A new 4c–2e bond in $B_6H_7^-$ †

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For $N(C_4H_9)_4B_6H_7$ a proton is shown to be localised above one of the faces of the distorted octahedron, and rhomboid rings are formed as shown by topological analysis of charge densities.

Several different types of 4c–2e bonds have been analysed in the literature. The most recent is the new description of Hoffmann and Balakrishnarajan of a planar rhomboid of four boron atoms.[1] Simon *et al.* observed triangles of metal atoms centred by a hydrogen atom.[2] And not long ago, Schleyer *et al.* discussed the pseudo-tetrahedral B_3H motif in a polyhedral borane and hydroborate, CB_5H_7 and $B_6H_7^-$, on the basis of HF and DFT calculations.[3] Such molecules can be derived from the highly-symmetric, octahedral $B_6H_6^{2-}$ ion by adding a proton. The authors concluded that a face-capping position should be more favourable for the extra hydrogen atom than a bridging situation (3c–2e BHB bond). There exists no experimental data to verify this. Hoffmann and Balakrishnarajan[1] concluded from extended Hückel calculations that sodium boride Na_3B_{20} should contain additional, statistically disordered boron atoms capping the boron atom polyhedra.[4] Such a situation would be very difficult to prove experimentally. It is therefore reasonable to address the question of whether a pyramidal 4c–2e bond exists for boron clusters by analysing the $B_6H_7^-$ ion, firstly by a conventional structure analysis to obtain information about the position of the hydrogen atom and secondly by a charge density determination. The latter was recently shown to be extremely useful in the investigation of $[Li(NH_3)_4]_2B_6H_6{\cdot}2NH_3$.[5] Charge density analysis based on multipole refinements and followed by a topological analysis according to the atoms-in-molecules (AIM)-method by Bader *et al.* permits a classification of the characteristics of interatomic areas of the electron density by means of critical points.[6] It becomes even more useful if the experimental work is supplemented by *ab initio* calculations (Gaussian03, AIM2000) of the geometry optimised clusters.[7,8]

$N(C_4H_9)_4B_6H_7$ has now for the first time been successfully crystallised and its crystal structure been determined at low temperatures.[9] It is hence now possible to collect data that are accurate enough to derive more detailed information concerning the position of the hydrogen atom and the bonding situation in $B_6H_7^-$, and to discuss the question as to whether a 4c–2e bond can be postulated for the pseudo-tetrahedral B_3H arrangement.

The *closo*-hydroborate, $B_6H_6^{2-}$ can add a proton like a Brønsted base, affording the $B_6H_7^-$ ion.[10] First observed in 1985,[11] this ion was investigated *via* ^1H NMR and infrared spectroscopy in solution.[12] The proton was found to fluctuate over multiple positions of the octahedron. A room-temperature structural investigation on crystals of the (disordered) $[Ni(phen)_3][B_6H_7]_2{\cdot}(CH_3)_2CO$ (phen = 1,10-phenanthroline) did not unambiguously answer the question as to whether the additional H atom binds to one of the faces.[11]

$N(C_4H_9)_4B_6H_7$ was prepared from $NaBH_4$, $BF_3{\cdot}O(C_2H_5)_2$, and $N(C_4H_9)_4Br$ as described in the literature.[13] Single crystals were isolated from the solvent and put into perfluorated oil. X-Ray data structure determination was performed at 103 K.[14–19] Fig. 1 shows that, in fact, the extra hydrogen atom was found to be located above one of the BBB faces (H^{fac}) of the polyhedron. The B_6H_6 cluster is formed by boron atoms at six crystallographically independent sites. This allows the cluster to deviate from the ideal octahedron. Three of the bond lengths differ significantly from "normal" values for BB bonds. While distances in the faces B1–B2–B3, B2–B3–B5, B3–B4–B5 and B2–B5–B6 exhibit typical values between 1.701(1) Å and 1.725(1) Å, those between B1, B4, and B6 are about 0.14 Å longer. These are the boron atoms that are capped by H^{fac}. It is interesting to note that such behaviour of the boron atom cluster was in fact predicted for the addition of an H atom: an elongation of the BB distances in the capped face by 0.136 Å from *ab initio* calculations in a geometry optimised cluster (calculated: B–B: 1.722 Å and 1.858 Å; B–H^{fac}: 1.412 Å).[3]

The distances between cations and anions do not suggest intermolecular interaction (shortest H(C)–B: 3.006(9) Å and 3.22(1) Å).

The multipole refinement was performed using the XD program, according to Hansen and Coppens, based on the structural model described above.[20–22] This had been preceded by a SHELX refinement confined to the high angle data (>41.64°/2θ) in order to locate and refine the atomic positions of the non-hydrogen atoms

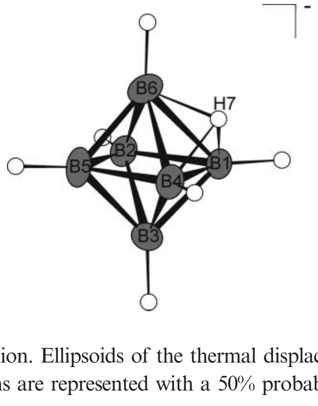

Fig. 1 $B_6H_7^-$ anion. Ellipsoids of the thermal displacement parameters of the boron atoms are represented with a 50% probability of finding.

