Photoisomerization

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Reversible Photochemical and Thermal Isomerization of Azaboratabisnorcaradiene to Azaborabenzotropilidene**

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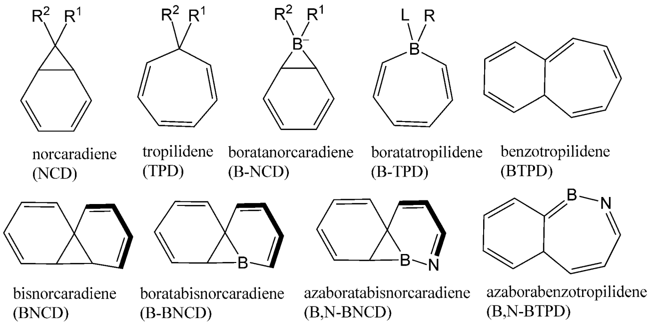
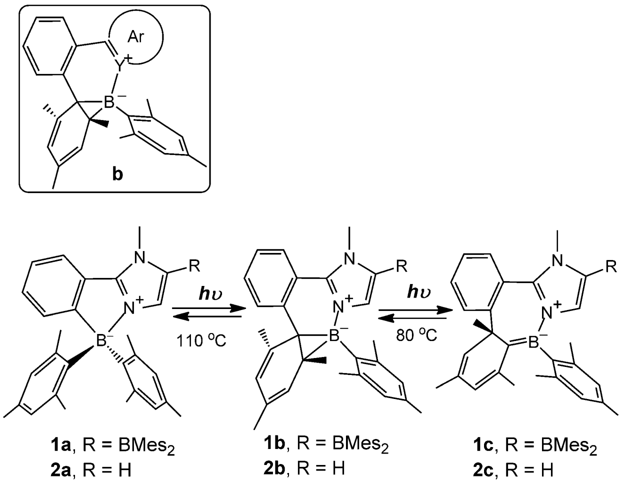
Abstract: *Two new tricyclic 1,2-azaboratabisnorcaradiene molecules (**1b** and **2b**) generated through the photoisomerization of N-methyl-2-phenylimidazolyl-chelated dimesitylboranes (**1a** and **2a**) have been found to undergo unusual photoisomerization, producing the first examples of 1,2-azaborabenzotropilidenes (**1c** and **2c**), accompanied by a distinct color change, upon irradiation at 350 nm. Compounds **1c** and **2c** contain a conjugated alkylideneborane unit and can be fully reverted back to **1b** and **2b**, and subsequently to **1a** and **2a** upon heating. The mechanistic pathway of the new isomerism has been established to involve "walk" rearrangements by DFT computational studies.*

Organic frameworks incorporating a boron atom with an empty p_z orbital have many distinct optoelectronic properties such as intense fluorescence,[1] near-infrared emission,[2] and large two-photon absorption cross sections.[3] Organoboranes have also been found recently to display photochromism,[4] and unusual photochemical and thermal structural transformations.[5] Although in many instances, the structural transformation of organoboranes is similar or analogous to that of their carbon analogues, the incorporation of boron does introduce unique electronic, optical, and chemical properties to the molecule. One extensively studied organic rearrangement system is the tropilidene (TPD)–norcaradiene (NCD) isomerization and "walk" rearrangement (Scheme 1).[6] The isoelectronic boron analogues, B-TPD[7] and B-NCD,[8] have been known for several decades. Depending on the substituent groups, one isomer is usually greatly favored over the other, and interconversion between the two isomers has not been observed directly. A related isomerism is the bisnorcaradiene (BNCD)–benzotropilidene (BTPD) rearrangement[6c,d] shown in Scheme 1. We reported the first examples of boron-containing BNCD, which can be described as an 1,2-azaboratabisnorcaradiene (1,2-B,N-BNCD), obtained through photoisomerization of a four-coordinate $BMes_2$ compound (Mes = mesityl) with a 2-phenylpyridyl backbone (**b** with Ar = py in Scheme 2).[4c] The replacement of the N donor by a N-heterocyclic carbene (NHC) donor leads to the formation of 1,3-azaboratabisnorcaradiene (1,3-B,N-BNCD).[5b,c] In contrast to BNCD, which display mainly the BNCD–BTPD rearrangement, B,N-BNCD displays a multitude of photochemical and thermal isomerizations including enantiomer interconversion via 1,5-sigmatropic shift[4c,5d] and intramolecular H-atom transfer[5d]/activation,[5b] depending on the nature of the Ar σ donor group in **b**.



