# Diboryldiborenes: $\pi$-Conjugated $B_4$ Chains Isoelectronic to the Butadiene Dication

Alexander Hermann, Jessica Cid, James D. Mattock, Rian D. Dewhurst, Ivo Krummenacher, Alfredo Vargas,* Michael J. Ingleson,* Holger Braunschweig*

***Abstract:*** *$sp^2$–$sp^3$ diborane species based on bis(catecholato)diboron and N-heterocyclic carbenes (NHCs) are subjected to catechol/bromide exchange selectively at the $sp^3$ boron atom. The reduction of the resulting 1,1-dibromodiborane adducts led to reductive coupling and isolation of doubly NHC-stabilized 1,2-diboryldiborenes. These compounds are the first examples of molecules exhibiting $\pi$-electron delocalization over an all-boron chain.*

Molecules featuring two-atom $2\pi$-electron systems (e.g. alkenes, diazo compounds) are well known. However, addition of further $\pi$ orbitals to a $2\pi$-electron system makes the resulting molecules less stable and consequently much rarer. While aromatic, cyclic three-atom $2\pi$-electron systems such as cyclopropenium cations (*cyclo*-$[C_3R_3]^+$), their heavier analogues[1] and borirenes (*cyclo*-$[BC_2R_3]$)[2] are relatively stable, acyclic examples such as the allyl cation ($[C_3R_5]^+$),[3] its trisila analogue ($[Si_3R_5]^+$),[4] *cyclo*-($E_3R_3$) dianions (E = B, Ga),[5,6] and a triborane(3)[7] are either transient or highly reactive. Adding a further empty $\pi$ orbital, resulting in a four-atom $2\pi$-electron system, is even less favorable in terms of stability. Syntheses of cyclobutadiene dications (**A**, Figure 1) have been reported,[3a] however, despite their nominal aromaticity, their instability has precluded structural authentication. Neutral, Group 13 analogues of cyclobutadiene dications, such as 1,3-diboretes (**B**, Figure 1)[8] and a 1,2-dialuminacyclobutene (**C**)[9] have been structurally confirmed, although both feature strongly puckered structures suggesting reduced delocalization and aromaticity.

