SUPPORTING INFORMATION FOR:

A Photochromic System among Boron Hydrides: The Hawthorne Rearrangement

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1. Computational Details

1.1. Ground-state geometry optimizations and single-point computations

The minima (**I** and **II**) and transition state (**TS**) were optimized by means of the DFT/B3LYP method as implemented in the GAUSSIAN 09 software package,¹¹ imposing symmetry constraints (C_{2h} point group) and using the standard 6-31G* basis set. The DFT/B3LYP/6-31G* level of theory has described properly the structures of related polyhedral borane hydrides.^{12–15} The **TS** was obtained using the QST2 method, using **I** as the geometry of reactant and **II** as the product structure. On the other hand, the intermediate **INT** structure was optimized without any symmetry restriction. Frequency calculations were performed to check the correct nature of the critical points of the potential energy hypersurfaces (PEHs). All frequencies were positive for the minima, and only one imaginary frequency was found for **TS**, confirming the saddle point nature of this stationary point. Intrinsic Reaction Coordinate (IRC) calculations were performed to connect the **TS** with the **I** and **INT** minima. Note that axial borons are not involved in the corresponding multicenter bonding in the latter. Since such computations in the direction towards **INT** converged

to a minimum with a similar energy and geometry as compared to the **TS**, linear interpolation of internal coordinates (LIIC) computations were carried out between **TS** and **INT**. The wave function stability at the **TS** and the nearby minimum was analyzed by comparing the close-shell and open-shell solutions as described elsewhere.¹⁶ Negligible energy differences were detected (<0.014 eV). Further re-optimization of the **TS** using the determined open-shell wave function and releasing the symmetry constraints (C_1 point group) lead to the same **TS** solution (energy difference of 0.0017 eV achieved in four iterations; same imaginary frequency).

1.2. Excited-state geometry optimizations

The minimum-energy crossing point (MECP) between the S_0 and the S_1 states, *i.e.* **S_0/S_1 CI** geometry, was optimized with the multiconfigurational CASSCF method¹⁷ in conjunction with the 6-31G basis set. The energy degeneracy between the S_0 and the S_1 states was imposed by means of the restricted Lagrange multipliers technique. An active space of 8 electrons distributed into 8 molecular orbitals [hereafter, CASSCF(8,8)] delocalized over the borane backbone was used for the CI geometry optimization, and three states were computed in the state-average (SA)-CASSCF procedure. The convergence criterion with respect to the energy change and the norm of the gradient was set to 10^{-6} and 10^{-2} a.u., respectively. The CI nature of the converged structure was confirmed *via* single-point calculations using a higher level of theory, as described as follows.

1.3. Excited-state single-point calculations

The ground- and excited-state energies on top of the optimized geometries were calculated using the CASSCF method with a larger active space of CASSCF(12,12) and demanding six roots in the SA-CASSCF procedure. The CASSCF(12,12) natural orbitals of **I** are displayed in Figure S1. At the region of isomer **I**, **S_0/S_1 CI** and **INT**, the orbitals are well localized in the borane cluster. However, at the **II** region, a diffuse orbital (see Figure S2) is needed to describe the high excited states of the system S_3 and S_4 (see Table 1 of the main text). Attempts to exclude the diffuse orbital from the CASSCF(12,12) active space when computing 6 states were not successful. These high-energy states of **II** are however not relevant for the present determination of the thermal and photo-induced isomerization mechanisms mainly involving the low-lying excited states of **I**.

The atomic natural orbital (ANO) S-type with a contraction scheme B[3s,2p,1d]/H[2s1p], hereafter ANO-S-VDZP, was used for all energies reported in this work, given its repeatedly demonstrated ability to provide accurate excited-state energies of borane hydrides.^{12,14,18} The dynamic electron correlation was computed with the CASPT2 method using the SA-CASSCF(12,12) wave functions as a reference. According to previous studies on related systems,^[8,10,14] the ionization-potential electron-affinity parameter (IPEA) was set to the recommended value of 0.25 au, and an imaginary level shift of 0.2 au was used to minimize the presence of weakly intruder states. Oscillator strengths (f) at the FC region of **I** and **II** were calculated according to the formula $f = \frac{2}{3} E_{VA} TDM^2$, where E_{VA} stands for the CASPT2 vertical absorption energy, and TDM refers to the transition dipole moment between the initial φ_1 and final φ_2 SA-CASSCF wave functions, according to the formula $TDM = \langle \varphi_1 | \vec{d} | \varphi_2 \rangle$, where $\vec{d}$ is the dipole moment operator.

