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Reversible Photoisomerization from Borepin to Boratanorcaradiene and Double Aryl Migration from Boron to Carbon

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Abstract: B(npy)Ar$_2$ (npy = 2-(naphthalen-1-yl)pyridine) compounds bearing various non-bulky aryl groups have been found to undergo a clean and sequential two-step photoisomerization in which two aryl substituents on boron migrate to a carbon atom of the naphthyl moiety. The 2nd isomerization step is the first example of a reversible photoisoermization between a borepin and a borirane. Both steric and electronic factors have been found to have a great impact on this photoreactivity. Furthermore, the borirane isomer reacts with oxygen, forming a rare oxaborepin dimer.

Organoboron compounds play a significant role in a number of important fields, including optoelectronic devices,[1] responsive and sensory systems,[2] metal-free bond activation and catalysis.[3] Another interesting aspect is the photoreactivity of organoboron compounds that lead to rare chemical reactions or structural transformation.[4] Reversible photoisomerization mediated by boron is especially interesting because it allows access to new and rare boron-based photochromic materials.[5]-[8] Kawashima et al reported a boron and azobenzene-based photochromic system that relies on *trans*/*cis*-isomerization of an azo unit and reversible B←N coordination.[5] Yamaguchi et al reported a BMes$_2$ substituted borepin system that undergoes thermally reversible bora-Nazarov photocyclization with distinct colour change.[6] We reported several thermally reversible photochromic boron systems that rely on BN-heterocycle ring expansion/contraction rearrangements.[7] These systems demonstrate the propensity of boron to facilitate complex structural transformations and the possibility of creating rare species such as BN-tropilidenes and BN-cyclooctatrienes ((a) and (b) in Scheme 1) *via* photoisomerization. Herein we present another unprecedented bora-heterocycle phototransformation involving a BN-fluorene annulated borepin species **a** and a BN-fluorene annulated boratanorcaradiene **b** (Scheme 1). Unlike most of the previously reported photoisomerization systems such as (a) and (b), which can only be reversed by heating, this new photochromic system can be operated in both directions with light. Furthermore, the **a** to **b** transformation involves reversible aryl migration between a boron and a carbon atom. In fact, from the starting isomer B(npy)Ar$_2$, the sequential photoisomerization shown in Scheme 1(c) involves double aryl

migration from boron to carbon, which, to the best of our knowledge, is a previously unknown reactivity for boron compounds. This rare two-step photoisomerization of B(npy)Ar$_2$ can be precisely controlled by the wavelength of light used. In a previous report,[8a] a related molecule B(npy)Mes$_2$ (**7**) was found to undergo the first stage photoisomerization only, forming species **a**. Given the rare occurrence of reversible, light-driven isomerization of bora-heterocycles and reversible double aryl migration involving boron as shown in Scheme 1, we conducted a comprehensive study on this system. The substituents on boron were found to have a significant impact on both the boron-insertion reaction and the **a** to **b** transformation. The details are presented herein.
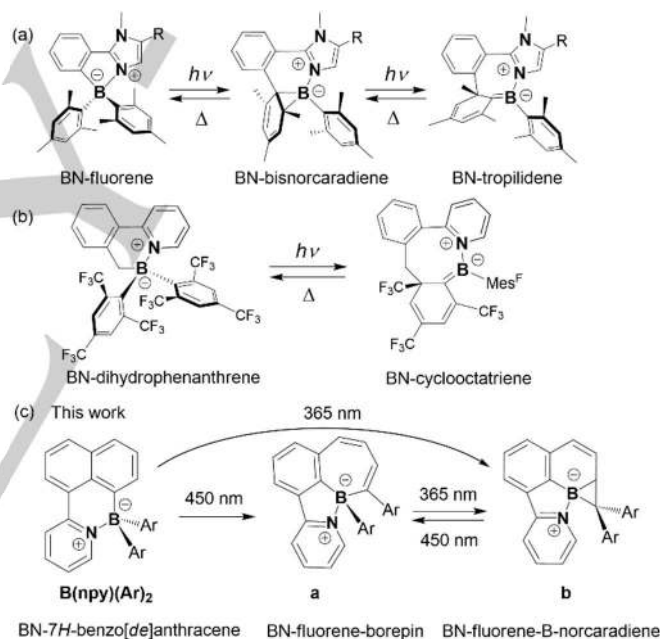
Scheme 1. (a) and (b): Representative examples of reversible BN-heterocycle ring expansion/contraction photoisomerization. (c): Sequential photoisomerization of B(npy)Ar$_2$ and the first example of reversible photoisomerization of borepin **a** to boratanorcaradiene **b** examined in this work.

