dihydro-1,2-azaborinine **1** to its Dewar valence isomer **2**.

The replacement of two adjacent carbon atoms in benzene by the isoelectronic BN unit leads to 1,2-dihydro-1,2-azaborinines, heterocyclic compounds that have in common with benzene a considerable degree of aromaticity.^[7] The polarity of the BN unit modifies electronic properties^[8] and this heterocycle is therefore of interest in biomedical research^[9] and materials science.^[10] First

syntheses of substituted 1,2-dihydro-1,2-azaborinines were reported by Dewar^[11] and White^[12] in the 1960s. Further progress was made by Ashe,^[13] Perepichka,^[10] Yamaguchi^[10a], Liu^[7a, 14] and Braunschweig.^[10d, 15] Liu developed the first synthesis for the parent 1,2-dihydro-1,2-azaborinine (**1**).^[7a] The photochemistry of the 1,2-dihydro-1,2-azaborinine (**1**) under matrix isolation conditions was investigated by our group (Scheme 2).^[16] The irradiation of **1** isolated in a neon matrix with light of wavelength 254 nm shows full conversion exclusively to the Dewar isomer **2**.



Scheme 1. Valence isomer pairs studied in the context of energy storage.



Scheme 2. Photoisomerization of 1,2-dihydro-1,2-azaborinine to the Dewar valence isomer.

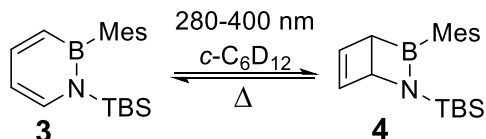
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We also explored the thermal ring opening reaction of **2** by computational chemistry techniques.^[17] Beside the classical conrotatory and disrotatory transition states, two further *stepwise* ring opening pathways were identified which were found to be lower in energy than the conrotatory ring opening. With an activation barrier of 22.2 kcal·mol⁻¹ [CCSD(T)/cc-pVQZ//CCSD(T)/TZ2P], the life time of **2** should be long enough to allow its detection in solution. It was also found computationally that the polarity of the BN unit would lead to very facile dimerization or oligomerization of **2**.^[17a]

Encouraged by the finding of a sizable barrier for thermal ring opening of **2**, we investigated the photochemistry of 1,2-dihydro-1,2-azaborinines in solution. We reasoned that oligomerization of the aminoborane moiety could be suppressed by kinetic stabilization through bulky substituents at B and N. Herein we report the photoconversion of 1,2-dihydro-1-*tert*-butyldimethylsilyl-2-mesityl-1,2-azaborinine^[10e] (**3**) to the

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corresponding Dewar valence isomer (**4**) in cyclohexane solution at room temperature (Scheme 3). To our surprise, **4** turns out to be stable for weeks at room temperature under inert conditions and reacts back to **3** only slowly.



Scheme 3. Photoisomerization of 1,2-dihydro-1-*tert*-butyldimethylsilyl-2-mesityl-1,2-azaborinine to the Dewar isomer.

We irradiated with 280-400 nm light a solution of **3** in deuterated cyclohexane ($c\text{-C}_6\text{D}_{12}$) in a J. Young quartz tube to follow the reaction progress by NMR spectroscopy. The NMR spectra show decreasing signals of **3** and new increasing signals of **4** without formation of any byproducts. After extended irradiation, full conversion to **4** was observed. The quantum yield of the transformation was determined to be 0.46 ± 0.08 (See Supporting Information for details). The NMR signals of **4** were unambiguously assigned through 2D NMR spectroscopy experiments and compared with DFT computations of chemical shifts at the B3LYP/6-311+G** level of theory (see Table S2 and S4). For example, the boron NMR shows a new signal at 52.9 ppm ($c\text{-C}_6\text{D}_{12}$) which is in accordance to the computed downfield shift of 13.0 ppm compared to the signal of **3** at 40.3 ppm ($c\text{-C}_6\text{D}_{12}$). The bridge head protons were observed at 3.00 ppm and at 4.75 ppm (Figure 1) as expected for nonaromatic methine protons and showed the corresponding coupling in the COSY NMR spectrum (see Figure S9). The two methyl groups of the TBS substituent are diastereotopic due to the adjacent bridgehead stereocenter.