PEH of the ground and low-lying four excited states were mapped by means of the LIIC technique between the **I**, **S₀/S₁ CI**, **INT**, and **II** structures. This strategy provides connected but non-optimized paths, therefore, the energy barriers must be considered as upper bounds.

All multiconfigurational calculations reported in this work were carried out with the MOLCAS 8 software package.¹⁹

2. Experimental section

2.1. NMR Computations and Geometry Verification

¹¹B NMR spectra of the both isomers under scrutiny were computed at the GIAO-B3LYP/II//B3LYP/6-31G* level and the reasonable agreement with the experimental values (the shielding tensors were computed at the GIAO-B3LYP level employing a IGLO-II basis set by Huzinaga¹⁰ on the basis of the B3LYP/6-31G* geometries, see also ref. ¹¹). For the computed ¹¹B NMR chemical shifts see Tables S1 and S2. A relatively good accord between the computed and experimental ¹¹B NMR chemical shifts provides a good ground for accepting the corresponding internal coordinates computed at the 6-31G* level as good representations of the molecular geometries in solution. The effect of electron dynamic correlation for computing magnetic shielding of such large clusters is found to be marginal, see refs. 2–4,11.

2.2. Synthesis

I was prepared according to the literature procedure.¹²

2.3. NMR measurements

¹¹B NMR spectra were measured in CD₃ CN using a Varian XL-500 instrument at 11.75 T. The chemical shifts were referenced to BF₃·OEt₂.

2.4. Absorption Spectra and Irradiation

UV-vis absorption spectra of solutions were recorded on a Perkin Elmer Lambda 35 spectrometer. A 300 W Xenon lamp source (ozone-free lamp, Newport) equipped with a longpass filter (305 nm cut-on wavelength) was used for continuous irradiation. Acetonitrile solution of **I** was placed in an NMR tube and irradiated for 25 min at room temperature. The reverse reaction was performed after evaporation of acetonitrile in an NMR tube. The tube was placed in an oven preheated at 140 °C for 5.5 h.

trans-B₂₀H₁₈²⁻ (**I**)

Table S1. Computed and experimental ¹¹B nuclei chemical shifts (ppm) for isomer **I**, *trans*-[B₂₀H₁₈]²⁻, computed at the GIAO-B3LYP/II//B3LYP/6-31G* level of theory.

¹¹ B Nuclei	δ _{comp} (¹¹ B) (ppm)	δ _{exp} (¹¹ B) (ppm)
B(1) = B(1')	26.2	29.9
B(2) = B(3) = B(2') = B(3')	-19.7	-16.7
B(4) = B(5) = B(4') = B(5')	-23.9	-20.1
B(7) = B(9) = B(7') = B(9')	-17.2	-13.1
B(8) = B(8')	-9.1	-7.6
B(6) = B(6')	16.9	15.3
B(10) = B(10')	-29.6	-26.3

photo-B₂₀H₁₈²⁻ (II)

Table S2. Computed and experimental ¹¹B nuclei chemical shifts (ppm) for isomer **II**, *photo*-[B₂₀H₁₈]²⁻, computed at the GIAO-B3LYP/II//B3LYP/6-31G* level of theory.

¹¹ B Nuclei	δ _{comp} (¹¹ B) (ppm)	δ _{exp} (¹¹ B) (ppm)
B(1) = B(10) = B(1') = B(10')	-8.4	-3.4
B(3) = B(9) = B(3') = B(9')	-33.9	-29.2
B(4) = B(8) = B(4') = B(8')	-32.0	-27.9
B(5) = B(7) = B(5') = B(7')	-29.3	-26.0
B(2) = B(6) = B(2') = B(6')	-24.8	-26.0

3. CASSCF molecular orbitals

Figure S1. SA-CASSCF natural orbitals (NO) of the CASSCF(12,12) active space of the isomer **I**, using the ANO-S-VDZP basis set.

Figure S2. SA-CASSCF natural orbitals (NO) of the CASSCF(12,12) active space of the isomer **II**, using the ANO-S-VDZP basis set.

4. Transition state structure

Figure S3. (a) Optimized geometry of the C_{2h} transition state (TS) related to the thermal conversion between isomers I and II, with straight and curved blue arrows indicating the displacements of atoms following the imaginary frequency (left), and (b) aligned structures of TS (orange) and S_0/S_1 CI (blue) with a fitted RMSD value of 0.14 Å.

5. Energy gradients along the thermal isomerization path

Figure S4. Energy gradients computed at the interpolated points 16 (a), 21 (b), and 25 (c) of Figure 4 with the DFT/B3LYP/6-31G* methodology.

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