On the nature of chemical bonding in Γ-boron

Piero Macchi

*Department für Chemie und Biochemie, Universität Bern, Freiestrasse 3,
CH3018 Bern Switzerland*

Abstract:

The chemical bonding in γ-Boron is discussed, based on the known crystal structures of the new phase, recently discovered. The unexpected polarity of some B-B bonds and a sensible electron counting scheme are presented. The relationship between the chemical bonding and the material hardness is also discussed.

Keywords: Boron, Chemical Bond, Bond Polarity

Introduction

Recently, an high pressure form of Boron (γ-B) has been structurally characterized and reported by Oganov and coworkers [1] and later by Zarechnaya and coworkers [2].

Oganov *et al.* [1] used the *evolutionary algorithm* [3] in combination with solid state density functional theory (DFT) calculations to predict the structure, confirmed by X-ray diffraction on a polycrystalline sample. The interesting feature is the presence of B_2 moieties embedded in a lattice formed by the most common B_{12} icosahedra, see Figure 1. Based on different partitioning schemes of the electron density distribution, Oganov *et al.* [1] concluded that there is a partial charge transfer from B_2 to B_{12}, and they called the compound a "boron-boride". A segregation of ions would be quite interesting, because it would show that the pressure is able to stabilize electronic configurations (and corresponding structures) that are not stable at room conditions, in particular the B_2^{2+} cation. However, the same authors warned that the calculated charge transfer is only partial and therefore an oversimplification may be dangerous. They anyway stressed on the high polarity of some bonds between the two sub-units.

Zarechnaya *et al.* [2] reported a structure solution of γ-Boron from single crystal and powder X-ray diffraction data, together with theoretical calculations. The structural features are substantially similar to those anticipated by Oganov *et al.*, [1] however some controversy was raised because of the different interpretation of the chemical bond between B_{12} and B_2 units, especially based on deformation densities, electron localization function (ELF) and implications from the measured hardness of the material.

Häusserman and Mikhaylushkin (hereinafter H&M) [4] analyzed the γ-B structure by means of DFT calculations and proposed a rationalization of the chemical bonding. Although they confirmed a positive charge for the B_2 dumbbell, they proposed an electron counting scheme that does not comply with the ionic configuration of γ-Boron suggested by Oganov *et*

al. [1]. H&M postulated the covalence of all the bonds between the dumbbell and the icosahedron within the first coordination sphere, as revealed by deformation densities. H&M criticized the meaning of a space partitioning based on the Quantum Theory of Atoms in Molecules (QTAIM) [5] which produces the charge separation between the sub-units. Very recently Mondal *et al.* [6] reported QTAIM results from X-ray diffraction on γ-Boron and recognized the polarity of some B-B bonds. ==The discovery of γ-Boron and the discussion on the chemical bonding is reported in the first article of this special issue [7].==

This paper reports on some further speculations about the nature of the chemical bonding in γ-Boron, in particular concerning the polarity. An alternative electron counting scheme is proposed and connection with the material hardness is tentatively established.

Computational details

DFT calculations reported in this paper were carried out with Gaussian09 [8], using the B3LYP hybrid functional and 6-311++G(2d,2p) basis set, and with ADF2010.2 [9], using the BLYP functional and quadruple-ζ, quadruple polarization Slater Type Orbital basis (QZ4P). All results were comparable between the two methods and, unless otherwise stated, B3LYP/6-311++G(2d2,p) are reported in the text. For the reference B_2F_2 molecule, complete active space (CAS) and Quadratic configuration interaction, including single and double substitution (QCISD), in order to include a sufficient amount of electron correlation in the calculated wave function. CAS and QCISD calculations were carried out with 6-311++G(2d,2p) basis set and performed with Gaussian09. QTAIM analysis was performed using AimAll [10].

