B,N Azo Dyes Hot Paper

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Formation of BN Isosteres of Azo Dyes by Ring Expansion of Boroles with Azides**

Holger Braunschweig, Mehmet Ali Celik, Florian Hupp, Ivo Krummenacher, and Lisa Mailänder*

Abstract: *Herein, we present the results of our investigations on the effect of ortho substitution of aryl azides on the ring-expansion reaction of boroles, five-membered unsaturated boron heterocycles. These studies led to the isolation of the first 1,2-azaborinine-substituted azo dyes, which are bright yellow solids. One of the derivatives, (E)-2-mesityl-1-(mesityldiazenyl)-3,4,5,6-tetraphenyl-1,2-azaborinine, was found to be unstable in solution and to transform through a Jacobsen-like reaction into an indazole and 1-hydro-1,2-azaborinine. DFT calculations were performed to shed light on possible mechanisms to rationalize the unexpected azo-azaborinine formation and to draw conclusions about the role played by the ortho substituents in the reaction.*

The concept of isosterism, first introduced by Irving Langmuir in 1919,[1] continues to be a valuable stimulus for enhancing the chemical, biological, or physical properties of a given compound without making significant changes to its chemical structure. In inorganic chemistry, C=C and B=N bonds are two well-established examples of isosteric groups, meaning that they contain the same number of atoms and the same number and arrangement of electrons.[2] Whereas the analogy manifests itself in their similar structures, the polar B=N bond imparts different chemical and physical properties. Thus, the prospect of modifying existing properties in various organic architectures by partially replacing C_2 with BN units has led to burgeoning interest. As a result, many improved and new synthetic methodologies, particularly in the preparation of BN isosteres of aromatic hydrocarbons, have been developed.[2b,3] With regard to the simplest arene, benzene, different routes to singly BN-substituted derivatives, commonly referred to as azaborinines, have been described.[2b] However, despite major advances in their preparation, monocyclic azaborinines constitute challenging synthetic targets and available derivatives remain limited in their scope of substitution. In the case of the 1,2-isomers, suitable precursors exist, from the work of Liu et al., for the facile functionalization at both boron and nitrogen positions,[4] but introduction of substituents such as aryl groups at the carbon framework remains difficult. In addition to the report by Taniguchi and Yamaguchi on a 3,6-diarylated 1,2-azaborinine,[5] our group has recently found new entries to derivatives with substituents on the C_4 backbone, a) by a rhodium-catalyzed [2+2]/[2+4] cycloaddition reaction of di-*tert*-butyliminoborane with alkynes[6] and b) by a ring-expansion reaction of free boroles with organic azides.[7] The synthesis from boroles, five-membered unsaturated boron heterocycles,[8] offers a facile approach to perarylated 1,2-azaborinines, which are not available by other methods. As a result of their pronounced anti-aromatic[9] and Lewis acidic character, boroles readily bind to nucleophiles[10] and are susceptible to ring-expansion reactions,[7,11] thereby alleviating their unfavorable 4π-electron delocalization in the ring.

Experimental and theoretical insight into the mechanism of borole ring expansion by organic azides was provided by the group of Martin.[11f] Based on DFT calculations, it was proposed that azide coordination by the α-nitrogen atom to the empty p_z orbital on boron constitutes the first step in this process. Given that organic azides ($R-N_3$) have multiple donor sites,[12] we wondered if the reaction outcome can be altered by forcing adduct formation to occur at the terminal nitrogen atom. Herein, we report how the reaction pathway in the ring-expansion of boroles with organic azides is redirected by systematic variation of the steric nature of the substrates. The products formed in this new process are 1,2-azaborinine-substituted azo derivatives, and thus hitherto unknown BN analogues of diaryl azo dyes.

To favor complexation at the less nucleophilic, terminal nitrogen atom of the azide, blocking of the α-nitrogen site by *ortho*-substituted aryl azides seemed to be a viable strategy.[7] We have thus investigated the reactivity of 1,2,3,4,5-pentaphenylborole (**2**) toward mesityl azide (**1**, Scheme 1). The product (**3**) of this transformation was obtained as a colorless solid in good yield (67%). Its ^{11}B NMR signal ($\delta(^{11}B) = 35.9$ ppm) and UV/Vis absorption maximum ($\lambda_{max} = 316$ nm, $\varepsilon = 19\,600\ L\,mol^{-1}\,cm^{-1}$) are in agreement with ring expansion and formation of an 1,2-azaborinine.[7,13] An X-ray analysis further confirmed the proposed structure (Figure 1). Despite the steric shielding of the α-nitrogen atom by the mesityl substituent, the reaction still follows the established pathway of 1,2-azaborinine formation.