The Dewar isomer **4** could be isolated after the photoreaction. The compound was obtained as a colorless oil in all attempted syntheses and it was not possible to grow crystals suitable for single crystal X-ray analysis despite a considerable number of attempts using various techniques including the crystalline sponge method^[18] and the *in situ* crystallization technique (see Figure S23 for a computed structure).

Further, we investigated the thermal ring opening of Dewar isomer **4** back to the starting material **3** by NMR spectroscopy. Due to the high thermal stability, deuterated 1,1,2,2-tetrachloroethane ($[D_2]TCE$) was chosen as solvent. The ^1H NMR spectrum only shows growth of signals due to **3**, without any formation of byproducts. The half-life at 100 °C is around 25 minutes. The kinetics of ring opening were studied by NMR in $[D_2]TCE$ over a rather narrow temperature range (358 – 373 K). An Arrhenius treatment of the first-order reaction data gave an activation energy E_a of 27.0 ± 1.2 kcal·mol⁻¹ and a preexponential factor of $\log A = 12.5 \pm 0.7$ s⁻¹.

The experimentally determined activation energy is much higher than the barrier computed previously for the ring opening of **2**.^[17a] As these data were obtained with coupled cluster theory, the "gold standard" of quantum chemistry, it is worthwhile to investigate the origin of the difference. As **4** is much too large for a computational treatment at the coupled cluster level, we have re-investigated the ring opening of **2** using density functional theory (DFT) at the B3LYP/6-311+G** level. Gratifyingly, the DFT results are in very good agreement with the computationally significantly more involved CCSD(T) method (see Table S10) reported earlier.^[17a] Hence, we investigated the ring opening of **4** at the B3LYP/6-311+G** level. In the presence of the bulky

substituents, the thermal ring opening reaction is no longer stepwise, but rather concerted with a strongly distorted transition state (see Fig. S24) as evidenced by computation of the intrinsic reaction coordinate. The lowest energy barrier of 26.1 kcal·mol⁻¹ obtained is in very good agreement with experiment and shows that the bulky substituents not only stabilize the Dewar isomer with respect to oligomerization, but also retard ring opening. This is most likely due to the increased steric repulsion of the adjacent bulky groups in the planar geometrical arrangement in **3** as the computed heat of reaction is lowered by more than 10 kcal·mol⁻¹ for the isomerization of **4** → **3** vs. **2** → **1** (see Table S10).

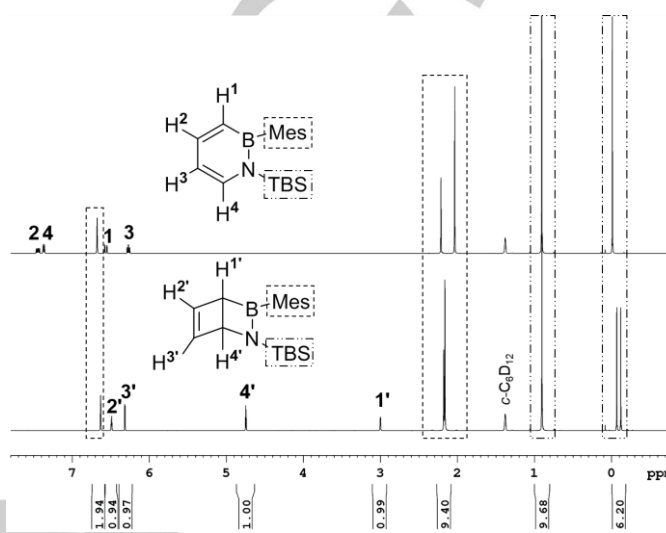


Figure 1. ^1H NMR spectra in $c\text{-C}_6\text{D}_{12}$ of 1,2-dihydro-1-*tert*-butyldimethylsilyl-2-mesityl-1,2-azaborinine (top trace) and of its Dewar valence isomer after irradiation with 280-400 nm light (bottom trace).

