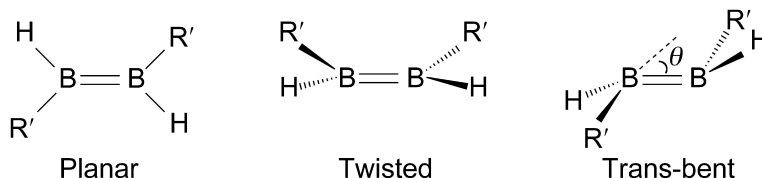


Planar, Twisted, and Trans-Bent: Conformational Flexibility of Neutral Diborenes

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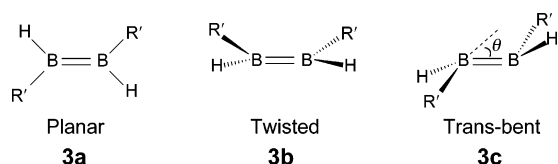
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Realization of the fascinating potential of boron homonuclear multiple bond chemistry has long frustrated chemists.^{1–3} Boron–boron double bonds are represented by two olefin-like classes of compounds: (1) the isoelectronic diboron dianions, $[R_2BBR_2]^{2-}$, and (2) the Lewis base-stabilized neutral diborene complexes, $L(H)B=B(H)L$ (L = Lewis base). Although diboron dianions and their alkali metal salts were proposed as promising $B=B$ double bond candidates two decades ago,⁴ corroborating synthetic and structural evidence has been rare.^{5–7} In contrast, neutral Lewis base-stabilized diborenes are attractive alternatives. While the highly reactive parent neutral diborene(2), $HB=BH$,⁸ has only been characterized in matrices,⁹ complexation with appropriate Lewis base ligands is a promising approach to viable $L(H)B=B(H)L$ derivatives. Although the theoretical development of BCO chemistry^{10–14} included the computational prediction of the carbonyl-stabilized diborene, $OC(H)B=B(H)CO$,¹² such complexes have not been experimentally realized. In this regard, bulky N-heterocyclic carbene (NHC) ligands are attractive due to their strong electron-donating properties coupled with their ability to provide effective protection to the $HB=BH$ core.^{15,16}

Our recent potassium graphite reduction of $RBBR_3$ ($R = :C\{N(2,6-Pr^i_2C_6H_3)CH\}_2$) afforded $R(H)B=B(H)R$, **1**, the first structurally characterized neutral diborene as well as a diborene complex, $R(H)_2B-B(H)_2R$, **2**.¹⁷ We now utilize a less bulky NHC ligand ($R' = :C\{N(2,4,6-Me_3C_6H_2)CH\}_2$) to prepare the second neutral diborene, $R'(H)B=B(H)R'$, **3**, as well as the corresponding $R'(H)_2B-B(H)_2R'$ diborene, **4**. In contrast to planar diborene **1**, the new diborene, **3**, exhibits remarkable conformational variations in the solid state. X-ray determinations of three different crystals reveal not only planar (**3a**) but also twisted (**3b**) and trans-bent (**3c**) molecular structures! Herein we report these results and the computational examination of **3** and **4**.^{18,19}



While trans-bent geometries of the heavier group 13 dianionic alkene analogues, $[H_2E=EH_2]^{2-}$ ($E = Al, Ga, In$), are predicted to be favored over planar alternatives,²⁰ both diboron dianions ($E = B$)^{4–7} and the Lewis base-stabilized neutral diborenes (**1** and $OC(H)B=B(H)CO$)^{12,17} prefer planar geometries. Hence, the twisted (**3b**) and trans-bent (**3c**) structures of **3** are unexpected. The pyramidal tricoordinate boron atoms in **3c** contrast with the predominant trigonal planar geometries. Indeed, pyramidal boron environments have only been reported in cyclic systems.²¹

Our earlier study showed that the $RBBR_3:KC_8$ ratio affects the diborene yield.¹⁷ The reaction of $R'BBR_3$ with KC_8 in a 1:5 ratio in