To further increase the steric demand of the reaction partners we have included 1-mesityl-2,3,4,5-tetraphenylborole (**4**), which bears a bulky mesityl substituent at the boron center. Using borole **4** in the reaction with mesityl azide (**1**) indeed leads to a different outcome (Scheme 1). In this case,

[*] Prof. Dr. H. Braunschweig, Dr. M. A. Celik, F. Hupp, Dr. I. Krummenacher, L. Mailänder
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
E-mail: h.braunschweig@uni-wuerzburg.de
Homepage: http://www-anorganik.ak-braunschweig.chemie.uni-wuerzburg.de/

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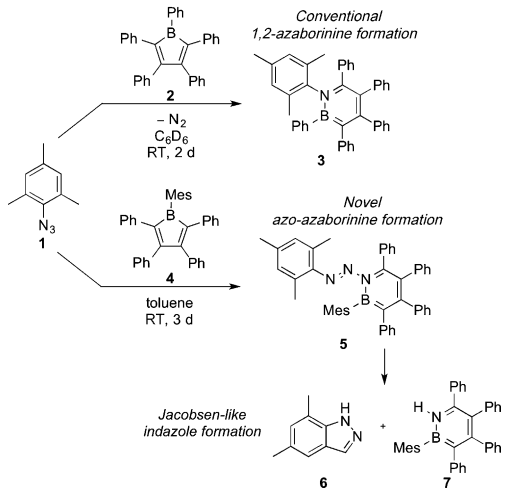


Scheme 1. Two possible pathways for the reaction of mesityl azide with boroles.

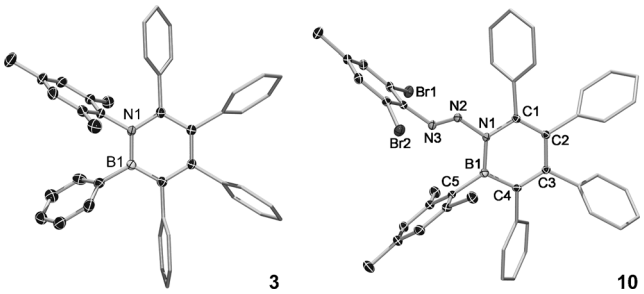
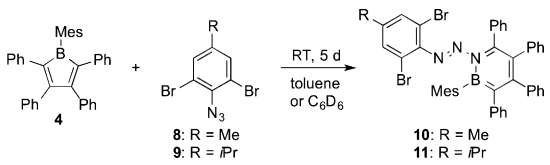


Figure 1. X-ray crystal structures of **3** and **10**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids set at 50% probability. Owing to substitutional disorder in the molecular structure of **3**, the data for **3** can only serve as proof of connectivity and does not allow for a discussion of bond parameters. Selected bond lengths [Å] and angles [°] of **10**: N2–N3 1.241(2), N1–N2 1.435(2), B1–N1 1.443(3), N1–C1 1.396(2), C1–C2 1.373(3), C2–C3 1.443(3), C3–C4 1.384(3), B1–C4 1.525(3); N1-N2-N3 110.2(2), N1-B1-C4 114.3(2), N1-B1-C5 121.8(2), C4-B1-C5 123.4(2), C1-N1-B1 124.3(2), C1-N1-N2 112.6(2), B1-N1-N2 122.7(2).

no evolution of nitrogen gas was observed and an intensely yellow colored product was obtained in good yield (53%) after stirring the reaction mixture for 3 days at room temperature. The ^{11}B NMR chemical shift does not change significantly ($\delta(^{11}B) = 35.1$ ppm) and appears in the range typical for 1,2-azaborinine compounds.[7,13] Analysis by single-crystal X-ray crystallography confirms the formation of an 1,2-azaborinine scaffold (Figure S8), in which the formerly γ-nitrogen atom is incorporated into the six-membered BN-containing heterocycle. Interestingly, the three-nitrogen-atom N_3 arrangement of the former azide unit remains intact. This situation is in contrast both to the conventional de-dinitrogenative ring expansion reported by our group[7] and a result from the group of Martin et al. in which formal three-atom azide incorporation into the five-membered borole ring was observed, resulting in an eight-membered C_4BN_3 heterocycle.[11f] Compound **5** is identified as an 1-(arylazo)-substituted 1,2-azaborinine, which can also be described as a triazene, as it contains a RN=N–NR_2 motif. These classes of compounds are versatile reagents that serve many roles in organic synthesis[14] and are furthermore biologically active.[15] As highlighted below, compound **5** and its more stable derivatives resemble classical azo compounds in many of their properties, such as their optical absorption characteristics and electrochemical behavior.[16] The analogy reflects the isosteric relationship of 1,2-azaborinines and arenes, in which a C=C bond is swapped with an isoelectronic B=N bond.