We also investigated the photochemistry of the related chloro derivative 1,2-dihydro-1-*tert*-butyldimethylsilyl-2-chloro-1,2-azaborinine (**5**) and found that it also undergoes photoisomerization in solution. The corresponding Dewar isomer **6** was also obtained as an oil that is however quite readily hydrolyzed by trace amounts of water. As **5** is a thermal precursor to BN-aryne studied by matrix isolation techniques,^[19] we also investigated its photochemistry in argon matrix. Photolysis of **5** with 280-400 nm irradiation quickly leads to the formation of the Dewar valence isomer based on comparison of experimental and computed IR spectra as the only photo product. UV spectra show disappearance of **5** due to photolysis with 280-400 nm and a formation of a new band at 215 nm (Figure S21) that can be assigned to **6** based on the behavior deduced by IR spectroscopy. A weak absorption ($S_0 \rightarrow S_1$) is computed for **6** at 216 nm ($f = 0.013$) at the TD-B3LYP/6-311+G** level of theory.

Irradiation of **5** with 254 nm light also quickly results in photoisomerization to **6**, but upon extended 254-nm-photolysis the Dewar isomer slowly undergoes cycloreversion to the corresponding iminoborane (**7**) and cyclobutadiene. The latter undergoes a further cycloreversion upon prolonged irradiation to two acetylene molecules (Scheme 4).^[20] The IR signals of **7** could be assigned by comparison with a computed spectra [B3LYP/6-311+G**] and show the natural ratio of the ^{10}B and ^{11}B isotopes (Figure S22).

We previously observed that the parent Dewar isomer **2** also undergoes a slow photodecomposition reaction, and hence re-investigated this in light of the results described above. Indeed, prolonged irradiation of the parent systems (both the B-H/N-H and

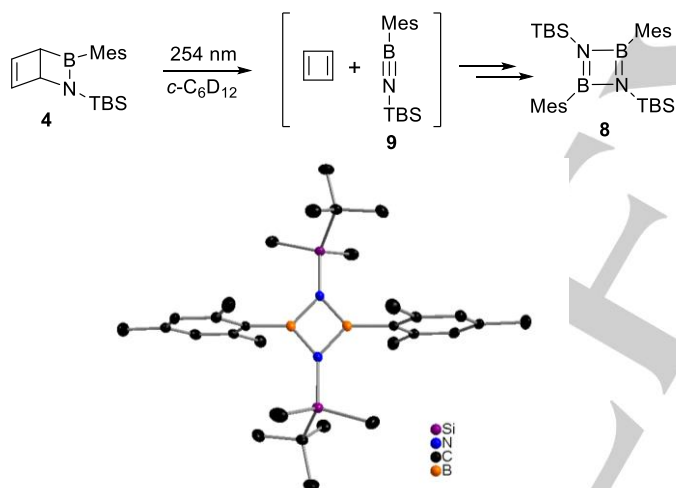
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B-D/N-D isotopologues were investigated) result in the formation of cyclobutadiene and acetylene. However, the corresponding parent iminoboranes HBNH and DBND cannot unambiguously be observed as the degree of photoisomerization and photodecomposition is lower for the parent system.



Scheme 4. Photochemistry of 1,2-dihydro-1-*tert*-butyl(dimethylsilyl)-2-chloro-1,2-azaborinine under matrix isolation conditions.

Motivated by the matrix isolation study, we explored the photochemistry of **4** in solution. The NMR spectra after irradiation with 254 nm light showed the disappearance of **4** and formation of new compounds. One of them is 1,3,2,4-diazadiboretidine **8** (Scheme 5) that is stable under conventional conditions and can be purified by column chromatography. A single crystal suitable for X-ray crystallography was obtained by slow evaporation of *n*-pentane (Scheme 5).^[21] The ¹¹B NMR shows a signal at 17.4 ppm after irradiation that is in the typical range of N-silyl substituted iminoboranes (16–22 ppm).^[21b, 22] The computed chemical shift of 17.2 ppm supports the assignment of the intermediate to iminoborane **9**. Other photo products could not be identified.