Scheme 1. Selected isomers of NCD, BNCD, and BTPD and their boron and B,N analogues.



Scheme 2. Photochemical and thermal rearrangements of **1a** and **2a**.

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We have now discovered a new isomerism phenomenon based on a new class of B,N-BNCD compounds (**1b** and **2b** in Scheme 2) that reveals for the first time the reversible photothermal interconversion of B,N-BNCD and B,N-BTPD (**1c** and **2c**). Taking advantage of this unusual isomerization, we have isolated and characterized the first examples of B,N-BTPD molecules. The details are reported herein.

Compounds **1b** and **2b** were generated through photoisomerization of the N,C-chelated BMes$_2$ compounds **1a** and **2a**, respectively (Scheme 2). Compounds **1a** and **2a** were obtained in 44 % and 17 % yield, respectively, from a one-pot reaction that involves the lithiation of 2-phenyl-*N*-methylimidazole with *tert*-butyllithium, followed by addition of BMes$_2$F at −78 °C in diethyl ether. 2-Phenyl-5-BMes$_2$-*N*-methylimidazole was also obtained as a side product from the same reaction. Compounds **1a** and **2a** were fully characterized by NMR, elemental, and single-crystal X-ray diffraction analyses (see the Supporting Information). Because of their high air-sensitivity, **1b** and **2b** were characterized by NMR spectroscopy data and the crystal structure of **2b** was determined by single-crystal X-ray diffraction analysis.

The photochemical reactivity of **1a** and **2a** was monitored by ^{1}H and ^{11}B NMR spectroscopy (Figure 1 and the Supporting Information). Irradiation of a C$_6$D$_6$ solution of **1a** at 350 nm resulted in a new set of distinct olefinic proton peaks at 5.5 and 5.7 ppm in the ^{1}H NMR spectrum, and a shift of the ^{11}B NMR signal from 2.4 ppm (**1a**) to −11.8 ppm, which is assigned to isomer **1b**. Compound **2a** displayed the analogous photoisomerization to **2b**. The molecular structure of **2b** (Figure 2) resembles those of our previously reported B,N-BNCD analogues.[4c,d,5b] The B,N-cyclohexadienyl ring and the cyclohexadienyl ring in **2b** are approximately perpendicular to the shared boratacyclopropyl ring.

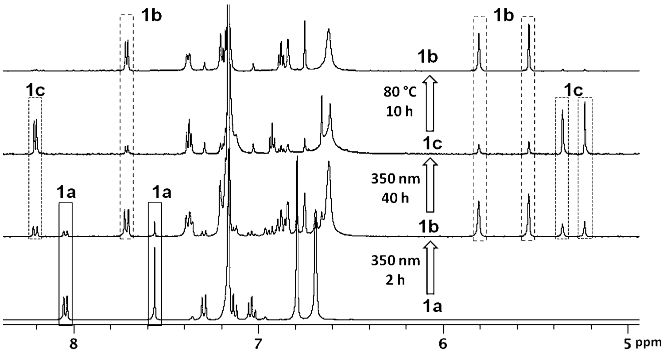


Figure 1. Stacked ^{1}H NMR spectra of the olefinic and aromatic region showing the conversion of **1a**→**1b**→**1c**→**1b** in C$_6$D$_6$ upon irradiation or heating. The key peaks of the different isomers are in frames.

Remarkably, upon prolonged irradiation, the characteristic ^{1}H NMR peaks of **1b** diminished and were replaced by a new set of peaks belonging to **1c** (Figure 1). The photoisomerization of **2b**→**2c** was also observed, albeit it proceeds at a much slower rate, and was also accompanied by formation of considerable amounts of degradation products after extended irradiation (see the Supporting Information).