The structure of γ-Boron

The determination of γ-B has been a very important discovery that contributed to solve the puzzle accompanying this element for long time. Apart for the historical reasons, the structure is also very interesting and a rationale for the chemical bonding is not so immediate. The structure can be described as formed by two structural sub-units (Figure 1): a) B_{12} icosahedra, quite typical in the chemistry of Boron and present in other known solid state phases; b) a B_2 "dumbbell", embedded in channels produced by the packing of the B_{12} units.

H&M have interestingly compared the bond distances in α-B and γ-B, identifying localized some 2center-2electron (2c2e) extra cage bonds and some delocalized 3center-2electron (3c2e) extra cage bonds together with the delocalized multicenter bonds of the B_{12}

skeleton (see Table 1). 2c2e bonds are the shortest, in the range 1.6-1.7 Å. This could be a reasonable estimation of a B-B single bond. The bonding distance in B_2 ($^3\Sigma_g^-$) is ca. 1.6 Å, although this molecule is not really associated with a genuine single B-B bond [11]. Moreover, it should be taken into account that B-B is quite flexible and a larger range of distances is actually possible.

H&M also pointed out the rather uneven coordination number (CN) of the 5 independent atoms in γ-B. Based on the distance ranges, they dismissed the hypothesis that a $(B_{12})^{2-}$ unit could be a constituent part of the structure and actually computed an inverse polarity for the two sub-units, $(B_{12})^{+2/3}(B_2)^{-2/3}$. H&M's hypothesis is based on the assumption that 3c2e type connections link B_{eq2}, B_{eq3} and B_{db}, although B_{eq3}-B_{db} and B_{eq2}-B_{db} distances are in excess of 1.98 Å (single crystal data) or 1.90 Å (ab initio predictions). In addition, one feature has probably escaped attention: at variance from all other known forms of B, the B_{12} unit in γ-B has 12 *exo* B-B bonds, almost "radially" oriented, as expected in the all-*exo* B_{12}^{2-} moieties, like $[B_{12}H_{12}]^{2-}$ (see Figure 2). This similarity was originally suggested by Oganov *et al.* [1]. The *pseudo*-radial B-B bond distances are not homogeneous and they can be grouped as: a) 2 short bonds (B_{ap}-B_{ap}) connect the B_{12} units along the crystallographic *a* direction of the orthorombic phase; b) 8 relatively weaker bonds (B_{eq2}-B_{eq3}) connect B_{12} units obliquely (and classified by H&M as part of 3c2e bonding); c) 2 short bonds (B_{eq1}-B_{db}) connect B_{12} with the B_2 dumbbell along crystallographic *b* direction. In Table 1 details are given. In α-Boron instead, there are only 6 *exo* B-B bonds (1.67 Å) radially oriented and therefore a proper B_{12}^{2-} unit is not recognized. The other B-B extra cage bonds of α-B are longer (2.01 Å) and assigned by H&M as part of a symmetric 3c2e extra cage system, in agreement with Müller [12]. H&M admit that for γ-B, the extra cage 3c2e bonds are rather asymmetrical, inserted in triangles with two long edges (B_{eq2}-B_{db} and B_{eq3}-B_{db}) and a much shorter one (B_{eq2}-B_{eq3}), see Table 1.

An alternative counting scheme could be considered, under the following assumptions (see Table 1): there is a B_{12} cage with the classical 26 skeleton electrons; all *exo* radial bonds are 2c2e, even if their distances are rather spread; the B_{db}-B_{db} is a 2c2e bond; all distances above 1.98 Å (or 1.90 Å from *ab initio* prediction) are closed shell type interactions. The latter assumption would be in agreement with what calculated by Oganov *et al.*[1], that B_{eq2}-B_{db} and B_{eq3}-B_{db} are highly polar interactions with scarce charge concentration. With these assumptions, one would easily recover a B_{12}^{2-} and a B_2^{2+} sub-unit, see Table 2. However, one should not conclude that there are only ionic interactions between them, given that this counting scheme in fact assumes a 2c2e bond between B_{eq1} and B_{db}.

