9054 *J. Am. Chem. Soc.* **2000,** *122,* 9054−9055

An Intramolecular Boron−Boron One-Electron σ-Bond

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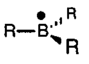
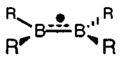
Received May 19, 2000

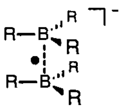
Owing to their isoelectronic relationship to neutral methyl radicals, the chemistry of stable boron-centered radical anions $R_3B^{\bullet-}$ has been intensively investigated. These compounds are usually prepared by chemical or electrochemical reduction of neutral tris(aryl)boranes (**A**).[1−6] Although delocalization of the radical over the aryl rings accounts for the stability of such systems,[7,8] EPR studies show that, in some instances, the unpaired electron is mainly localized at boron.[9] In organodiboranes, one-electron reduction leads to the formation of a one-electron π−bond formed by the overlap of the parallel p_z boron orbitals (**B**).[10,11] Interestingly, the isolation of boron radicals in which the unpaired electron occupies a σ molecular orbital formed by the combination of overlapping collinear atomic orbitals is much more elusive (**C**). In fact, while it has been proposed that such species occur in mixtures of Ph_3B and $Ph_3B^{\bullet-}$,[12] prior reports are limited to the $B_2H_6^{\bullet-}$ [13] and $B_2(OMe)_6^{\bullet-}$ [14] radicals that have been observed at low temperature or transiently. Motivated by the importance of stable radicals to the field of material science, we have set out to prepare a stable boron radical of type **C** and report on the formation of a radical that features a boron−boron one electron σ-bond.



A



B



C

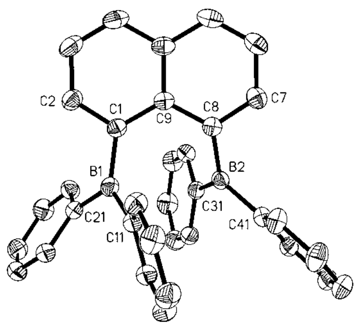


Figure 1. ORTEP view of **1** (30% ellipsoids).

Table 1. Metrical Parameters for the Structures of **1** and **2**[18]

	1 (X-ray)	**1** (DFT)	**2** (DFT)
av B−C (Å)	1.569	1.573	1.582
B−B (Å)	3.002	3.161	2.820
Σ(C−B(1)−C) (deg)	359.1	359.1	355.9
Σ(C−B(2)−C) (deg)	358.8	359.1	355.9
B(1) (Å)[18b]	51.2	51.2	58.3
B(2) (Å)[18b]	53.5	51.2	58.4

1,8-Diboryl-naphthalene derivatives have been shown to chelate small anions.[15] It has been suggested that the proximity of the boron atoms in these derivatives could enable intramolecular interactions of the boron p_z-orbitals,[15] thus providing a scaffold for the formation of a one-electron bond. The realization of this objective necessitated the synthesis of a 1,8-diboryl-naphthalene derivative that is stable toward reduction. To this end, 1,8-dilithionaphthalene was treated with 2 equiv of diphenylboron-bromide to afford 1,8-bis(diphenylboryl)-naphthalene (**1**). A single-crystal X-ray analysis[16] revealed the existence of a sterically congested structure (Figure 1, Table 1). The tight geometrical constraints present in the structure of **1** induce distortions of the naphthalenediyl fragments. Especially noteworthy are the C(9)−C(1)−B(1) (127.07(11)°), C(9)−C(8)−B(2) (125.53(11)°) angles which are larger than the ideal value of 120°. Each boron center adopts a trigonal planar arrangement. All carbon−boron distances in **1** are comparable to those found in the structure of other triarylboranes such as triphenylboron[17] (av 1.58 Å). It is interesting to note that each of the trigonal coordination planes of the B(1) and B(2) centers, respectively, forms a large dihedral angle with the plane containing the naphthalene backbone. The large values of this angle suggest that conjugation of the boron empty p_z-orbital with the π-system of the naphthalene backbone can only be modest. Finally, as a result of this unique molecular structure, the boron centers are separated by 3.002(2) Å.