Et_2O resulted in isolation of red-colored **3** (15.8%), together with colorless **4**, $R'(H)_2B-B(H)_2R'$. Reduction using a $R'BBR_3:KC_8$ ratio of 1:6.2 only resulted in **4**. Similar to the formation of **1** and **2**,¹⁷ the preparation of **3** and **4** involves the well-documented hydrogen abstraction from ethereal solvents in the presence of alkali metals. Both **3a**, as black red crystals, and **3b**, as ruby-colored crystals, were isolated from the 1:5 Et_2O /hexane solvent mixture, while **3c** was crystallized from the parent Et_2O solution. Despite their three different conformations in the solid state, **3a–c**, exhibit identical 1H and ^{11}B NMR spectra in C_6D_6 solution. Furthermore, the broad singlet ^{11}B NMR resonance of **3** (+23.45, $w_{1/2} = 587$ Hz) corresponds to that of diborene **1** (+25.30, $w_{1/2} = 946$ Hz). The 1H NMR imidazole resonances of **3** and **4** are 5.96 and 5.91, respectively. There is no evidence for different isomers or states of **3** in solution. We conclude that **3a–c** are polymorphs—the same compound crystallizing in different forms.²² The space groups for **3a–c** are $P2_1/c$, $P-1$, and $P2_1/c$, respectively, and their packing patterns are completely different.¹⁸

The ^{11}B signal of **4** (–31.20) is a triplet ($J_{BH} = 83.38$ Hz) like that of diborene **2** (–31.62).¹⁷ The core of **4** consists of two tetrahedral $C(H)_2B$ units connected by a boron–boron single bond (1.795(5) Å).¹⁸ Evidently due to the smaller steric repulsion between the carbene ligands, the B–B distance in **4** is shorter than that in **2** (1.828(4) Å).

The trans-bent $C(H)B=B(H)C$ boron–boron double bond is the most remarkable structural feature of **3c** (Figure 1). Its trans-bending angle, $\theta = 36^\circ$, is the same as that in the heavier Group 14 ethylene congener, $[R(Mes)Ge=Ge(Mes)R]$ ($R = 2,6-Pr^i_2C_6H_3$).²³ The central B=B bond distance in **3c** (1.679(9) Å) is 0.116 Å shorter

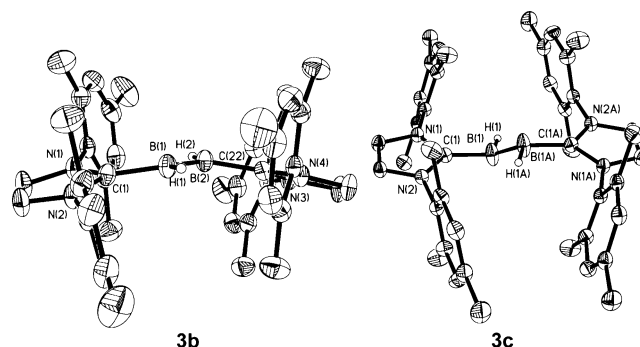


Figure 1. Molecular structures of **3b** and **3c** (thermal ellipsoids represent 30% probability; hydrogen atoms on carbon are omitted for clarity). Selected bond distances (Å) and angles (deg): For **3b**, B(1)–B(2) 1.582(4), B(1)–C(1) 1.541(4), B(2)–C(22) 1.541(4), B(1)–H(1) 1.117(17), B(2)–H(2) 1.12(3); C(1)–B(1)–B(2) 125.0(2), C(1)–B(1)–H(1) 109.9(16), B(2)–B(1)–H(1) 124.9(16), C(22)–B(2)–B(1) 125.1(2), C(22)–B(2)–H(2) 107.0(15), B(1)–B(2)–H(2) 127.2(15). For **3c**, B(1)–B(1A) 1.679(9), B(1)–C(1) 1.565(5), B(1)–H(1) 1.109(18); C(1)–B(1)–B(1A) 118.6(5), C(1)–B(1)–H(1) 107.7(19), H(1)–B(1)–B(1A) 118(2).