A comparison with $[B_{12}H_{12}]^{2-}$ is quite interesting (see Figure 2): in this borane hydride species, the only strongly localized bonds are the 12 *exo* B-H, whereas the B-B skeleton bonds are multicenter (B-B distance 1.78 Å). Within QTAIM, a useful indicator is the so called bond delocalization index δ [5], that measures the fraction of electron pairs shared by two atomic basins. Despite the name, a large δ indicates a strong localization of a 2c bond. DFT calculations give δ(B-H) = 0.7 whereas each skeleton B-B bond is associated with δ(B-B) = 0.47. A delocalization index smaller than 1, but significantly larger than 0, is typical of strongly polarized bonds, having a 2c2e character but a quite asymmetric distribution of the electron density shifted towards the hydrides. Based on QTAIM at various DFT level of calculations, the charges are ca. +0.45 (B) and -0.6 (H). It is a general tendency of B_{12} to localize electrons in the radial exo bonds, a feature that should be considered with care in γ-B. The small δ(B-B), instead, reflects the multicenter nature of the skeleton bonds, in the absence of any polarity for obvious symmetry reasons.

More intriguing is the electronic structure of the B_2 dumbbell. Oganov *et al.* compared the short B-B distance with that in known B_2X_4 species, like B_2F_4. The correct counter ion of the $[B_{12}]^{2-}$ is of course $[B_2]^{2+}$, but this cation is extremely elusive: in isolation its ground state is not stable against dissociation into $2B^+$ and only excited states, singlets or triplets, have minima on the potential energy surface with rather short B-B bond distances [13]. Even though solid state and high pressure are certainly able to stabilize electronic configurations otherwise instable, the presence of an unperturbed B_2^{2+} cation is quite unlikely, especially in view of the very short B_{eq1}-B_{db} bond. As a matter of facts, calculations in the solid state predict only a partial charge separation between B_2 and B_{12} sub-units [1,4]. The nature of B_{eq1}-B_{db} is evident from the electron localization function (ELF) [14] and the deformation density [2,4]. As anticipated above, a strongly localized *exo* bond B_{eq1}-B_{db}, radially oriented, is in fact necessary to stabilize the B_{12}^{2-} unit.

Another feature is important: the B_{eq1}-B_{db}-B_{db} angle is quite small (ca. 117°), see Figure 1, which is unexpected for the hypovalent B_2^{2+} cation that would preferentially bind along the B-B axis, to form a linear geometry. However, a bent structure for the molecule B_2F_2 can be optimized with B-B-F angle of ca. 127°, whereas a linear B_2F_2 conformer is not stable against bending. This can be proved by DFT calculations and also at post Hartree Fock level including a considerable amount of electron correlation (for example at QCISD level). At CAS[6,6] level, a linear geometry is calculated as a stable conformer, but the bent geometry is anyway more stable. By introducing electron correlation, the B-B distance becomes somewhat longer (ca. 1.78), but the features of the electron density distribution are unchanged. In Figure

3, the DFT $\nabla^2\rho(\mathbf{r})$ and the molecular graph are reproduced. The molecular graph of B_2F_2 clearly shows the strong tension in this molecule, with the B-B-F bond path angles being quite larger than the geometrical angles (see Figure 3). A strong charge separation is computed [$q(B) = +0.84$; $q(F) = -0.84$] in agreement with the ideal oxidation states of these atoms. Nevertheless the B-F bond is also strongly localized and according to different DFT or correlated methods, δ (B,F) $\sim$ 0.7, whereas δ (B,B) $\sim$ 1.15.