To establish the scope of the sequential phototransformation, six new B(npy)Ar$_2$ molecules with various aryl substituents on boron were prepared by lithiation of 2-(8-iodonaphthalen-1-yl)pyridine, followed by the addition of an appropriate ClBAr$_2$ reagent using the general procedure shown in Scheme 2 (see the Supporting Information (SI) for details). Compound **1** has two phenyl groups on boron while **2**, **5** and **6** have electron-donating and electron-withdrawing groups on the phenyl ring, respectively, for the purpose of examining the electronic influence on the photoreactivity in this system. Compound **3** and **4** have *p*-tolyl and 2,4-dimethylphenyl groups on boron, respectively, for the purpose of studying steric effects of the

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photoreaction. All six compounds were fully characterized by NMR and HRMS spectroscopic analysis. Their ^{11}B NMR spectra display a sharp peak between −3.7 and 2.2 ppm, characteristic of four-coordinated boron. The crystal structure of **1** was determined by X-ray diffraction analysis (see SI).[9] The B–N and B–C bond lengths in **1** are all much shorter than those in B(npy)Mes$_2$ (**7**) owing to the reduced steric congestion.[8a] The naphthyl and py rings in **1** are also more coplanar compared to **7**, as indicated by the smaller dihedral angle in the former (~9 *vs.* 30°).[8a] As observed in **7**, the two phenyl rings in **1** occupy an axial (ph$_a$) and an equatorial (ph$_e$) position, respectively. The chelate feature of **1** resembles that of bis-BPh$_2$ chelated 9,10-di(pyrid-2-yl)anthracene reported by Jäkle and coworkers.[8b]
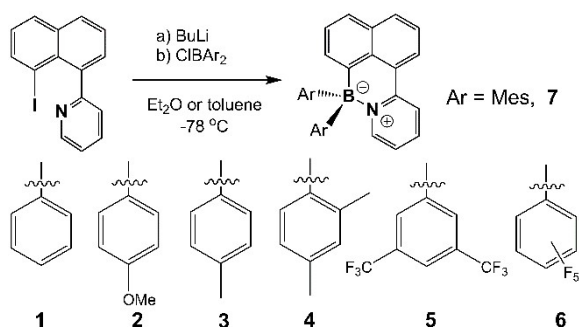
Scheme 2. Examples of B(npy)Ar$_2$ investigated in this work.

Compounds **1** – **6** have intense and broad absorption bands in the region of 330 nm to 460 nm as well as distinct fluorescent colours. **1**, **5** and **6** are bright blue emitters in toluene (λ_{em} = 465 nm, 449 nm, and 450 nm, respectively) with Φ_{FL} = 0.58, 0.97 and 0.96, which can be ascribed to π - π^* transitions of the npy unit. In contrast, **2** – **4** display green or blue-green emission colours (λ_{em} = 509 nm, 488 nm, and 527 nm) with much lower Φ_{FL} (0.21, 0.33 and 0.15, respectively), which are attributed to charge transfer transitions from Ar to the npy unit. These assignments are in agreement with the computed TD-DFT data (see SI). By comparison, **7** is barely emissive with a low Φ_{FL} of 0.02. Consistent with their bright fluorescence, **5** and **6** do not show any photoreactivity upon irradiation at 365 nm or 450 nm. Surprisingly, however, molecule **1** undergoes clean isomerization upon irradiation at 365 nm, forming boratanorcaradiene (borirane) **1b** quantitatively, accompanied by a distinct colour change from light yellow to bright orange, without observable intermediates by NMR spectroscopy (see SI). The photoisomerization quantum yield for **1** to **1b** conversion at 365 nm in toluene was determined to be 14%. Interestingly, irradiating a benzene solution of **1** at 450 nm (a LED lamp with a FWHM value of ~50 nm) for about 4 hrs yields a clean mixture of borepin **1a** and borirane **1b** in a ratio of 1:1.2 (Figure 1(a)). Under ambient conditions **1a** is stable and can be separated from **1b** by column chromatography, while **1b** gradually degrades. **1a** has structural features similar to that of the bis-mesityl borepin analogue **7a** obtained from the photoisomerization of **7**. [8a] The ^{11}B NMR chemical shift (2.2 ppm) of **1a** is ~1 ppm down-field shifted from that of **1** (1.3 ppm), and similar to that of **7a** (2.5 ppm). Significantly, irradiating the