Compound **5** is unstable in solution at room temperature, decomposing into indazole **6** and 1-hydro-1,2-azaborinine **7** (Scheme 1). The formation of the two products, which is supported by GC/MS (**6**: *m*/*z* 146 [M^+]; **7**: *m*/*z* 501 [M^+]), NMR and UV/Vis spectroscopy (Figure S1–4), involves C–H activation of one of the *ortho* methyl groups on the mesityl residue of the azo substituent. This type of reaction can be described as a Jacobsen-like indazole formation, which usually proceeds from diazoesters of the general formula "Ar-N=N-OR".[17] Similar reactivity has been observed by Erker et al. for a five-membered C_2BNP heterocycle, in which the terminal nitrogen atom of the mesityl azide is analogously incorporated into the ring.[18] Furthermore, in an attempt to characterize **5** in the solid-state by X-ray diffraction, analysis of the crystallographic data revealed that the asymmetric unit not only consists of **5** but also contains about 10% of the reaction products **6** and **7** (Figure S9).

To suppress the subsequent transformation of the azo-azaborinine motif, we replaced the methyl groups in *ortho* position of the aryl azide with bromide substituents. Treatment of 2-azido-1,3-dibromo-5-methylbenzene (**8**) and 2-azido-1,3-dibromo-5-isopropylbenzene (**9**), respectively, with **4** afforded the stable 1,2-azaborinine-substituted azo dyes **10** and **11** in good yields (**10**: 74%, **11**: 61%) after 5 days at room temperature (Scheme 2). Both compounds were isolated as



Scheme 2. Synthesis of azo dyes **10** and **11**.

bright yellow solids and exhibit similar ^{11}B NMR chemical shifts at δ = 36.6 ppm (**10**) and δ = 36.0 ppm (**11**), respectively. In contrast to compound **5**, the 1,2-azaborinine-substituted azo dyes **10** and **11** proved to be stable, with no decomposition observed, even upon heating at 80 °C.

X-ray diffraction analysis of single crystals of **10** and **11** confirmed the formation of azo-azaborinines (Figure 1; see also Figure S10). As a representative example, the solid-state structure of **10** is discussed. All bond lengths and angles within the 1,2-azaborinine core compare well to other reported examples.[4a,7,19] The initially linear N_3 moiety becomes bent (N1-N2-N3 110.2(2)°), adopting a *trans* configuration with a single bond between N1 and N2 (1.435(2) Å) and a double bond between N2 and N3 (1.241(2) Å).[20] In the case of **10** and **11**, the aryl and azaborinine substituents of the azo bridge adopt an angle of 83.4(6)° and 80.9(5)°, respectively, to each other, whereas for **5** an angle of only 48.5(1)° is found

(Figure S11). This structural difference may account for the instability of **5**. The close interaction between the β-N atom and an *ortho*-methyl proton of the mesityl ligand of the azide facilitates C–H bond activation and indazole formation. All the azo compounds (**5**, **10**, and **11**) are in a *trans* configuration, presumably favored by the steric constraint imposed by the bulky substituents on B1 and N3, which also makes photo-induced *trans–cis* isomerization unachievable.[21] Accordingly, the corresponding ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra display only one set of signals and show no evidence of the *cis* isomer.

The UV/Vis spectra of **3**, **10**, and **11** are depicted in Figure 2. The absorption band of **10** and **11** at $\lambda_{max} = 286$ nm (**10**: $\varepsilon = 17707\ L\,mol^{-1}\,cm^{-1}$, **11**: $\varepsilon = 22350\ L\,mol^{-1}\,cm^{-1}$), which can be assigned to the 1,2-azaborinine chromophore, is shifted to slightly smaller wavelengths compared to compound **3** ($\lambda_{max}(\varepsilon) = 314$ nm ($19600\ L\,mol^{-1}\,cm^{-1}$)). Both **10** and **11** show broad absorption maxima in the range typical for aryl azo compounds (**10**: $\lambda_{max}(\varepsilon) = 365$ nm ($4804\ L\,mol^{-1}\,cm^{-1}$), $\lambda_{max}(\varepsilon) = 425$ nm ($2354\ L\,mol^{-1}\,cm^{-1}$); **11**: $\lambda_{max} = 366$ nm ($5988\ L\,mol^{-1}\,cm^{-1}$), $\lambda_{max}(\varepsilon) = 425$ nm ($2910\ L\,mol^{-1}\,cm^{-1}$)) in *trans* configuration, although their corresponding molar extinction coefficients vary significantly (for example, 1,2-dimesityldiazene: $\lambda_{max}(\varepsilon) = 328$ nm ($17500\ L\,mol^{-1}\,cm^{-1}$), $\lambda_{max}(\varepsilon) = 455$ nm ($850\ L\,mol^{-1}\,cm^{-1}$)).[16,21]