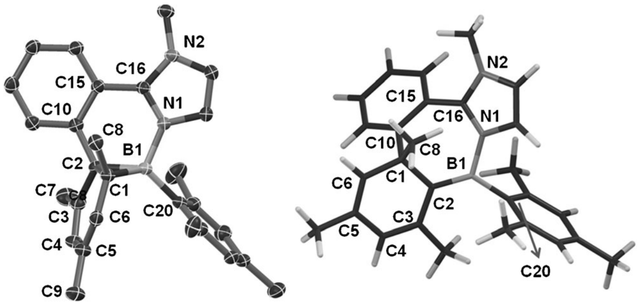


Figure 2. Left: Crystal structure of **2b** (left, H atoms are omitted for clarity) with 35 % thermal ellipsoids and labels for the key atoms. Right: DFT-optimized structure of **2c** (right, CAM-B3LYP/SVP level of theory). Important bond lengths [Å] and angles [°] for **2b**: B1-C1 1.587(3), B1-C2 1.629(3), B1-N1 1.555(3), B1-C20 1.598(3), C1-C2 1.601(3), C2-C3 1.488(3), C3-C4 1.345(3), C4-C5 1.450(3), C5-C6 1.329(3), C1-C6 1.480(3), C2-C10 1.488(3), C10-C15 1.416(3), C15-C16 1.455(3), N1-C16 1.345(3), C2-B1-C1 59.7(1), C1-C2-B1 58.8(1), C2-C1-B1 61.4(1); for **2c:** B1-C2 1.468, B1-C20 1.594, B1-N1 1.547, C1-C2 1.558, C2-C3 1.467, C3-C4 1.358, C4-C5 1.453, C5-C6 1.339, C1-C6 1.518(3), C1-C10 1.539, C10-C15 1.412, C15-C16 1.459, N1-C16 1.340, C2-B1-N1 119.28, C2-B1-C20 131.59, N1-B1-C20 109.07.

Compounds **1b** and **2b** have two quaternary B-bonded C atoms, C1 and C2 (43.6 and 30.4 ppm for **1b**, 42.4 and 27.4 ppm for **2b**) in the cyclohexadienyl ring. In contrast, the 2D ^{1}H^{13}C HMBC NMR spectra of **1c** and **2c** showed that only one C atom (C1) remains quaternary, displaying a chemical shift at 46 ppm. The ^{11}B NMR spectra of **1c** and **2c** exhibit a broad peak at 32 ppm, which is similar to those reported previously for $[R_2C{=}BR'_2]^-$ and $A_2C{=}BR(L)$ ($A = SiR_3$, SnR_3, L = Lewis donor).[9–11] These data led us to propose the B,N-TPD structure that is fused with a cyclohexadienyl ring for **1c** and **2c** as shown in Scheme 2. The chemical shift of the C atom in the B=C bond in **1c** and **2c** was determined to be at 122 ppm from ^{1}H^{13}C HMBC spectra, which is much further downfield than those reported for $A_2C{=}BR(L)$ ($A =$ SiR_3, SnR_3, L = nitrogen donor).[10] The calculated ^{1}H, ^{13}C, and ^{11}B NMR shifts match very well with the experimentally observed data (see the Supporting Information). As shown by the calculated structure of **2c** in Figure 2, the B=C bond is coplanar with the cyclohexadienyl unit and the seven-membered B,N-heterocycle is isoelectronic with TPD. The calculated B=C bond length for **2c** is 1.47 Å, which is much longer than that of methyleneborane derivatives (1.37 Å),[10] but comparable to those of alkylidenborates $[R_2C{=}BR'_2]^-$ or methyleneborane adducts with a Lewis base donor.[9,10b]

The transformation of the **b** isomer to the **c** isomer is accompanied by a distinct color change (olive-green to red for **1b** to **1c**, and red to reddish brown for **2b** to **2c**). As shown in Figure 3, **1b** has a broad absorption band at $\lambda_{max} = 590$ nm, while **2b** has an intense absorption peak at $\lambda_{max} = 495$ nm, which is characteristic for azaboratabisnorcaradienes. The red shift of this absorption band of **1b** by roughly 100 nm relative to that of **2b** is caused by the BMes$_2$ unit in the backbone of **1b** which is known to significantly lower the absorption energy through π-conjugation with the N,C-chelate backbone.[4c] In contrast to **1b** and **2b**, the absorption bands of **1c** and **2c** move to lower energy for **1c** (750 nm) and **2c**

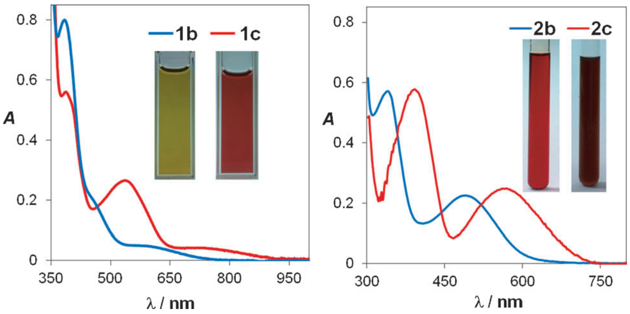


Figure 3. UV/Vis absorption spectra of **1b** and **1c** (left), **2b** and **2c** (right) in toluene (1×10^{-4} M). Inset: photographs showing the colors of **1b**, **1c**, **2b**, and **2c** in solution.