benzene solution of the isolated **1a** or the 1:1.2 mixture of **1a** and **1b** at 365 nm converts **1a** to **1b** quantitatively, establishing that **1a** is an intermediate in the photoisomerization pathway of **1** to **1b**. Interestingly, irradiating **1b** at 450 nm reproduces the 1:1.2 mixture of **1a** and **1b**, as shown in Figure 1(a).
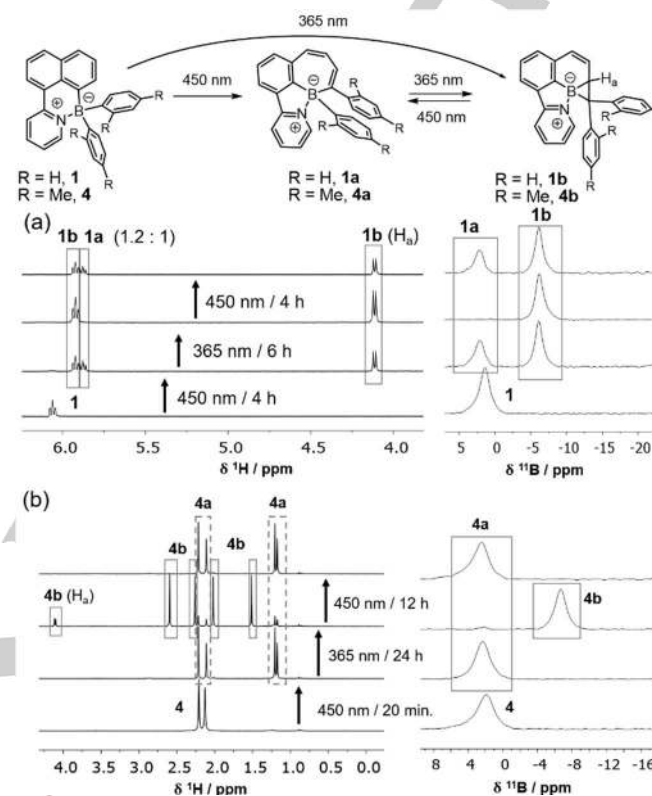
Figure 1. [1]H (partial spectra) and ^{11}B NMR spectra showing the sequential structural change of **1** (a) and **4** (b) in C$_6$D$_6$ (1.0 x 10^{-3} M) upon irradiation at different wavelengths (450 and 365 nm). Utilizing 450 nm irradiation on **1/4** yields a mixture of **1a** + **1b** (1:1.2) and **4a**, respectively, while 365 nm irradiation converts all of **1a** to **1b** and **4a** to a 1:5.2 mixture of **4a** + **4b**. This second transformation can be reversed with a second round of 450 nm irradiation, yielding a 1:1.2 mixture of **1a** + **1b** and **4a**, respectively.