A cyclic voltammogram recorded on a 3 mM solution of **1** at 20 °C in THF (scan speed: 250 mV/s) revealed the presence of a reversible reduction wave at −1.81 V (vs SHE) followed by an irreversible wave at −2.28 V. The potential of the first reduction is less negative than that reported for triphenylboron (−1.97 V) suggesting that the reduction of **1** is a more facile process. Treatment of THF solutions of **1** with an equimolar quantity of K/18-C-6 leads to the rapid formation of paramagnetic dark purple solutions. These solutions are stable for several weeks at −25 °C but decompose when stored at room temperature or when exposed to air. To gain insights into the nature of the radicalar species (**2**) formed by the reduction of **1**, an EPR spectrum was recorded (Figure 2). While the best resolution was obtained with a 10 mM solution in THF at 25 °C, the spectra exhibited a seven-line signal ($g = 2.002$) in agreement with the hyperfine coupling

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(16) Crystal data for **1**: $C_{34}H_{26}B_2$, *M* 456.17, triclinic, space group *P*-1, $a = 10.866(2)$ Å, $b = 11.157(2)$ Å, $c = 12.322(2)$ Å, $\alpha = 65.644(3)°$, $\beta = 83.339(3)°$, $\gamma = 67.130(3)°$, $V = 1252.1(4)$ Å^3, $Z = 2$, $\rho_{calc} = 1.210$ g cm^{-3}. Siemens SMART-CCD area detector diffractometer, Mo Kα radiation ($\lambda = 0.71069$ Å), $T = 300$ K. Crystal size 0.53 × 0.40 × 0.21 mm, ω-scan mode, measurement range $1.82 \leq \theta \leq 25.00°$, 4342 unique reflections, 3393 reflections with $I > 2\sigma(I)$, $\mu = 0.067$ mm^{-1}. The structure was solved by direct methods and refined by full-matrix least squares against F^2 using the SHELXTL/PC (ver. 5.10) package, 60 parameters, R1 = 0.0483, wR2 = 0.1122 (all data).

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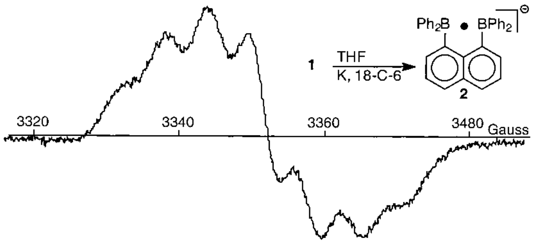

Figure 2. X-band EPR spectrum of **2** at 25 °C.

of the electron spin with the nuclear spin 3/2 of the two ^{11}B centers. The magnitude of the boron hyperfine coupling constant ($a_B = 5.9$ G) is smaller than those reported for $B_2H_6^{\bullet-}$ (10.88 G),[13c] $Ph_3B^{\bullet-}$ (7.84 G).[3] and $Mes_3B^{\bullet-}$ (10.32 G).[9] Also, it drastically differs from that measured for $B_2(OMe)_6^{\bullet-}$ (46.3 G) which possesses a B−B σ-bond with a strong s character.[14] Thus, while the multiplicity of the observed signal indicates that the SOMO (semi-occupied molecular orbital) of **2** involves both boron centers, the magnitude of ^{11}B hyperfine coupling constant suggests the preponderant participation of the boron p-orbitals.