(580 nm). DFT calculations indicate that for **1b** and **2b** the HOMO is localized on the boranorcaradiene unit while the LUMO is localized on the Ph-imidazolyl($BMes_2$) backbone. For **1c** and **2c**, the energy levels and compositions of LUMO and LUMO + 1 are similar to those of **1b** and **2b**; however, the HOMO is localized on the conjugated B=C bond and the cyclohexadienyl moiety and is destabilized by about 0.50 eV relative to the situation in **1b** and **2b** (Figure 4). Based on TD-DFT data, the two lowest absorption bands in **1c** and **2c** were assigned to HOMO→LUMO, and HOMO→LUMO + 1 charge-transfer transitions. The patterns of the calculated UV/Vis spectra of **1c** and **2c** match the experimental spectra very well, further validating the proposed structures for **1c** and **2c** (see the Supporting Information).

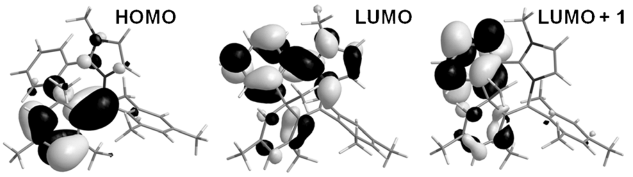
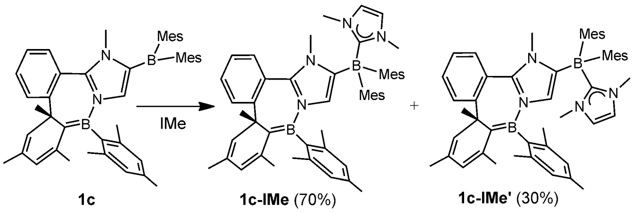


Figure 4. HOMO, LUMO, and LUMO + 1 diagrams of **2c**.

Compounds **1c** and **2c** rapidly decompose upon exposure to air. The destabilized HOMO level makes the molecule prone to oxidation by oxygen. **1c** and **2c** are also highly reactive to water and alcohols but are stable to diethylamine. However, unlike the previously reported reactive $A_2C{=}BR$ species ($A = SiR_3$ and SnR_3),[10] the B=C bond in compounds **1c** and **2c** did not show any [2+2] cycloaddition reactivity with benzophenone, acetone, or iminoborane *t*BuB≡N*t*Bu. Several factors are believed to contribute to the stabilization and significant deshielding of the carbon atom (122 ppm) in the B=C bond of **1c** and **2c**, which include the bulky mesityl group on the boron atom, the strong imidazolyl σ donor, and the extended π-conjugation of the B=C bond with the two C=C bonds in the cyclohexadienyl ring. **1c** and **2c** are rare examples of $R_2C{=}BR(L)$ species, and to the best of our knowledge, the first examples in which alkylideneborane units[9–11] are an integral part of conjugated π systems, illustrating the possibility of using the alkylideneborane unit as a building block for B-containing π-conjugated materials.

Compound **1c** was found to react with a strong σ donor, 1,3-bismethylimidazol-2-ylidene (IMe), forming the reddish brown adduct **1c-IMe**. All methyl groups of the $BMes_2$ unit in **1c-IMe** displayed distinct ^1H NMR chemical shifts. A new and sharp peak at −12 ppm in the ^{11}B NMR spectrum of **1c-IMe** was observed, along with a broad peak at 32 ppm for the B=C bond, supporting the unusual attachment of IMe to the sterically crowded $BMes^2Ar$ unit,[12] rather than [2+1] addition to the B=C bond. Because of steric congestion, two isomeric structures for **1c-IMe** were observed in the NMR spectra (Scheme 3), which undergo a slow exchange in solution, with the major isomer about 8 kJ mol^{-1} lower in energy, based on DFT data (see SI).