The structure of **1b** was established by 2D NMR spectroscopy and X-ray diffraction analysis. [9] The [11]B chemical shift of **1b** (-6.1 ppm) is shifted upfield relative to that of **1** and **1a**, but in the expected region for cyclohexadienyl-fused boriranes.[10] The only aliphatic H$_a$ atom located on the borirane ring of **1b** has a distinct doublet peak at 4.11 pm (^{3}J = 6.5 Hz). The most unusual feature unveiled by the crystal structure of **1b** shown in Figure 2 is the boratanorcaradiene unit, and the migration of both phenyl groups from boron in **1** to the C(10) atom of the naphthyl ring. The ^{13}C chemical shift (153 ppm) of the quaternary C(9) atom bonded to B was assigned based on HMBC spectral analysis and is broad due to the quadrupole moment of the boron atom. The calculated ^{1}H and ^{13}C chemical shifts of **1b** match well with the experimentally observed data (see the SI). In contrast to previously known examples of boratanorcaradienes where the boron atom is facially-bound to the cyclohexadienyl ring (see examples shown in Scheme 1(a)), the boron atom in **1b** is embedded within the bora-cyclohexadienyl ring and acts as one of the bridge atoms for fusing with the borirane ring. To the best

of our knowledge, **1b** is the first example of a boracyclo-hexadienylborirane with this type of bonding arrangement, thereby representing a rare boratanorcaradiene isomer. Nonetheless, the internal bond angles and lengths of the borirane ring are comparable to those of previously reported borirane structures.[7a, 10a-b, 10d] The fact that **1a** and **1b** are interconvertible using two different wavelengths can be ascribed to their well separated absorption bands with λ_{max} = 330 nm for **1a** and 440 nm for **1b** (Figure 3(a)).
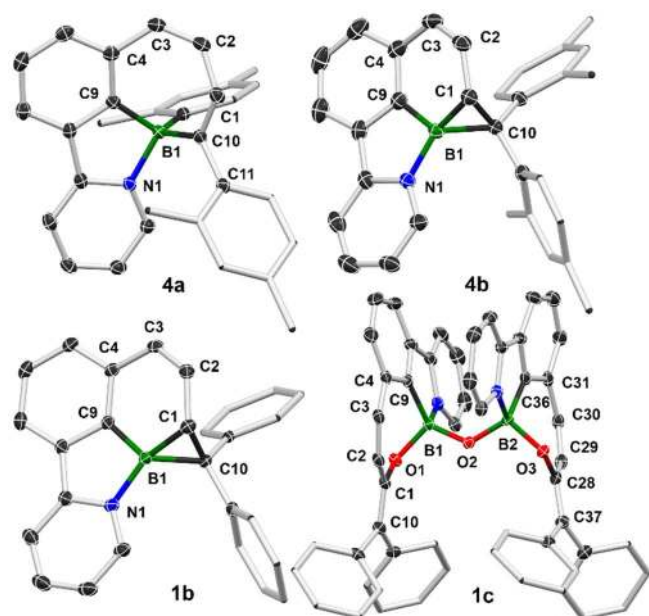

Figure 2. Crystal structures of **4a**, **4b**, **1b** and **1c** with 35% thermal ellipsoids and H atoms omitted for clarity. Selected bond lengths for **1b** (Å): B1 – N1 1.566(2), B1 – C1 1.640(3), B1 – C9 1.531(3), B1 – C10 1.600(3), C1 – C10 1.531(2), C1 – C2 1.481(2), C2 – C3 1.346(3), C3 – C4 1.455(3), C4 – C9 1.400(2); **4a**: B1 – N1 1.621(3), B1 – C9 1.593(3), B1 – C10 1.621(3), B1 – C10 1.621(3), C1 – C10 1.350(3), C1 – C2 1.455(3), C2 – C3 11.343(4), C3 – C4 1.459(3), C4 – C9 1.402(3); **1c** (for the B1 unit / O2 atom connectivity only): B1 – O1 1.463(4), B1 – O2 / B2 – O2 1.425(4) / 1.421(4), B1 – N1 1.637(4), B1 – C9 1.586(4), C1 – C10 1.363(4)), C1 – O1 1.359(4), C1 – C2 1.456(4), C2 – C3 1.354(4), C3 – C4 1.450(5).