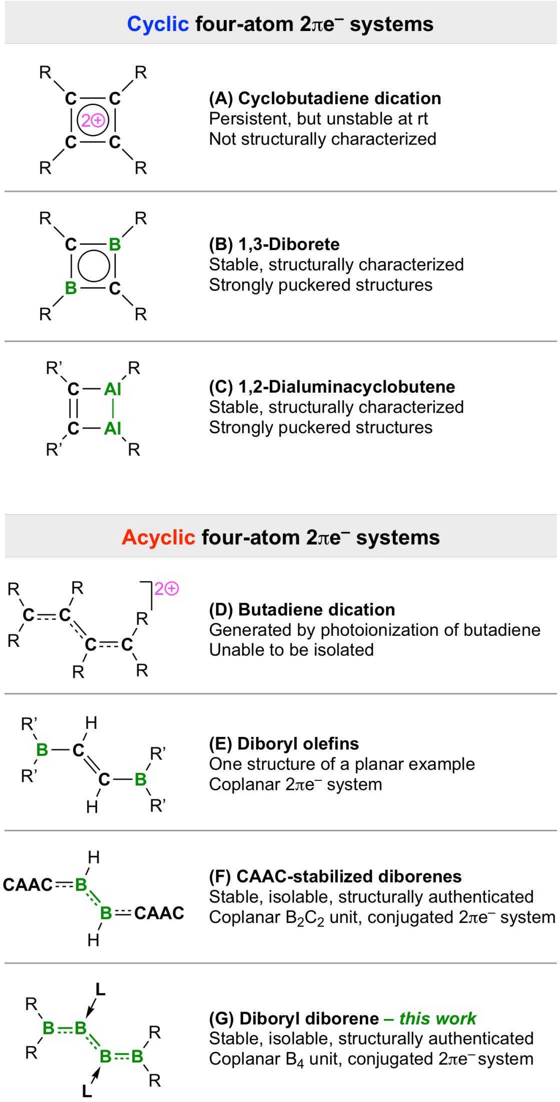

**Figure 1**. Cyclic (top) and acyclic (bottom) four-atom $2\pi$-electron systems. CAAC = cyclic (alkyl)(amino)carbene.

The relative instability of these cyclic, formally aromatic species makes it somewhat unsurprising that *acyclic* compounds featuring conjugated, four-atom $2\pi$-electron systems are even less well represented. The generation of the butadiene dication ($[C_4R_6]^{2+}$; **D**, Figure 1) – the acyclic derivative of **A** – has been inferred by its decomposition products after double photoisomerization of butadiene. However, such a species has thus far not been isolated.[10] While diboryl olefins such as **E** (Figure 1) almost exclusively feature non-coplanar $B_2C_2$ units, one example (*E*-CatBC(H)C(H)BCat) has been uncovered with a coplanar $B_2C_2$ unit.[11] A dihydrodiborene species stabilized by two strongly $\pi$-withdrawing cyclic (alkyl)(amino)carbene[12] (CAAC[CAAC]) donors (**F**, Figure 1)[13-15] is a further example of a

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[*] A. Hermann, Dr. R. D. Dewhurst, Dr. I. Krummenacher, Prof. Dr. Braunschweig
Institute for Inorganic Chemistry
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
E-Mail: h.braunschweig@uni-wuerzburg.de
and
Institute for Sustainable Chemistry & Catalysis with Boron
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)

Dr. J. Cid, Dr. M. J. Ingleson
School of Chemistry, University of Manchester
Manchester, United Kingdom
E-Mail: michael.ingleson@manchester.ac.uk

J. D. Mattock, Dr. A. Vargas
Department of Chemistry, School of Life Sciences, University of Sussex, Brighton BN1 9QJ, Sussex, United Kingdom
E-Mail: alfredo.vargas@sussex.ac.uk

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four-atom ($B_2C_2$) 2π-electron system. The extreme rarity of molecules with conjugated four-atom 2π-electron systems thus makes the isolation of such compounds a worthy synthetic goal.

Chains of *sp*$^2$-hybridized boron atoms by definition have a contiguous π system comprising the *p* orbitals of the boron atoms, although the degree to which these orbitals are conjugated will likely be attenuated by steric concerns and the π-donor strength of the atoms attached to the boron atoms. Nevertheless, such compounds present the exciting possibility of filling (or partially filling) their extended π systems with electrons. Such a goal is as yet unrealized, as compounds with B(*sp*$^2$) chains are exceedingly rare and difficult to prepare.[14] Only five structurally-characterized compounds exist containing a chain (or ring) of four or more tricoordinate boron atoms, the longest being the *cyclo*-hexaborane $B_6(NMe_2)_6$.[16] While all of these compounds feature electronic stabilization from π-donor substituents, none of them feature π electrons in the $B_4$ π system or any degree of B-B multiple bonding.

In this work we present the synthesis of doubly carbene-stabilized diboryl diborenes, of the form $[B_2(BCat)_2(NHC)_2]$ (BCat = catecholboryl; NHC = N-heterocyclic carbene; **G**, Figure 1). In these compounds, the two diborene π electrons are significantly delocalized towards the adjacent boryl groups, leading to a reduced central B-B bond order and increased outer B-B bond orders. The compounds are very rare examples of acyclic compounds featuring conjugated four-atom 2π-electron systems and the first examples of molecules exhibiting π-electron delocalization over an all-boron chain.

The addition of a single molar equivalent of a strong donor ligand to diboranes(4) has recently become an area of interest in organoboron chemistry, leading in many cases to sp$^2$–sp$^3$ diborane species with nucleophilic boron atoms.[17] In 2015, Ingleson, Radius and Marder reported that reaction of equimolar amounts of bis(catecholato)diboron ($B_2Cat_2$) with the relatively small and strongly σ-donating NHC 1,3,4,5-tetramethylimidazol-2-ylidene (IMe$^{Me}$) provided the sp$^2$–sp$^3$ diborane **1a** (Figure 2).[18] The stability of this species led us to attempt the exchange of one of its catecholyl groups with halides, in order to open up one or both boron atoms for further functionalization. Thereby, equimolar amounts of **1a** and $BBr_3$ were combined at –30 ºC, providing a colorless solid (**2a**) with $^{11}$B NMR spectroscopic signals at δ 36.3 and –13.7. While the position of the low-field signal of **2a** is little changed from that of its precursor **1a** (δ 38.6, 7.11), the high-field signal has shifted significantly upfield, suggesting that catechol/halide exchange had occurred exclusively at one boron atom.

