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Electron Density and Bonding in Borates: An Experimental Study of Tetrabutylammonium Heptahydridohexaborate, $[(C_4H_9)_4N][B_6H_7]$

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An experimental study of a high-resolution X-ray data set of the *closo*-boranate $[B_6H_7]^-$ was performed. The charge density distribution and its topological properties were analyzed according to the "Atoms in Molecules" theory of R. W. Bader. The $[B_6H_7]^-$ anion forms an octahedral boron cage with one of the six faces capped by an additional proton. The unusual bonding situation of the threefold capping hydrogen atom is of special interest and is discussed in detail. Three new B–H bonds form, while the B–B bonds in the capped boron triangle vanish. The reactivity of the $[B_6H_7]^-$ anion is visualized by the electrostatic potential.

Results and Discussion

The very stable $[B_nH_n]^{2-}$ anions form *closo* clusters with spherical aromaticity.[1,2] $[B_6H_6]^{2-}$, $[B_7H_7]^{2-}$, $[B_8H_8]^{2-}$ and $[B_{10}H_{10}]^{2-}$ can be protonated forming stable monoanions.[3,4] The structures of $[B_6H_7]^-$ and $[B_{10}H_{11}]^-$ have been determined by X-ray diffraction[3] and nonempirical calculations.[5–7] During our experimental charge density studies of compounds with multi-center two-electron bonds like B_2H_6[8] we became interested in the charge-density distribution $\rho(\mathbf{r})$ and its topological analysis of $[B_6H_6]^{2-}$ and $[B_6H_7]^-$.[9] Herein, we report on the results of a study based on a high-resolution low-temperature X-ray diffraction experiment of $[Bu_4N]^+[B_6H_7]^-$, where the $[B_6H_7]^-$ anion crystallizes with one tetrabutylammonium cation in the asymmetric unit. Figure 1 shows the structure of the $[B_6H_7]^-$ anion and its numbering scheme.[10]

A multipole refinement based on the Hansen–Coppens formalism[14] and a topological analysis were performed using the program package XD.[15] A known problem in X-ray structure solution and charge-density analysis is the determination of the position of the hydrogen atoms. Thus, in this study the terminal hydrogen atoms H_{term} of the borate were fixed at neutron distances, taken from neutron diffraction data of decaborane.[16] Mebel et al. published a theoretical study of the structure and migrational non-rigidity of the $[B_6H_7]^-$ anion (Gaussian80, SCF/4-31G).[5] They found five stable states whose total energy levels are very close together. The global minimum has C_{3v} symmetry. A geometry optimization of the title anion was performed (Gaussian98,[17] B3LYP/6-311G**), starting at experimental geometry which converged with a C_s symmetry as depicted in Figure 2. Therefore, the anion packed with

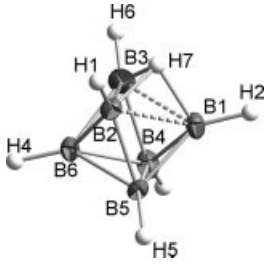

Figure 1. The structure and labeling scheme of the $[B_6H_7]^-$ anion; Diamond[11] drawing.

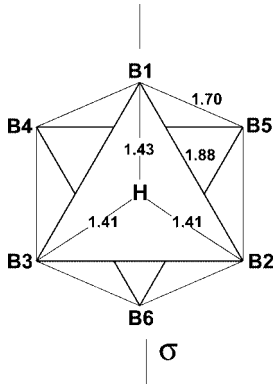

Figure 2. Symmetry scheme of the $[B_6H_7]^-$ ion according to the geometry optimization. View from above the capped boron triangle.

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$[Bu_4N]^+$ in $P2_1/n$ presents a local energy minimum. The B–H_{term} distances obtained by ab initio calculations correspond exactly to neutron values of $B_{10}D_{14}$, while the theoretical optimized B–B distances differ only in the fourth decimal place from the experimental results of $[B_6H_7]^-$. Thus, it seemed to be justified to fix the bond lengths to the capping hydrogen atom, B–H7 to the corresponding values of the ab initio calculation (at 1.41 Å from B2 and B3, and 1.43 Å from B1, see Figure 2) for the multipole refinement.

The topological analysis of the charge density was carried out using the formalism of the theory of "atoms in molecules" (AIM) developed by Bader.[12,13] The values of the electron density ρ_{bcp} and the Laplacian $\nabla^2\rho_{bcp}$ at the bond critical points (bcp) enable a quantitative description of the bonds. They are given in Table 1. The topological parameters of the capping bonds B–H_{cap} and the region they influence reveal several interesting aspects.