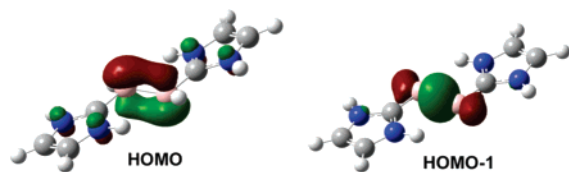


Figure 2. Representation of the frontier orbitals of trans-bent **3c**.

than that of the corresponding B–B single bond of **4** (1.795(5) Å), but it is about 0.1 Å longer than those in **1** (1.560(18) Å, av), in dianionic (tetraamino)diborates⁷ (1.566(9) to 1.59(1) Å), and in OC(H)B=B(H)CO (1.590 Å, computed).¹² Notably, the B=B bond distance of **3c** is only about 0.05 Å longer than in [Mes₂BB-(Mes)Ph]²⁻ (1.636(11) Å)⁵ and [{Ph(Me₂N)BB(NMe₂)Ph}]²⁻ (1.627 Å, av).⁶ Each boron atom in **3c** is pyramidal with a 344.3° bond angle sum. As far as we are aware, **3c** is the first example of pyramidal tricoordinate boron in an acyclic environment. The cyclic silaborirane, CH₂SiH₂BH,²⁴ and its analogs have been computed to have pyramidal geometries due to heteroatom–boron p orbital interactions. Constrained systems like 1-boraadamantane²⁵ necessarily have nonplanar boron geometries.

In contrast to the trans-bent structure of **3c**, isomer **3a** possesses the same planar C(H)B=B(H)C core as observed in **1**.¹⁸ Each boron atom in **3b** (Figure 1) also has a planar tricoordinate environment. However, **3b** adopts a twisted geometry with a 18.1° dihedral angle between the two CBH planes. The B=B double bond distance of **3b** (1.582(4) Å) is similar to those of **1** (1.560(18) Å (av)) and **3a** (1.602(5) Å). Remarkably, the B=B bond distance in the crystal structure of **3c** (1.679(9) Å) is about 0.1 Å longer. The boron–boron double bond character of **3** is further supported by the $\pi_{B=B} - \pi_{*B=B}$ absorption ($\lambda_{\max} = 574$ nm).

The B3LYP/6-311+G** DFT optimization of **3c**,¹⁹ starting with the X-ray coordinates, led to a planar geometry and a B=B bond distance of 1.605 Å, essentially identical with the experimental value (1.602(5) Å) of planar **3a**. The polymorphism exhibited by **3** may be attributed to the combination of a number of factors including (1) the flat potential energy surface; (2) the packing effects in crystals;^{26,27} (3) the polarity of the solvent used for crystallization; and (4) the intramolecular steric repulsion of the carbene ligands. The different packing patterns of **3a–c** suggest that the associated distinct packing effects may contribute to the stabilization of these polymorphs.¹⁸ Differences in solvent polarity are known to significantly affect conformational isomerism of molecular²⁸ and supramolecular²⁹ systems. Indeed, **3a** and **3b** were isolated from 1:5 Et₂O/hexane solvent mixtures, whereas **3c** was crystallized from pure Et₂O. Compared to the more sterically demanding ligands in **1**, the smaller ligands in **3** can adjust their orientations more easily to packing forces.

Our numerous computations¹⁹ employing simplified ligand models R''(H)B=B(H)R'' (R'' = :C(NRCH)₂, with R = H or CH₃) confirmed the flatness of the potential energy surface. The planar **3a** models had C_{2h} symmetry. The C_i models for trans-bent **3c** optimized to the same C_{2h} geometries. The only minimum (in C₂ symmetry) corresponding to **3b** (R = CH₃) had a small planarization barrier. Consequently, the X-ray coordinates of **3c** were used for the MO model shown in Figure 2. Boron–boron π -bonding dominates the HOMO, while the HOMO-1 has mixed B–B and B–H σ bonding character (Figure 2). The Wiberg (1.445) and NLMO/NPA (1.515) B–B bond indices, comparable to those

reported for **1** (1.408 and 1.656, respectively), support the presence of a B=B double bond in **3c** despite its ca. 0.1 Å boron–boron elongation and trans-bent geometry. The distortion exhibited by **3c** does not decrease the boron–boron bond order substantially and supports the dictum “the electronic structure, rather than bond distances, determines the nature of multiple bonds”.³⁰

The experimental realization of three distinct polymorphic structures of diborene **3** may be attributed to a combination of, inter alia, packing effects in the crystal, crystallizing-solvent polarity, and intramolecular ligand steric effects.

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Supporting Information Available: Full details of the syntheses, computations, and X-ray crystal determination, including the cif files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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