These synthetic protocols were extended to the synthesis of three further sp$^2$–sp$^3$ diboranes, **1b-d** (Figure 2), bearing NHCs 1,3-dimethylimidazol-2-ylidene (IMe), 1,3-di*iso*propylimidazol-2-ylidene (I*i*Pr), and 1,3-dimesitylimidazol-2-ylidene (IMes), respectively. The dicatechol sp$^2$–sp$^3$ diboranes **1b-d**[19] were subsequently subjected to catechol/halide exchange, forming dibromo sp$^2$–sp$^3$ diboranes **2b-d** (Figure 2) in excellent yields (82-99%). The dicatechol sp$^2$–sp$^3$ diboranes **1b-d** showed $^{11}$B NMR spectral features analogous to those of **1a** (**1b**: δ 37.1, 6.82; **1c**: δ 37.6, 7.43; **1d**: δ 35.2, 5.90). Likewise, the $^{11}$B NMR data of dibromo sp$^2$–sp$^3$ diboranes **2b-d** matched those of **2a** (**2b**: δ 36.5, –14.7; **2c**: δ 36.0, –14.0; **2d**: δ 35.3, –14.7). The crystallographically-derived solid-state structures of **2a-c** (Figure 3) confirmed the successful catechol/halide exchange.

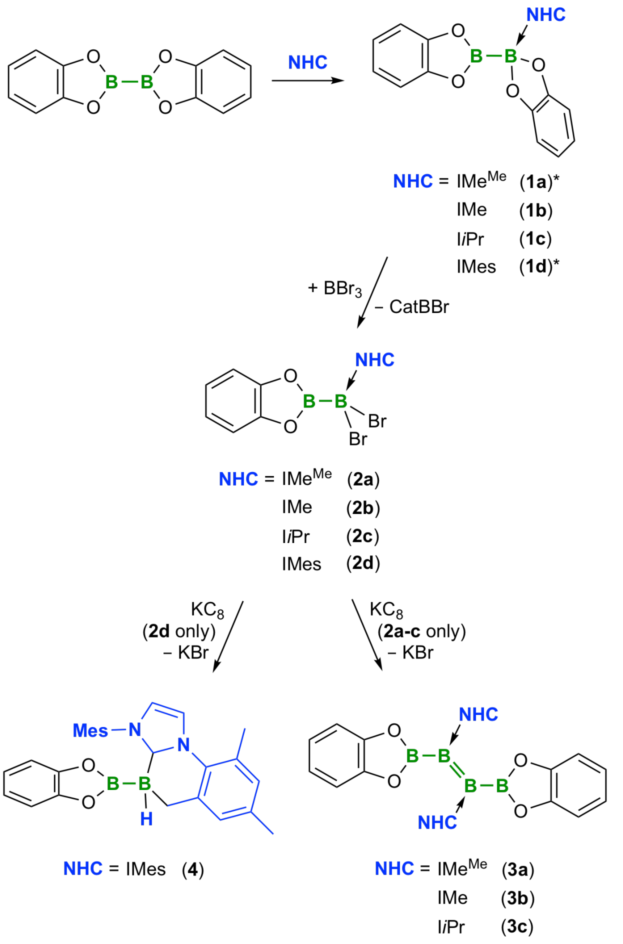

**Figure 2**. Synthesis of diborane carbene monoadducts **1a-d**, their double halide exchange products **2a-d**, diboryl diborenes **3a-c** and C-H activation product **4**. *The syntheses of compounds **1a,d** were reported previously.[18,19]

