J|A|C|S
COMMUNICATIONS

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

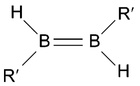
Yuzhong Wang, Brandon Quillian, Pingrong Wei, Yaoming Xie, Chaitanya S. Wannere,
R. Bruce King, Henry F. Schaefer, III, Paul v. R. Schleyer,* and Gregory H. Robinson*

*Department of Chemistry and the Center for Computational Chemistry, The University of Georgia,
Athens, Georgia 30602-2556*

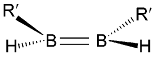
Received January 11, 2008; E-mail: robinson@chem.uga.edu

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]

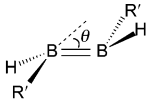
Our recent potassium graphite reduction of $RBBr_3$ (R = :C{N(2,6-$Pr^i_2C_6H_3$)CH}$_2$) afforded R(H)B═B(H)R, **1**, the first structurally characterized neutral diborene as well as a diborane complex, $R(H)_2B-B(H)_2R$, **2**.[17] We now utilize a less bulky NHC ligand (R′ = :C{N(2,4,6-$Me_3C_6H_2$)CH}$_2$) to prepare the second neutral diborene, R′(H)B═B(H)R′, **3**, as well as the corresponding $R'(H)_2B-B(H)_2R'$ 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]



Planar
3a



Twisted
3b



Trans-bent
3c

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 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, $\theta = 36°$, 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

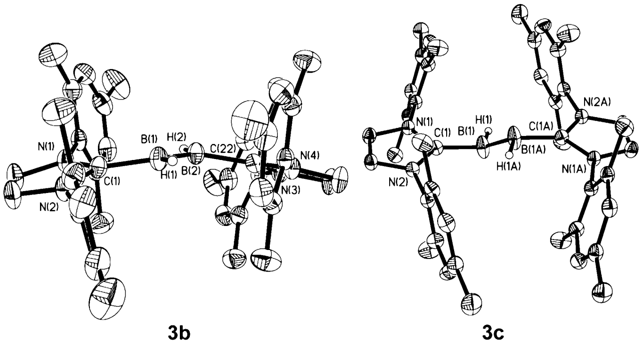


Figure 1. Molecular structures of **3b** and **3c** (thermal ellipsoids represent 30% probability; hydrogen atoms on carbon are omitted for clarity). Selected bond distances (Å) and angles (deg): For **3b**, B(1)−B(2) 1.582(4), B(1)−C(1) 1.541(4), B(2)−C(22) 1.541(4), B(1)−H(1) 1.117(17), B(2)−H(2) 1.12(3); 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).

10.1021/ja800257j CCC: $40.75

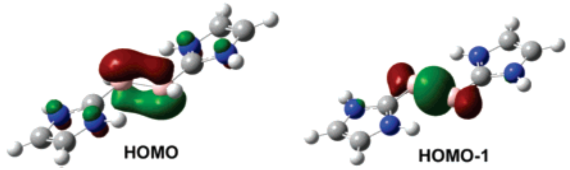


Figure 2. Representation of the frontier orbitals of trans-bent **3c**.

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)diborates[7] (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 [Mes$_2$BB-(Mes)Ph]$^{2-}$ (1.636(11) Å)[5] and [{Ph(Me$_2$N)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, CH$_2$SiH$_2$BH,[24] and its analogs have been computed to have pyramidal geometries due to heteroatom−boron p orbital interactions. Constrained systems like 1-boraadamantane[25] 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 molecular[28] and supramolecular[29] systems. Indeed, **3a** and **3b** were isolated from 1:5 Et$_2$O/hexane solvent mixtures, whereas **3c** was crystallized from pure Et$_2$O. 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 computations[19] 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 = CH$_3$) 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.

Acknowledgment. We are grateful to the National Science Foundation (Grants CHE-0209857, CHE-0451445, and CHE-0608142) for support.

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.