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and their anisotropic thermal displacement parameters, which then remained fixed for the localisation of the hydrogen atoms. The hydrogen atoms were found by a difference Fourier analysis of all data. The positions of the non-hydrogen atoms, the anisotropic thermal displacement parameters and the multipoles (up to octupoles for non-hydrogen atoms) were freely refined using all data up to a resolution of $\sin(\theta_{\max}/\lambda) = 0.992$. By subtracting the resulting multipoles from the total electron density we obtain the static deformation density. Analysing the latter permits a more in-depth study of the valence electrons in bonding and non-bonding areas.[23] Fig. 2 shows the static deformation density for one of the BBB planes of the polyhedron and the H^{fac} atom. The aspherical deformation of the density towards the capping hydrogen atom is clearly seen.

According to Bader's theory, the analysis of the charge density distribution can be used to define critical points that indicate a bonding situation. For example, the conventional 2c–2e bonds between the boron and hydrogen atoms of the B_6H_6 cluster are characterised by (3,−1) bond critical points (BCP). Bond critical points also occur between the B atoms of the uncapped BBB planes. The hydrogen-capped BBB face (B4, B6, B1), however, has no BCPs between boron atoms: it exhibits BCPs between boron atoms and H^{fac}. Three rhomboid, almost planar BBBH rings are thus formed, very similar to the B4 rhomboids that were recently discussed by Hoffmann and Balakrishnarajan[1] It is justified to describe the arrangement as a 4-membered rhomboid (Fig. 3a), since we found (3,+1) ring critical points (RCP) in each of them. The bond paths shown in Fig. 3b also confirm these rings.

The absence of (3,−1) bond critical points between the boron atoms and the presence, on the other hand, of (3,+1) ring critical points between the atoms H7–B6–B4–B5, H7–B1–B4–B3, and H7–B1–B6–B2 experimentally indicate the existence of a 4c–2e bond. The picture derived from the conventional structure analysis (Fig. 1), which was discussed above, is therefore misleading in terms of a deeper understanding of the bonding situation of $B_6H_7^-$. A better description is shown in Fig. 4, which also gives the position of the critical points between B and H. The electron density at the critical points is given in Table 1.[19] In addition to these, a cage critical point was found. It is located slightly off the centre of the polyhedron. This compares with a cage critical point in $B_6H_6^{2-}$ that is exactly in the centre, thus reflecting the higher symmetry of the polyhedron. The electron densities at the cage critical points in $B_6H_6^{2-}$ and $B_6H_7^-$ have very similar values (ρ = 0.517 *vs.* 0.460 e$Å^{-3}$).

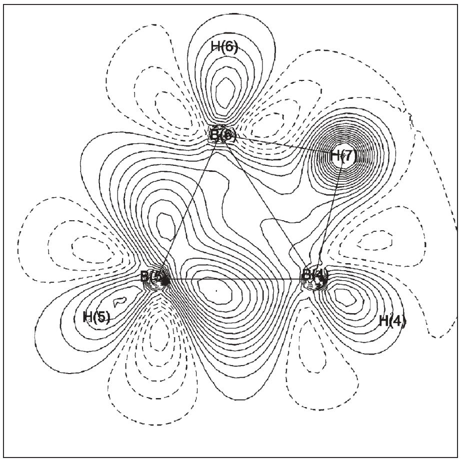

Fig. 2 Experimentally determined static deformation density in the B5–B4–B6–H7 rhomboid of $N(C_4H_9)B_6H_7$. The contour intervals are 0.1 e$Å^{-3}$, negative lines dashed.

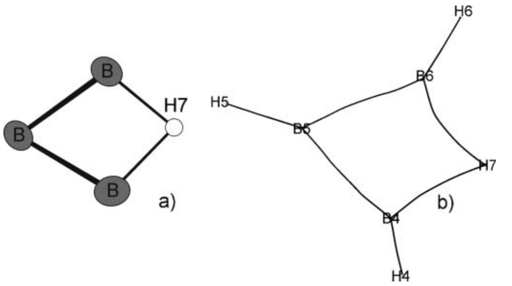

Fig. 3 (a) Rhomboid ring; (b) bond paths between B5, B4, B6, and H7.

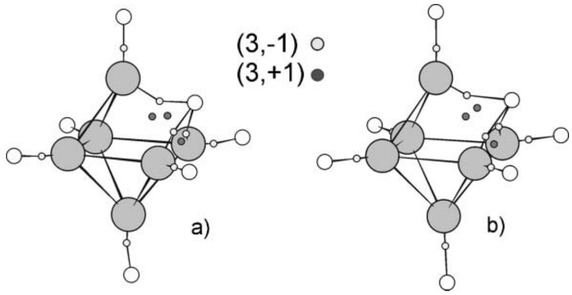

Fig. 4 (a) Experimental bond and ring critical points; (b) calculated bond and ring critical points.