Electrochemical characterization by cyclic voltammetry is also in line with the description of **10** and **11** as BN analogues of aromatic azo compounds (Figure S6 and S7). The voltammetric data show an irreversible oxidation around +1.0 V versus Fc/Fc^{+} ($Fc = [(\eta\text{-}C_5H_5)_2Fe]$) characteristic for 1,2-azaborinine structures,[22] and an irreversible reduction peak (**10**: −2.1 V, **11**: −2.0 V, potentials vs. Fc/Fc^{+}), which can be ascribed to reduction of an azo functional group (cf. azobenzene, $E_{1/2} = -1.81$ V vs. Fc/Fc^{+}).[23]

To elucidate the mechanism of azo-azaborinine formation, we carried out DFT calculations for the reaction between azide **8** and the model compound 1-mesityl-2,3,4,5-tetramethylborole (**R2**). The calculations were performed using the B3LYP[24] hybrid functional. The calculated reaction profile is shown in Figure 3. The theoretical data show that the construction of the azo-azaborinine **P1** is initiated by formation of the adduct **I1** (Figure S13), in which borole **R2** binds to the terminal N atom of the azide. The calculated free energy of **I1** is 21.7 kcal mol^{-1}. All attempts to locate a transition state for the formation of **I1** have failed. A systematic scan of the potential energy surface from **8** and **R2** to **I1** showed that it is a barrierless process and that the energy is decreasing in this direction (Figure S16). After initial Lewis acid–base complexation, the reaction proceeds through an early transition state (**TS1**) that resembles the adduct **I1** to afford the azo-azaborinine **P1**. The calculated free energy of activation with respect to **I1** is 3.7 kcal mol^{-1} and the overall activation barrier with respect to **8** and **R2** is 25.4 kcal mol^{-1}. This relatively high free-energy barrier is in good agreement

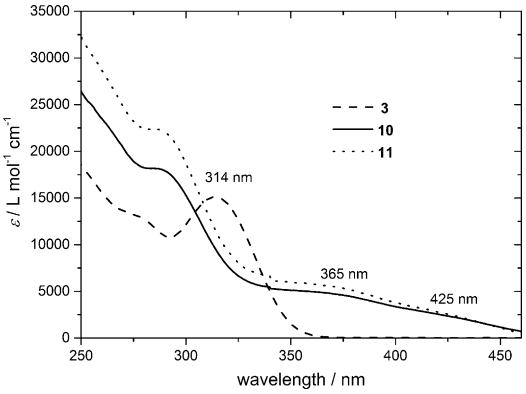


Figure 2. UV/Vis absorption spectra for solutions of **3**, **10**, and **11** in CH_2Cl_2.