Bond critical points can be found on all B–B contacts except those capped by the hydrogen atom. Thus, the capping of the triangular face results in the loss of three covalent bonds [distances B1–B2 1.867(1) Å, B2–B3 1.863(1) Å and B3–B1 1.874(1) Å], so that four-membered rings are formed by H7 and three boron atoms, e.g. B1–H7–B3–B4, characterized by ring critical points (rcp) located in the center. The experimentally derived bond topological properties are in very good agreement with the theoretical ones. For the B–B bonds the mean deviation for ρ_{bcp} and $\nabla^2\rho_{bcp}$ between theory and experiment is 0.05(2) e Å^{-3} and 0.5(3) e Å^{-5}, even for the ring critical points the deviation is small, 0.05(1) e Å^{-3} and 0.17(2) e Å^{-5}. In case of the B–H bonds the differences between theory and experiment are slightly higher. For terminal B–H_{term} bonds it is 0.05(3) e Å^{-3} and 7.0(8) e Å^{-5}, while the capping B–H_{cap} bonds differ by 0.10(2) e Å^{-3} in ρ_{bcp} and 1.6(8) e Å^{-5} in the Laplacian values.

Figure 3 shows the contour line Laplacian diagram of the capped boron plane B1–B2–B3 (left) compared to the plane spanned by the atoms B4–B5–B6 (right). In contrast to the capped plane the uncapped one shows shared interaction on the B–B bonds, indicated by a charge concentration on the B–B bond path, bordered furthermore by the zero Laplace line (black). As a consequence of the missing bcp values, the coordination number of B1, B2 and B3 is 4, while B4, B5 and B6 are bonded to five neighboring atoms.

Table 1. Topological properties of $[B_6H_7]^-$.

Bond	Bond length r [Å]	ρ [e/Å^3] exp.	theor.	$\nabla^2\rho$ [e/Å^5] exp.	theor.
Triangle B–B bonds; 2e-3c bonds					
B1–B4	1.7066(6)	0.93(2)	0.90	–4.3(2)	–3.9
B1–B5	1.7037(7)	0.93(2)	0.90	–3.9(3)	–4.1
B2–B5	1.7071(6)	0.97(2)	0.90	–4.9(2)	–3.9
B2–B6	1.7081(6)	0.92(3)	0.89	–3.6(4)	–3.8
B3–B4	1.7112(9)	1.00(3)	0.90	–4.6(3)	–3.9
B3–B6	1.7098(7)	0.95(3)	0.89	–4.5(3)	–3.8
B4–B5	1.7284(7)	0.90(3)	0.86	–3.5(4)	–2.8
B4–B6	1.7276(6)	0.94(3)	0.86	–3.8(3)	–2.9
B5–B6	1.7224(6)	0.91(4)	0.87	–3.7(3)	–3.0
av. all[a]	1.714(9)	0.94(3)	0.89(2)	–4.1(5)	–3.6(5)
Terminal B–H_{term} bonds; 2e-2c bonds					
B1–H1	1.19	1.13(1)	1.15	–9.8(2)	–3.5
B2–H2	1.19	1.16(1)	1.15	–9.6(2)	–3.5
B3–H3	1.19	1.16(1)	1.15	–9.5(2)	–3.4
B4–H4	1.19	1.21(2)	1.13	–10.4(2)	–2.6
B5–H5	1.19	1.21(2)	1.13	–10.5(2)	–2.6
B6–H6	1.19	1.19(2)	1.13	–10.4(2)	–2.6
av. all[a]		1.18(6)	1.14(1)	–10.0(4)	–3(4)
Capping B–H_{cap} bonds; 2e-4c bonds					
B1–H7	1.43	0.70(1)	0.63	0.2(3)	–0.2
B2–H7	1.41	0.75(2)	0.63	–2.5(3)	–0.3
B3–H7	1.41	0.75(1)	0.63	–2.5(2)	–0.3
av. all[a]		0.73(2)	0.63(0)	–1.7(10)	–0.3(1)
Ring critical points in the capped B(1)–B(2)–B(3) plane					
B1–H7–B2–B5		0.66(2)	0.61	0.8(2)	0.8
B1–H7–B3–B4		0.64(2)	0.60	1.3(2)	0.8
B2–H7–B3–B6		0.68(2)	0.61	0.7(2)	0.7

[a] av. is the average of the values in the column.

Figure 4 shows the bending of the bond paths which is most pronounced for the B–H_{cap} bonds curved into the interior of the B_6 cage (see Figure 4, right). This results in longer bond-path lengths in comparison to the atomic distances, which is 0.002 Å for the B–B bonds and up to 0.2 Å for the B–H_{cap} bonds.