The **1a** to **1b** interconversion can be readily tracked by UV-Vis spectra (Figure 3(b)). Consistent with NMR tracking data, irradiating **1a** at 365 nm fully converts it to **1b**, while irradiating **1b** at 450 nm only partially converts it back to **1a**. The **1a** to **1b** interconversion can be repeated many times without significant decomposition, provided that the reaction vessel is well sealed to minimize exposure to oxygen. To demonstrate the robustness of this new reversible photochromic system, the fatigue resistance of compound **1a**/**1b** was examined using UV-Vis spectroscopy by cycling through the **1a**→**1b**→**1a** transformations repeatedly at 1.0 x 10^{-4} M in toluene. The data in Figure 3(c) show that the **1a**→**1b**→**1a** cycle has a good recoverability. Nonetheless, a notable absorbance decrease of **1b** is evident with increasing irradiation time, which is most likely caused by the slow leaking of the cuvette and degradation of **1b** by oxygen. The fate of **1b** in the presence of oxygen was established by several control experiments (see SI). When exposed to air in the

dark, the solution of **1b** changed colour from orange to yellow, and over the period of several days at 25 °C, yellow crystals of **1c** precipitated. This reaction could be greatly accelerated by heating and the crystals of **1c** were isolated in good yield (72%) (Scheme 3). The crystal structure of **1c** determined by X-ray diffraction [9] is shown in Figure 2. Remarkably, the borirane **1b** is transformed to an oxo-bridged dimer **1c** that contains two N^C^O-chelated boron atoms and two oxaborepin rings with the two boron units being related by an approximate C_2 symmetry. The B-O bond lengths involving the bridging oxygen atom are similar to those of previously known B-O-B units with tetrahedral boron centers.[11]
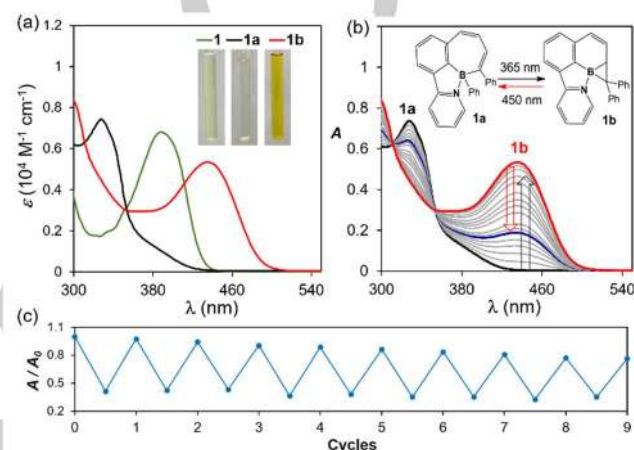
Figure 3. (a) UV-Vis spectra of **1**, **1a** and **1b** in toluene at 1.0 x 10^{-4} M and photographs showing their colours in benzene. (b) UV-Vis spectral tracking showing the full conversion of **1a** to **1b** at 365 nm and the partial conversion of **1b** to **1a** at 450 nm. (c) Fatigue resistance data obtained by recording the λ_{max} change of **1b**, after irradiating a mixture of **1a** and **1b** in toluene at 365 nm for 5 min. (**1a** → **1b**), followed by irradiating the resulting solution at 450 nm for another 5 min. (**1b** → **1a**). A_0 is the absorbance of **1b** at λ_{max} after 0.5 cycle.
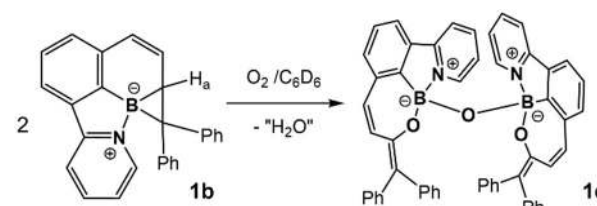
**Scheme 3.** **1b** to **1c** transformation via oxygen oxidation.