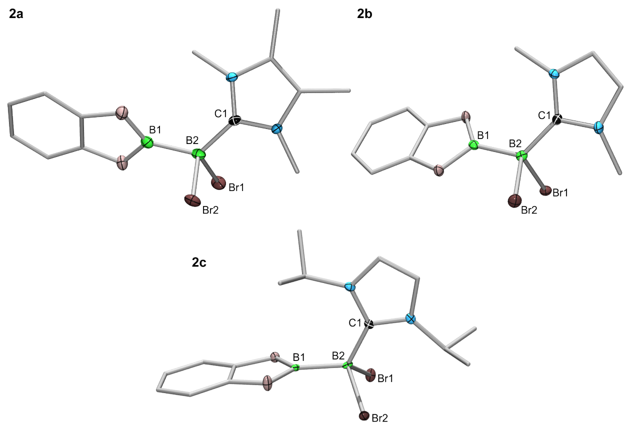

**Figure 3.** Crystallographically derived structures of **2a-c**. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms and solvent molecules (if present) have been removed for clarity. Selected bond lengths (Å) and angles (º) for **2a**: B1-B2 1.681(5), B2-C1 1.601(4). For **2b**: B1-B2 1.699(4), B2-C1 1.594(3). For **2c**: B1-B2 1.788(4), B2-C1 1.616(4).

The synthesis of dibromocatechol diborane adducts **2a-d** provided promising precursors for their chemical reduction. Reduction of NHC-stabilized dihalodiboranes is to date the most reliable method to prepare doubly NHC-stabilized diborenes.[13,14] However, extending this reduction strategy to their diborane analogues, 1,1-dihalo-1-NHC-diboranes, has thus far only led to C-H activated diborane(5) products with bridging organic and hydride groups.[20] We reasoned that by avoiding the use of IMes bound at or near the $BX_2$ site, we may be able to circumvent the C-H activation pathway and generate the hypovalent reduction products, either the doubly NHC-stabilized diborene or perhaps even the corresponding carbene-stabilized borylborylene invoked in previous studies.[20]

Reduction of mesityl-free $sp^2$–$sp^3$ diboranes **2a-c** provided highly-colored reaction mixtures and orange (**3a**, Figure 2) or bright yellow (**3b,c**) solids after filtration and crystallization in modest to good yields (26-76%). However, it should be noted that all samples contained small amounts of unidentified byproducts originating from the reduction process. These impurities could not be removed by recrystallization (with prolonged storage in solution leading to decomposition of **3a-c**) or other methods. The $^{11}$B NMR spectra of the solids each showed two broad singlets (**3a**: $\delta$ 43.5, 27.1; **3b**: $\delta$ 41.9, 27.5; **3c**: $\delta$ 42.1, 27.2). The high-field signal of each compound can be attributed to the diborene boron nuclei, although this signal is found slightly to lower field than those of reported diborenes bearing conventional NHC donors (i.e. with unsaturated backbones; ca. $\delta$ 19-25).[13,14] Interestingly, the $^{11}$B NMR resonances of the -BCat boron nuclei are shifted to low field upon reduction, suggesting depletion of electron density at these centers.

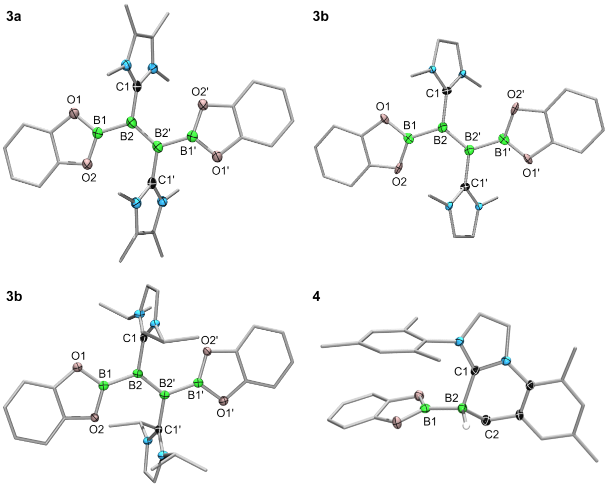

**Figure 4.** Crystallographically derived structures of diborenes **3a-c** and C-H activation product **4**. Ellipsoids shown at the 50% probability level. Some ellipsoids and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°) for **3a**: B1-B2 1.658(3), B2-B2' 1.582(4), B2-C1 1.579(3), ∠(CBB/OBO planes) 7.0. For **3b**: B1-B2 1.676(6), B2-B2' 1.592(9), B2-C1 1.600(6), ∠(CBB/OBO planes) 13.9. For **3c**: B1-B2 1.645(3), B2-B2' 1.596(4), B2-C1 1.582(2), ∠(CBB/OBO planes) 10.5. For **4**: B1-B2 1.691(6), B2-C1 1.591(5), B2-C2 1.638(5).