While it has so far not been possible to obtain single crystals of **2**, we have performed a series of DFT calculations on both **1** and **2**.[19] The calculated structure of **1** is in good agreement with that determined experimentally by diffraction methods (Table 1). While all bond distances and angles are in good agreement, we note that the calculated boron−boron intramolecular distance is slightly overestimated by the calculation. Nevertheless, examination of the DFT orbitals reveals that, in **1**, the p_z orbitals of the neighboring boron centers overlap substantially and contribute to the LUMO. The calculated structure from **2** differs from that of **1** in several aspects (Table 1). (i) Both boron atoms adopt a slightly pyramidal geometry and the boron carbon bonds are moderately lengthened in agreement with a small increase in p character; (ii) the dihedral angle formed by the naphthalene backbone and the planes containing the three carbon atoms bound to each boron increases and the boron−boron distance decreases substantially in agreement with the presence of a bonding interaction. As shown in Figure 3, both boron atoms are the dominant contributors to the SOMO, which has a strong boron−boron σ-bond character. This one-electron σ-bond can be viewed as resulting from the overlap of the formerly vacant boron p_z-orbitals. The minor contributions of the ring carbon atoms substantiate the importance of the stabilizing effect provided by aryl substituents in stable radicals. The calculated boron−boron bond distance of **2** is approximately 1 Å longer than that observed in compounds that feature single bonds between four coordinate boron atoms.[20] This difference likely arises from the negligible participation of the 2s boron orbital in the semi-occupied σ-bond of **2** as well as from the rigidity and steric congestion of the structure that prevent a closer approach of the two boron centers.

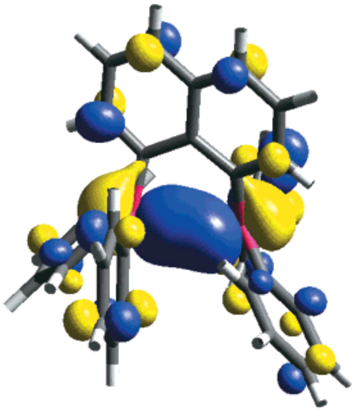

Figure 3. Orbital representation of **2** showing the SOMO.

While the search for unusual bonding situations in group 13 chemistry has focused on the formation of multiply bonded compounds, we document the formation and room-temperature observation of a compound that features a boron−boron one-electron σ-bond. One electron σ-bonding remains a rare phenomenon that has been investigated in group 14 chemistry[21] and has recently emerged as an object of fundamental concern in group 15 chemistry.[22] Our present efforts are focused on the preparation of a crystalline analogue of **2**.

Acknowledgment. We thank the Robert A. Welch Foundation (Grant A-1423) for generous financial support. The purchase of the CCD X-ray diffractometer was made possible by the NSF (CHE-98 07975). We thank the Laboratory for Molecular Simulation at Texas A&M, and the NSF for its funding (CHE-9528196). We thank Agnes Derecskei-Kovacs and Lisa M. Thomson for help with the calculations.

Supporting Information Available: Experimental details for the preparation of **1**; DFT orbital picture showing the LUMO of **1**; X-ray crystal analysis data for **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) (a) Distances in [Å] and angles in [deg]. (b) Dihedral angles: formed between the plane of the naphthalene and the plane defined by the three carbon atoms bound to boron.

(19) DFT calculations (full geometry optimization) were carried out by using the gradient-corrected Becke exchange functional (Becke, A. D., *J. Chem. Phys.* **1993**, *98*, 5648) and the Lee−Yang−Parr correlation functional (Lee, C.; Yang, W.; Parr, R. G. *Physical Review B* **1988**, *37*, 785) and Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200) (B3LYP). For carbon and hydrogen, a 6-31G (Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257) basis set was used, and a 6-31+G* (Hariharan, P. C. and Pople, J. A. *Theor. Chem. Acta* **1973**, *28*, 213, Clark, T.; Chandrasekhar, J.; Schleyer, P.v. R. *J. Comput. Chem.* **1983**, *4*, 294, Krishnam, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650, Gill, P. M. W.; Johnson, B. G.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1992**, *197*, 499) basis set was used for boron. All calculations were performed using the Gaussian94 suite of programs: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995. The orbital representation in Figure 1 was generated in the Cerius^2 program of MSI.

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