Compound **1b** is stable toward water. **1c** is therefore the result of oxygen insertion into the borirane in **1b**. NMR tracking experiments indicated possible formation of radical species in the reaction mixture of **1b** with O$_2$ due to the disappearance / broadening of peaks following O$_2$ exposure. Oxidation of boriranes by oxygen was reported previously for a few borirane species,[10b, 12] although isolated oxygen insertion products of boriranes are rare.[12b] MS spectroscopic analysis for **1c** recrystallized from CH$_2$Cl$_2$ in the presence of H$_2$^{18}O showed that one of the O atoms in **1c** (likely the bridging O atom) is exchangeable with that in water. Hence, H$_2$O involvement in **1c** formation could not be fully ruled out. Another interesting feature

is the cleavage of the borirane C-H$_a$ bond and the formation of a C=C bond in **1c**. The fate of the H$_a$ was not established, although it is most likely incorporated into H$_2$O as a by-product of the reaction.

Compounds **2** and **3** undergo photoisomerization at 450 nm irradiation in a similar manner as does **1**, forming a 2.8:1 mixture of **2a** and **2b**, and a 1.9:1 mixture of **3a** and **3b**, respectively. For **3**, the conversion is clean and quantitative while for **2**, the conversion is over 90%. The same mixtures can also be obtained by irradiating the isolated **2b/3b** at 450 nm. Compared to the 1:1.2 mixture of **1a** and **1b**, the introduction of electron-donating *p*-OMe or *p*-Me on the aryl substituents clearly favours the borepin species **2a/3a** over the borirane **2b/3b** in the photostationary state at 450 nm. As shown in Figure 1(b), **4** forms borepin **4a** exclusively at 450 nm. Under 365 nm irradiation, **2/3** or the isolated **2a/3a** can be converted to **2b** (94%) and **3b** (~100%), respectively. In contrast, irradiation of **4** or **4a** at 365 nm yields a photostationary state mixture of 1:4.9 of **4a** and **4b**. With 450 nm, compound **4b** converts back to **4a** quantitatively (Figure 1(b)). These results indicate that the *o*-Me group on the aryl likely stabilizes the borepin species. Consistent with this is the observation that irradiation of compound **7** at either 450 nm or 365 nm produces the borepin **7a** exclusively, which does not isomerize to the borirane **7b** at all, supporting that the borepin isomer is favoured by bulky aryls on boron. The structures of both **4a** and **4b** were determined by X-ray diffraction analyses (Figure 2).[9] The structure of **4a** is similar to that of **7a** while that of **4b** is similar to **1b**, with some minor variations of the internal bond lengths within the bora cycles. Like **1b**, compounds **2b** – **3b** degrade in the presence of oxygen, forming species similar to **1c**.

To understand the influence of aryl substituents on the sequential photoisomerization of B(npy)Ar$_2$, DFT computational analysis was performed for all isolated species involved in the photoisomerization of **1** – **4** and **7** along with the unobserved borirane species **7b**. The calculated Gibbs energy difference of the borepin isomer **a** and the borirane isomer **b** relative to the starting B(npy)Ar$_2$ isomer is shown in Figure 4(a). Strikingly, the relative stability of the borepin isomer **a** increases with increasing number of *o*-Me groups on the aryl group, which agrees with the preference for the **a** isomer observed for **4** and **7** at 450 nm excitation. The **b** isomers are the least stable, much higher in energy than the **a** isomers. The ratio of the **a** and **b** isomers at the photostationary state is certainly dependent on their energy difference and the excitation energy. The potential energy profile for the sequential transformation of B(npy)Ar$_2$ to the borepin and the borirane isomer has not been established by computational analysis owing to the complexity of the excited state calculations. Nonetheless, it is conceivable that **1** – **4** photoisomerize to **1a** – **4a** according to the mechanism of the **7** to **7a** isomerization,[8a] (Figure 4(b), using **1** as an example). Like **7**, the axial Ar in **1** – **4** has significant contributions to the HOMO. Photoexcitation could weaken this B-Ar$_a$ bond, inducing the axial Ar migration that ultimately leads to **a**. This step of the photoisomerization can be rationalized by a Zimmerman rearrangement (di-π-borate/methane rearrangement).[10a, 13, 14] In the HOMO of the **a** isomer, the key contributions are from the borepin C=C bonds and the B-C$_{Ar}$ bond (e.g. HOMO of **1a** in