The solid-state structures of **3a-c** (Figure 4) confirm the reductive coupling of two diboron units to form effectively coplanar $B_4$ chains, with very acute angles between the C1B2B2' and O1B1O2 planes (**3a**: 7.0°; **3b**: 13.9°; **3c**: 10.5°). The diborenes show short central B-B bonds (**3a**: 1.582(4) Å; **3b**: 1.592(9) Å; **3c**: 1.596(4) Å), with longer outer B-B bonds (**3a**: 1.658(3) Å; **3b**: 1.676(6) Å; **3c**: 1.645(3) Å). While the B=B distances of **3a-c** are indistinguishable with those of other doubly NHC-stabilized diborenes within experimental uncertainty,[14] the outer B-B bonds are slightly shorter than those of precursors **2a-c** (**2a**: 1.681(5) Å; **2b**: 1.699(4) Å; **2c**: 1.788(4) Å). The B=B distances of **3a-c** are, however, significantly shorter than that of a diborene stabilized by two strongly $\pi$-withdrawing cyclic (alkyl)(amino)carbene (CAAC) donors and featuring significant delocalization over the $B_2C_2$ unit (1.625(2) Å).[15]

In order to quantify the extent of delocalization of B=B $\pi$ electron density towards the $\pi$-withdrawing BCat groups, Kohn-Sham Density Functional Theory (DFT) calculations on **3a-c** were undertaken at the OLYP/TZ2P level. The calculated Mayer bond orders of the central B=B bonds of **3a-c** (**3a**: 1.480; **3b**: 1.477; **3c**: 1.479) lie between those of *iso*propyl- and 2-thienyl-substituted diborenes [$B_2$*i*$Pr_2$(I*i*Pr)$_2$] (**I**; 1.632) and [$B_2$(2-$C_4H_3S$)$_2$(I*i*Pr)$_2$] (**II**; 1.424), respectively, calculated for comparison (see Supporting Information). Where the diboryldiborenes **3a-c** significantly differ from the non-boryl examples **I** and **II** is in the Hirshfeld charge at the B=B atoms (**3a**: –0.173; **3b**: –0.172; **3c**: –0.169; **I**: –0.124; **II**: –0.116). The much more negative charge on the B atoms of **3a-c** can be ascribed to the better $\sigma$-donating properties of the attached boryl groups.

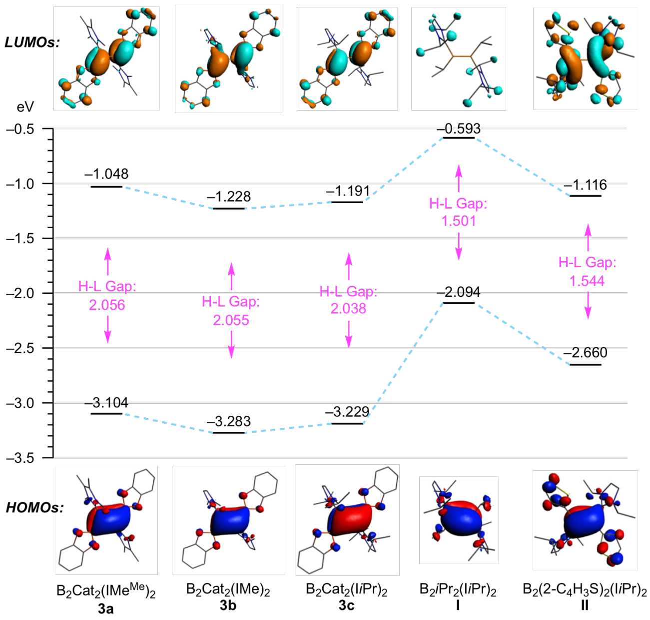

**Figure 5.** Depictions of the HOMOs and LUMOs of diborenes **3a-c**, **A** and **B**, their corresponding orbital energies and HOMO-LUMO (H-L) gaps, as derived from DFT calculations.