References

(1) Cowley, A. H. *J. Organomet. Chem.* **2004**, *689*, 3866−3872.
(2) Zhou, M.; Tsumori, N.; Li, Z.; Fan, K.; Andrews, L.; Xu, Q. *J. Am. Chem. Soc.* **2002**, *124*, 12936−12937.
(3) Maier, C.-J.; Pritzkow, H.; Siebert, W. *Angew. Chem., Int. Ed.* **1999**, *38*, 1666−1668.
(4) Kaufmann, E.; Schleyer, P. v. R. *Inorg. Chem.* **1988**, *27*, 3987−3992.
(5) Moezzi, A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 2715−2717.
(6) Moezzi, A.; Bartlett, R. A.; Power, P. P. *Angew. Chem., Int. Ed.* **1992**, *104*, 1082−1083.
(7) Noth, H.; Knizek, J.; Ponikwar, W. *Eur. J. Inorg. Chem.* **1999**, 1931−1937.
(8) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3402−3409.
(9) Knight, L. B., Jr.; Kerr, K.; Miller, P. K.; Arrington, C. A. *J. Phys. Chem.* **1995**, *99*, 16842−16848.
(10) Wu, H.-S.; Jiao, H.; Wang, Z.-X.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2003**, *125*, 4428−4429.
(11) Wu, H.-S.; Qin, X.-F.; Xu, X.-H.; Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2005**, *127*, 2334−2338.
(12) Wang, Z.-X.; Chen, Z.; Jiao, H.; Schleyer, P. v. R. *J. Theor. Comput. Chem.* **2005**, *4*, 669−688.
(13) Qin, X.-F.; Wu, H.-S.; Jiao, H. *J. Mol. Struct.* **2007**, *810*, 135−141.
(14) Qin, X.-F.; Wu, H.-S.; Jiao, H. *J. Mol. Model*. **2007**, *13*, 927−935.
(15) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815−1828.
(16) Arduengo, A. J., III *Acc. Chem. Res.* **1999**, *32*, 913−921.
(17) Wang, Y.; Quillian, B.; Wei, P.; Wannere, C. S.; Xie, Y.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2007**, *129*, 12412−12413.
(18) See the Supporting Information for synthetic and crystallographic details.
(19) Computations: The DFT calculations of **3** and **3c** were performed at the B3LYP/6-311+G** level with the Gaussian 03 program (computational details are in the Supporting Information): Frisch, M. J.; et al. *Gaussian 03, revision C.02*; Gaussian, Inc.: Wallingford, CT, 2004.
(20) Bridgeman, A. J.; Nielsen, N. A. *Inorg. Chim. Acta* **2000**, *303*, 107−115.
(21) Bouhadir, G.; Bourissou, D. *Chem. Soc. Rev.* **2004**, *33*, 210−217.
(22) Bernstein, J. *Polymorphism in Molecular Crystals*; Oxford University Press: Oxford, U.K., 2002.
(23) Power, P. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2939−2951.
(24) Giju, K. T.; Phukan, A. K.; Jemmis, E. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 539−542.
(25) Wrackmeyer, B.; Milius, W.; Tok, O. L.; Bubnov, Y. N. *Chem. Eur. J.* **2002**, *8*, 1537−1543.
(26) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*, 1st ed.; John Wiley & Sons, Ltd.: Chichester, U.K., 2000.
(27) Steed, J. W. In *Frontiers in Crystal Engineering*, 1st ed.; Tiekink, E. R. T., Vittal, J., Eds.; John Wiley & Sons, Ltd.: Chichester, U.K., 2006; pp 67−90.
(28) Kitamura, M.; Gao, G.; Nakajima, K.; Takahashi, T. *Chem. Lett.* **2002**, 1076−1077.
(29) Huang, X.-C.; Zhang, J.-P.; Lin, Y.-Y.; Chen, X.-M. *Chem. Commun.* **2005**, 2232−2234.
(30) Xie, Y.; Grev, R. S.; Gu, J.; Schaefer, H. F.; Schleyer, P. v. R.; Su, J.; Li, X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1998**, *120*, 3773−3780.

JA800257J