Scheme 3. Reaction of **1c** with IMe.

At 80 °C in C_6D_6, compounds **1c** and **2c** thermally revert back to **1b** and **2b**, respectively. At higher temperature (110 °C), isomers **b** can be fully converted back to isomers **a**, thus completing the remarkable molecular journey **a**→**b**→**c**→**b**→**a**. The NHC adduct **1c-IMe** is more inert toward thermal isomerization. Unfortunately, numerous attempts to collect the X-ray diffraction data of **1c-IMe** failed because the crystals are very small and display multiple twinning.

To understand the mechanism of this unusual isomerization, we examined the thermal pathway computationally with **2** as the model compound. The **2b** to **2a** thermal isomerization pathway follows the same pattern as established previously for the related N,C-chelated $BMes_2$ systems (see the Supporting Information for details). Two transition states and one intermediate (**Int**) were located along the reaction coordinates of **2c**–**2b** (Figure 5). The transformation of **2c** to **Int** is an electrocyclic ring-closing rearrangement, similar to that of TPD to NCD. Most significantly, the **Int** to **2b** reaction could be described as a new type of "walk" rearrangement[6] in which the walking unit is the cyclohexadienyl unit (type II′ in Scheme 4). Sigmatropic shifts in B-NCD were observed before (type I).[8c] In addition, 1,5-sigmatropic shifts were also observed for some B,N-BNCD compounds with the B,N-cyclohexadienyl as the walking unit (type II).[4c] It must be emphasized that with strong σ donors such as imidazolyl and NHC,[5b] the **b** isomers retain high thermal stability and do not undergo the type II "walk" rearrangement, but exhibit photoreactivity. The calculated transition states and the intermediate for the **2b**–**2c** isomerism involve the change of the B–N bond order and the dearomatization of the imidazolyl ring (Figure 5). The fact that the photoconversion rate of **1b**→**1c** is faster than that of **2b** to **2c** could be attributed to the $BMes_2$ substituent, which

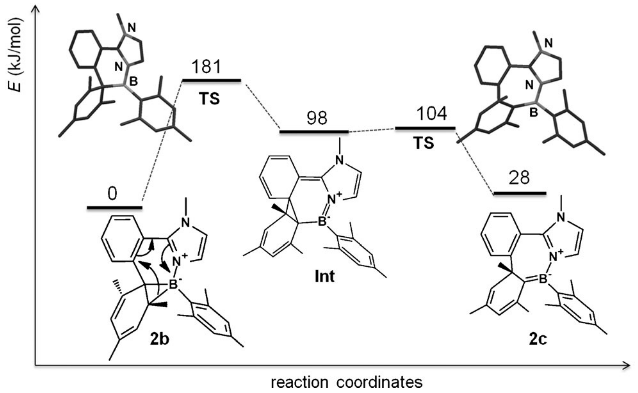
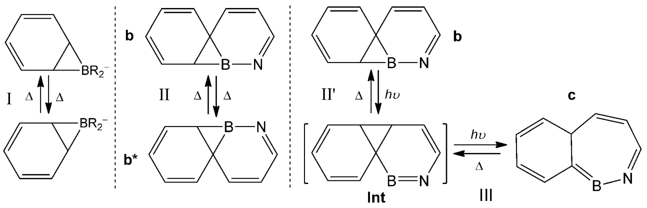


Figure 5. The thermal isomerization pathway between isomer **b** and **c**. The complete isomerization pathway of **a**, **b**, and **c** can be found in the Supporting Information.



Scheme 4. The "walk" rearrangement of B-NCD and B,N-BNCD and its role in the **b–c** isomerization.

lowers the aromaticity of the imidazolyl ring (see the Supporting Information for the NICS values).

In summary, a new reversible photochemical and thermal isomerization phenomenon involving three organoborane species with distinct colors has been discovered, which further illustrates the multitude of isomerism displayed by B,N-BNCD. The first example of reversible isomerization of B,N-BNCD and B,N-BTPD has been demonstrated and the mechanistic pathway has been established to involve a "walk" rearrangement around an B,N-cyclohexadienyl ring and the electrocyclic closure/ring opening of B,N-TPD. The σ-donating strength and the aromaticity of the heterocycle bound to the B atom are believed to play a key role in dictating the specific isomerization pathway among the competing pathways.

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