Scheme 5. Cycloreversion of the Dewar valence isomer of 1,2-dihydro-1-*tert*-butyl(dimethylsilyl)-2-mesityl-1,2-azaborinine leads to the formation of **8**.

This shows that 1,2-dihydro-1,2-azaborinines can undergo a stepwise photoinduced cycloreversion to the acetylene and iminoborane building blocks. The fragmentation discovered here is formally the reversion of azaborinine synthesis from iminoborane and acetylenes reported by Braunschweig et al.^[23]

Finally, we screened a variety of catalysts to promote the ring opening reaction at room temperature. In an initial survey of metal catalysts we found that Wilkinson's catalyst is uniquely effective, furnishing cleanly the 1,2-dihydro-1,2-azaborinine **3** from **4** in less than 1 hour at room temperature at 3 mol% catalyst loading (Table S11, entries 1–8 vs. entry 9). A more detailed screening of Rh-based catalysts revealed [Rh(C₂H₄)₂Cl]₂ as an equally effective catalyst (Table S11, entry 10). On the other hand, cyclooctadiene- or norbornadiene-containing neutral and cationic

Rh(I) complexes (entries 11–14) as well as the Rh(III) complex [Rh(Cp*)Cl₂]₂ (entry 15) are not suitable ring opening catalysts. In order to determine the energy stored in the photo-generated strained Dewar compound **4**, we measured the heat of the ring opening reaction in a reaction calorimeter. Thus, integration of the heatflow curve of the ring opening reaction catalyzed by 3 mol% Wilkinson's catalyst gave consistently a $\Delta H = -48 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$.^[24] This number compares favorably to other known MOST systems (e.g., $\Delta H = -21 \text{ kcal}\cdot\text{mol}^{-1}$ for norbornadiene/quadracyclane system;^[25] $\Delta H = -20 \text{ kcal}\cdot\text{mol}^{-1}$ for the fulvalenediruthenium system),^[5d] and agrees with our DFT computations (Table S10).

In summary, we have demonstrated the first isolation of the Dewar valence isomer of 1,2-dihydro-1,2-azaborinines in solution at preparative scale. Irradiation of a substituted 1,2-dihydro-1,2-azaborinine in a cyclohexane solution leads to a full conversion with high quantum yield ($46 \pm 8 \%$) exclusively to the Dewar valence isomer that is stable for weeks at room temperature under inert conditions. Further irradiation with shorter wavelength UV light leads to a cycloreversion of the Dewar valence isomer to the corresponding iminoborane and cyclobutadiene. The substituted Dewar isomer is kinetically stable towards thermal reversible reaction that has an activation barrier of $27.0 \pm 1.2 \text{ kcal}\cdot\text{mol}^{-1}$. The thermal ring opening reaction can be catalyzed efficiently by Wilkinson's catalyst. The energy stored in the strained bicyclic Dewar valence isomer has been determined by calorimetric measurement to be $48 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$. This work provides a proof-of-concept of the potential utility of using the valence isomer pair of 1,2-dihydro-1,2-azaborinines in molecular solar thermal system applications. Current efforts are directed toward tuning the absorption profiles of our system to the visible range.

Acknowledgements

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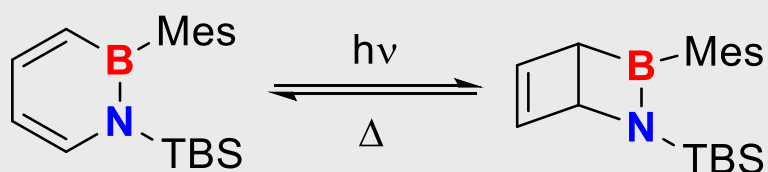
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COMMUNICATION

Entry for the Table of Contents

COMMUNICATION



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The Dewar isomer of 1,2-dihydro-1,2-azaborinines: Isolation, fragmentation, and energy storage.

BN-Dewar: The boron-nitrogen derivative of Dewar benzene can be generated by irradiation of a BN substituted benzene and is stable in solution. The thermally reversible reaction has a high activation barrier and can be catalyzed by Wilkinson's catalyst. The system comprises a new valence isomer pair that is in principle suitable for energy storage.