As a measure of conjugation across the $B_4$ chain, the outer B-B bonds were calculated to have orders above unity (**3a**: 1.141; **3b**: 1.128; **3c**: 1.141), suggesting significant $B^{inner}$-$B^{outer}$ multiple bonding and/or enhanced $\sigma$-bonding due to the strongly $\sigma$-donating BCat units. The calculated HOMO levels of **3a-c** effectively comprise the 2$\pi$-electron system stretched across the $B_4$ chain (Figure 5), while the energies of these orbitals (**3a**: –3.104; **3b**: –3.283; **3c**: –3.229 eV) are significantly lower than those of NHC-bound alkyl and aryl diborenes (**I**: –2.094; **II**: –2.660 eV). The low HOMO energies of **3a-c** are also reflected electrochemically, in the fact that **3b** (–0.95 V, see Supporting Information) is substantially more difficult to oxidise than other NHC-bound diborenes (e.g. **I**: –1.95 V; [$B_2Dur_2(IMe)_2$] –1.55 V).[21] As boryl units are known to be extremely strong $\sigma$-donors, one would expect the HOMO levels of **3a-c** to be destabilized, similar to that of the alkyl-substituted diborene **I**. That the HOMOs of **3a-c** are instead strongly stabilized suggests that the $\pi$ donation from the B=B bond to the outer boron atoms outweighs the $\sigma$ donation of the latter. Overall, the $\sigma$-acceptor / $\pi$-donor properties of the B=B unit are in line with the previously-discussed ability of hypovalent boron atoms to act as multisymmetry (i.e. $\sigma/\pi$) charge-flux-mediating centers.[2,22]

As expected, analogous reduction of mesityl-containing $sp^2$–$sp^3$ dibromodiborane **2d** led to C-H activation at one of the proximal methyl groups and formation of **4** (Figure 2), as evidenced by the absence of a highly colored reaction mixture, and by $^{11}$B NMR spectroscopy, which showed a clear doublet at high field due to B-H coupling ($\delta$ –33.0; $^1J_{BH}$ = 73.4 Hz) along with a broad singlet at low field ($\delta$ 42.1). Interestingly, the former signal is found significantly upfield, and the latter significantly downfield, of the corresponding signals of **2d** ($\delta$ 35.3, –14.7). The $^{11}$B NMR spectral features of **4** also distinguish this compound from the aforementioned reduction products featuring B-B units bridged both by organic groups and a single hydride ($\delta$ 53.1, 1.5 and $\delta$ 55.8, 2.6).[20] The solid-state structure of **4** (Figure 4) confirmed the C-H activation process and the presence of an unbridged B-B unit.

In conclusion, we have presented the synthesis of new $sp^2$–$sp^3$ diborane species based on bis(catecholato)diboron, their catechol/halide exchange products, and the reductive coupling products of the latter: doubly NHC-stabilized 1,2-diboryldiborenes. These compounds are the first examples of molecules exhibiting $\pi$-electron delocalization over an all-boron chain. The observed $\pi$-delocalization in these $B_4$ chains is an exciting discovery which points to the possible future synthesis of extended $\pi$-conjugated boron chains and polymers with interesting electronic properties. Furthermore, the presence of two BCat groups in these molecules presents interesting possibilities in terms of their further functionalization, analogous to the extensive use of boronate ester groups in organic chemistry.

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**Keywords:** diboranes; diborenes; N-heterocyclic carbenes; boron chains; $\pi$-conjugation

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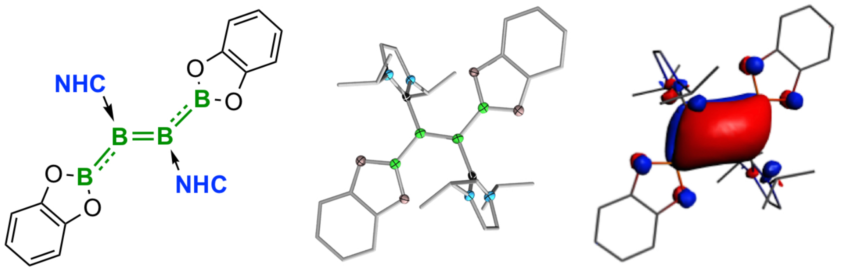

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