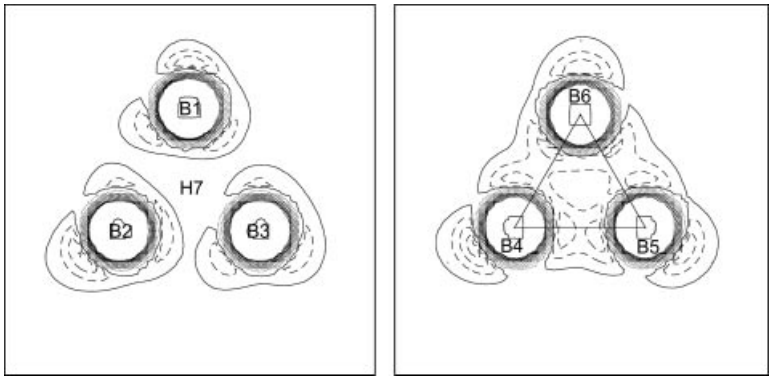

Figure 3. Contour line diagram of the Laplacian (dotted lines positive values, dashed lines negative, solid line zero Laplacian) of the capped B1–B2–B3 plane (left) and the uncapped B4–B5–B6 plane on the opposite side of the molecule (right).

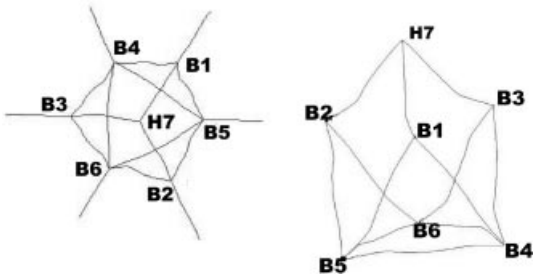

Figure 4. Bond paths of the title compound. Left: View from above the capped boron triangle, capping hydrogen atom in the center of the figure. Right: Side view, capping hydrogen atom on top of the figure.

The electrostatic potential (esp) was calculated by using the method of Su and Coppens[18] on the basis of experimental data. This calculation considers a $[B_6H_7]^-$ ion extracted from the crystal but still containing the polarization effects induced by intermolecular interactions. Figure 5 displays the electrostatic potential, mapped onto the isoelectron-density surface at $\rho(\mathbf{r}) = 0.5 e Å^{-3}$. The positive potential (red) is concentrated around the boron atoms and the negative potential around the terminal hydrogen atoms. There is a gradient of polarization between the hydrogen atoms. Thereby the terminal hydrogen atoms of the capped triangle are less polarized (green) than the hydrogen atoms on the opposite site of the molecule (blue). The remarkable effect of the capping H7 atom is also shown in the esp value. It shows a positive potential (red), indicating the reactivity of this hydrogen atom towards nucleophilic attack. $[B_6H_7]^-$ is very unstable and reacts in basic solution immediately by emitting a proton to form $[B_6H_6]^{2-}$.

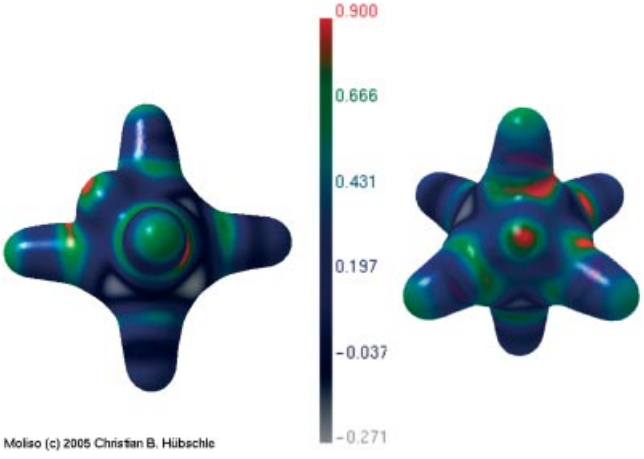

Figure 5. Electrostatic potential of the title compound; generated with the MolIso program.[19] Left: View from above the capped boron triangle, capping hydrogen atom in the center of the figure. Right: View from a terminal hydrogen atom of the non-capped triangle, capping hydrogen atom on top of the figure.

Acknowledgments

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[10] Crystals of $[Bu_4N][B_6H_7]$ were obtained by crystallization from methanol. Empirical formula: $[(C_4H_9)_4N][B_6H_7]$; formula mass [g mol^{-1}]: 314.37; crystal system: monoclinic; space group: $P2_1/n$ (no. 14); $Z = 4$; temperature: 98 K; cell parameters: a = 8.611(1) Å, b = 17.112(2) Å, c = 15.151(2) Å, β = 99.309(5)°, V = 2203.1(5) Å^3; density: 0.9478(2) g cm^{-3}; λ = 0.71073 Å; $2\theta_{max.}$ = 102.85°; 162395 reflections, 23027 unique reflections; completeness: 92.0%; redundancy: 7.0; $R(F^2)_{int.}$ = 0.039, $R(F)_{mul}$ = 0.026; residual density: –0.16/0.21 e Å^{-3}. CCDC-637977 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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