Figure 4). Photoexcitation could therefore initiate C-C bond formation between the C=C bond and the Ar group linked by boron *via* a di-π-borate rearrangement. Similarly, the HOMO of **b** is dominated by the "bent bonds" of the borirane ring, with substantial contribution from the π orbitals of one aryl ring. Photoexcitation could therefore induce the reverse isomerization of **b** back to **a**. Reversible di-π-methane rearrangement is unusual but a few examples were reported previously for bicyclic compounds.[15] The **a → b** isomerization is the first example of reversible di-π-borate rearrangement, and the first experimental demonstration of reversible borepin to borirane rearrangement.
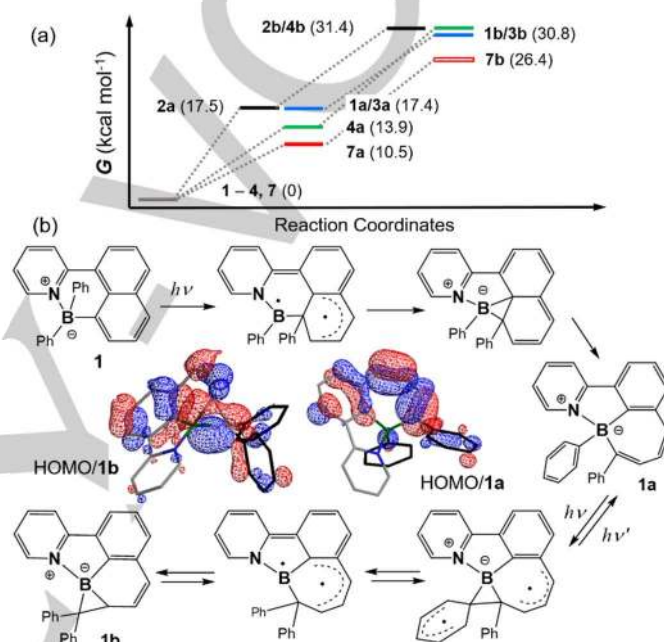
Figure 4. (a) A diagram showing the relative energy of **1a** – **4a/7a**, and **1b** – **4b/7b**, with respect to that of **1** – **4/7**, from DFT calculations (B3LYP/6-31g(d)). (b) The proposed sequential di-π-borate rearrangement for **1** to **1b** transformation along with the HOMO diagrams of **1a/1b** (iso-contour value = 0.04).

In summary, a stepwise phototransformation of B(npy)Ar$_2$ involving double aryl migration has been established to be a general phenomenon for Ar = phenyl or electron-rich aryl. Unprecedented interconversion between borepin and borirane derivatives has been established. The critical role of both electronic and steric factors in this rare structural transformation has been demonstrated. Formation of a rare oxaborepin species via oxygen insertion into the borirane ring has been established. Efforts are under way to build a full understanding of the mechanistic pathways in these rare photoreactions.

Acknowledgements

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Photoisomerization: Boron chelate compounds undergo two-stage photoisomerization, involving *double aryl migration* from boron to carbon, and an unprecedented reversible phototransformation of a borepin (**a**) to a new boratanorcaradiene species (**b**).
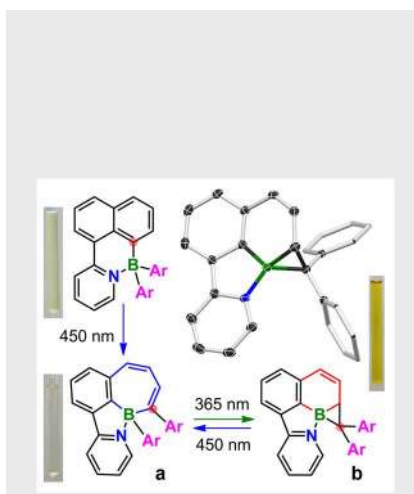
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Reversible Photoisomerization from Borepin to Boratanorcaradiene and Double Aryl Migration from Boron to Carbon