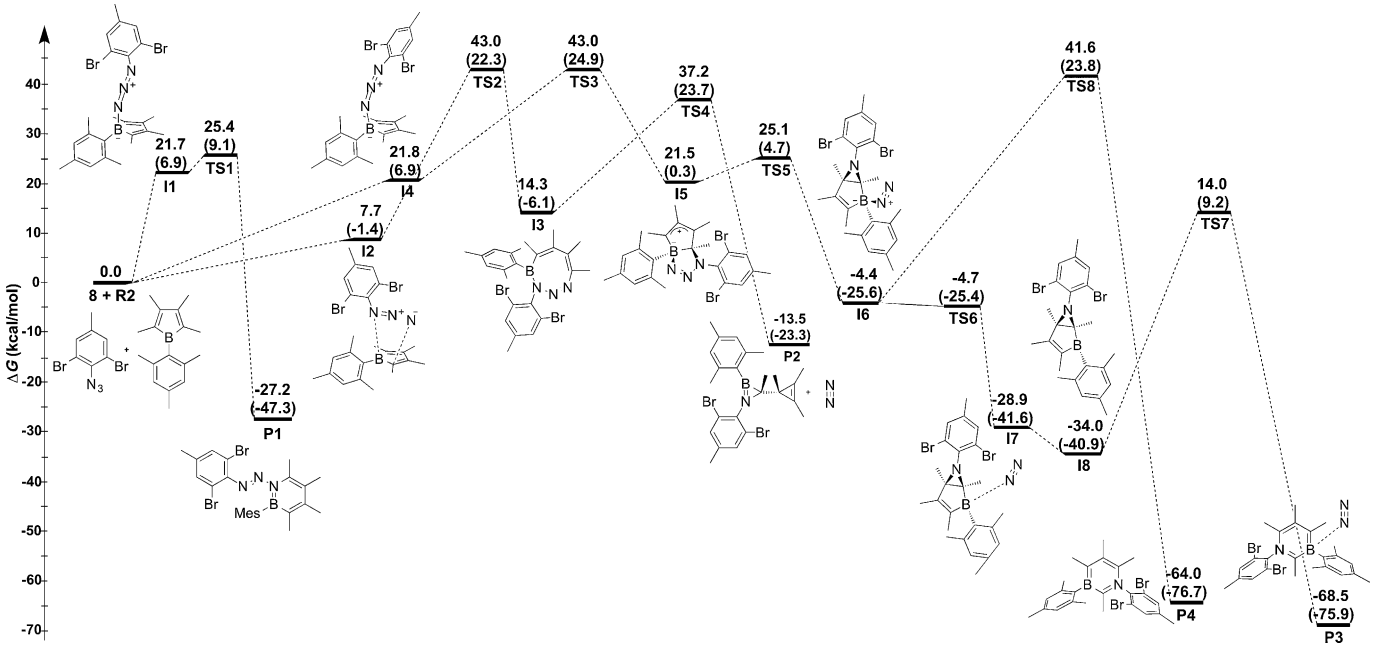


Figure 3. Calculated Gibbs free energy profile (kcal mol^{-1}) of azo-azaborinine formation together with two alternative pathways for the possible 1,3-dipolar cycloaddition reactions at B3LYP/def2-SVP. The energies are shown in parentheses.

with the experimental observation of a slow conversion of the reagents into the azo-azaborinine products, which is completed after 3–5 days at room temperature. The free energy of the reaction is exothermic by 27.2 kcal mol^{-1}.

We have also considered the attack of the α-nitrogen to the B atom, as previously reported,[11f] but all attempts to locate a transition state failed and a systematic scan of the potential energy surface from **8** and **R2** to the corresponding adduct showed that the energy is increasing in this direction (see Figure S17). During the geometry optimization of this adduct, the structure decomposed to form **8** and **R2**. We attribute this difference to steric repulsions between the *ortho* bromide substituents of the azide and the mesityl substituent at the boron center, thus preventing conventional adduct formation.

For a more complete picture, we have also considered the 1,3-dipolar cycloaddition reaction between **8** and **R2** (see the Supporting Information for details). Although the (3+2) cycloaddition across the B–C bond forms a more stable adduct (**I2**) compared to **I1**, its activation barrier (35.3 kcal mol^{-1}) along the reaction pathway to product **P2** is higher than for azo-azaborinine formation. Similarly, the overall barrier of the first step of a second possible 1,3-dipolar cycloaddition is considerably higher than the barrier of the azo-azaborinine formation reaction. Connected to this pathway are the thermodynamically most stable 1,3-azaborinine products **P3** and **P4**. Their formation from **8** and **R2** is, however, kinetically disfavored. It is worth noting that the 1,3-dipolar cycloaddition reaction between these sterically more hindered substrates does not lead to 1,2-azaborinines.

In conclusion, we have presented the synthesis of the first azo dyes based on 1,2-azaborinines by ring expansion of 1-mesityl-2,3,4,5-tetraphenylborole (**4**) with different *ortho*-substituted phenyl azides. The corresponding azo-azaborinines are bright yellow solids and show UV/Vis absorption bands typical of azo dye compounds. Theoretical mechanistic studies suggest that the reaction proceeds through a new type of borole ring expansion involving a key step consisting of the addition of the terminal N atom of the aryl azide to the Lewis acidic borole. The calculations showed that the steric restraints imposed by the *ortho* substituents on the aryl ligands of both the borole and azide molecule are the reasons for the kinetically favored azo-azaborinine formation. Our future efforts will include the investigation of the electronic structure and chemical reactivity of this new class of compounds.

Keywords: azo compounds · boron · heterocycles · reaction mechanism · ring expansion

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