Table 1 Bond and ring critical points for the anion and electron densities

BCP (3,−1)	$\rho(r)$/ e$Å^{-3}$ [a]	$\rho(r)$/ e$Å^{-3}$ [b]	RCP (3,+1)	$\rho(r)$/ e$Å^{-3}$ [a]	$\rho(r)$/ e$Å^{-3}$ [b]
B5/B3	0.863	0.844	B5–B3–B2	0.818	0.803
B3/B2	0.840	0.843	B4–B3–B5	0.837	0.803
B3/B4	0.865	0.879	B3–B2–B1	0.831	0.803
B3/B1	0.924	0.880	B6–B5–B2	0.786	0.803
B2/B6	0.890	0.880	H7–B6–B4–B5	0.695	0.630
B5/B2	0.881	0.843	H7–B1–B4–B3	0.712	0.628
B4/B5	0.918	0.890	H7–B1–B6–B2	0.622	0.628
B2/B1	0.874	0.879			
B6/B5	0.842	0.879			
B3/H3	0.995	1.132			
B5/H5	1.076	1.132			
B2/H2	1.092	1.132			
B4/H4	1.236	1.156			

[a] Experimentally determined.[26] [b] Calculated MP2.

There are no critical points between any atoms of the cation and the anion, which confirms what could be concluded from distances observed in the conventional structure analysis.

Calculations have been performed at the MP2 level of theory. For all atoms the standard 6-311+G(2d,2p) basis set has been employed. For calculations of energies, densities and gradients the Gaussian03 suite of programs has been used.[7] The energy minima with respect to the coordinates have been checked by frequency calculations yielding no imaginary frequency. Geometry optimisation of the $B_6H_7^-$ anion revealed a nearly C_{3v} symmetric structure with a distance B2–B3 of 1.712 Å, an elongated distance B1–B4 of

1.878 Å, and a distance B4–H7 of 1.416 Å. This is in accord with experimentally obtained parameters. The torsion angle B4–B3–B1–H7 was calculated to be 9.3°, which suggests a nearly coplanar arrangement of the three B atoms and the hydrogen atom H7. Topological analysis[8] revealed critical points and electron densities listed in Table 1. The calculated electron density for the cage critical point is $\rho = 0.430$ eÅ^{-3}. The calculated topological data is in very good agreement with data obtained from multipole refinement (Fig. 4). In agreement with the analysis of the experimentally obtained densities, no (3,−1) BCPs between the atoms B1–B4, B1–B6 and B4–B6 could be located from the calculated electron densities. Only (3,+1) ring critical points could be located, consistent with a rhomboidal 4c–2e multicentre bond description.

In conclusion, the structure of a salt containing the $B_6H_7^-$ ion has been determined for the first time in a manner that allows us to derive information about the position of the extra H atom. Neutron diffraction data are not at present available because of the difficult synthesis from isotopically pure ^{11}B compounds. But the BH distances found experimentally are very well reproduced by our calculations. The cluster deviates significantly from an octahedron. Rhomboid rings are found that are characterised by ring critical points and can be described as 4c–2e bonds. We would like to emphasise that this type of 4c–2e bond, as it is discussed here, is completely different from the initial picture of a B_3H pseudo-tetrahedron, which was the starting model for earlier calculations. There is some controversy in the literature about whether the observance of critical points indicates a bonding situation or not.[24,25] But, using the approach of topological analyses, we are able to derive a plausible description of the bonding situation. The tool of drawing critical points and bond paths helps us to see what was there from the beginning: BB distances in the octahedron that were considerably elongated by addition of a hydrogen atom to the cluster.

Future work will focus on a deeper analysis of the theoretical calculations of orbitals and related energies.

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18 Structure determination of $N(C_4H_9)_4B_6H_7$: molecular weight: 314.37 g mol^{-1}; crystal size: 0.26 × 0.22 × 0.11 mm; crystal system: monoclinic; space group: $P2_1/n$; $a = 8.6066(5)$ Å, $b = 17.118(1)$ Å, $c = 15.1724(9)$ Å, $\beta = 99.248(2)^\circ$; $V = 2206.22$ Å^3; $Z = 4$; $\rho_{calc} = 0.946$ g cm^{-3}, μ_{lin}: 0.05 mm^{-1}; $\lambda = 0.71073$ Å; $T = 103$ K; resolution: $\sin(\theta_{max}/\lambda) = 0.992$; no. of independent reflections: 17165 (R_{int}: 0.1455); no. of reflections collected: 149276; $R_1[I > 4\sigma]$: 0.0602; wR_2: 0.1362; GoF: 0.858. CCDC 639693. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704944g.

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