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

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Realization of the fascinating potential of boron homonuclear multiple bond chemistry has long frustrated chemists.¹⁻³ Boronboron 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 basestabilized 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)Lderivatives. Although the theoretical development of BCO chemistry¹⁰⁻¹⁴ 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 RBBr₃ (R = $:C\{N(2,6-Pr_{2}^{i}C_{6}H_{3})CH\}_{2})$ afforded R(H)B=B(H)R, **1**, the first structurally characterized neutral diborene as well as a diborane complex, R(H)₂B-B(H)₂R, **2**.¹⁷ We now utilize a less bulky NHC ligand (R' = $:C\{N(2,4,6-Me_{3}C_{6}H_{2})CH\}_{2})$ to prepare the second neutral diborene, R'(H)B=B(H)R', **3**, as well as the corresponding R'(H)₂B-B(H)₂R' diborane, **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 RBBr₃:KC₈ ratio affects the diborene yield.¹⁷ The reaction of R'BBr₃ with KC₈ in a 1:5 ratio in

Et₂O resulted in isolation of red-colored 3 (15.8%), together with colorless 4, R'(H)₂B-B(H)₂R'. Reduction using a R'BBr₃:KC₈ 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 Et₂O/hexane solvent mixture, while 3c was crystallized from the parent Et₂O solution. Despite their three different conformations in the solid state, 3a-c, exhibit identical ¹H and ¹¹B NMR spectra in C₆D₆ solution. Furthermore, the broad singlet ¹¹B 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 $3\mathbf{a} - \mathbf{c}$ 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 ¹¹B signal of **4** (-31.20) is a triplet ($J_{BH} = 83.38$ Hz) like that of diborane **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-Pri₂C₆H₃).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(1A) 118.6(5), C(1)–B(1)–H(1) 107.7(19), H(1)–B(1)–B(1A) 118(2).

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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 $[{Ph(Me_2N)BB(NMe_2)Ph}]^{2-}$ (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 boronboron 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 CH_3) 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 C_2 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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