A calculation on the species $[H_{11}B_{12}\text{-}B_2\text{-}B_{12}H_{11}]^{2-}$ is also useful, see Figure 4. The crystal geometry of the B cage was kept fixed, with H atoms used to saturate the valence and fixed at optimized B-H positions. The electron density was computed at DFT level. The bond paths connecting the B_2 dumbbell are similar to those of B_2F_2 and confirm the tension. At variance from B_2F_2 and from the crystal, the charges of B_{db} and B_{eq1} are similar and close to 0. The delocalization indices are also quite even: $\delta(B_{db},B_{db}) = 0.97$ and $\delta(B_{eq1},B_{db}) = 0.95$. The covalence of this unit is visualized by means of the energy density distribution (Figure 4, top) which has an uninterrupted negative region. Besides, the B_{eq1}-B_{db} bond is quite polar, as visualized by the interatomic surfaces shown in Figure 4, but with a reverse polarity because the $B_{eq1}|B_{db}$ interatomic surface is shifted towards B_{eq1}. This polarity is probably caused by the tendency of the B_{12} unit to concentrate the charge on the external atoms ($q(H) \sim -0.6$) through the localized 2c2e bonds, in keeping with $B_{12}H_{12}{}^{2-}$. Therefore, the charge of the dumbbell is almost neutralized. In the solid state form of γ-B, instead, each B_{12} unit is radially connected to another and there cannot be bond polarity toward the external atoms because of the crystal symmetry. In this case, the dumbbell remains positively charged and the B_{eq1}-B_{db} bond maintains a quite symmetric distribution (see ref [1], Supporting information). This is however the result of two opposite forces, namely the tendency to polarize the density of *exo* bonds toward the external atom and the positive charge of the dumbbell. All other longer bonds to the dumbbell Boron atoms in the solid are instead highly polarized [1], in agreement with the idea that they have scarce covalent character. In Table 2, charges calculated with different bonding schemes are reported.

Discussion

The structure of the new γ-B phase seems to be quite established, from different experimental and theoretical works, although the agreement for some geometrical parameter is not quantitative, see Table 1. In addition, it is obvious that the structure may be subject to some modifications as pressure is applied, beside the large Vickers hardness and bulk

modulus. The interpretation of bonding in this phase is not unanimous as anticipated in the previous section. Zarechnaya *et al.* [2] excluded polar interactions in γ-B, because of the charge accumulation in the strongly localized B_{eq1}-B_{db} bond. As demonstrated above, however, even strongly polar bonds like B-H or B-F are associated with bond localization and large electron pair sharing. In this respect, the classification of bonds proposed by Bersuker [15] is quite illuminating, because based on the actual electrons involved in a bond and its properties, instead of a genealogical approach.

It is important to stress that the nature of a bond between the atoms of two interacting moieties cannot be straightforwardly assigned from the starting electronic configuration of these moieties. Otherwise, a bond between two molecular *ions* would be necessarily *ionic*, a dangerous oversimplification. A glimpse at some well-known compounds would immediately clarify the problem. For example, coordination compounds involve transition metal cations and organic or inorganic closed shell molecules or ions. Applying the above oversimplification, one shall conclude that all these compounds are characterized by ionic metal-ligand bonds. This was in fact the initial interpretation that prompted to the so-called *crystal field theory* (CFT). With the CFT, some spectroscopic properties of transition metals are explained by the "d-orbital splitting" occurring to an ion surrounded by negative charges, breaking the spherical symmetry of the ion. Since more than 40 years, however, we know that this is not correct and that substantial covalent bonding has to be considered when describing these species, unless missing some important information. Thanks especially to the work by B. N. Figgis [16], a *ligand field theory* (LFT) was later developed, still valid within the molecular orbital frameworks, extensively used afterwards for more accurate calculation of the electronic states of these species.

The creation of charged atoms in Boron at high pressure is not unprecedented and one can find analogous examples in other elemental solids as well as in molecular crystals. Some metals have been reported to undergo a transition to a non metallic phase at high pressure, for example Na [17], that localizes regions of valence shell charge concentration in interstitial voids. An interesting example of a organic compound is oxalic acid di-hydrate [18,19], which transforms at high pressure into oxalate di-anion and hydronium species. Because the electronic configuration is mainly assigned from the location of H atoms, the formation of ionic units is unambiguous there. Again, the oversimplification of Zarechnaya *et al.* [2] would imply that the hydrogen bond between the two units is exclusively ionic at high pressure. On the other hand, the hydrogen bond is electrostatic when it is a weak interaction between neutral molecules, but it becomes more covalent as the HB is stronger and this often occurs

between ions, sometime even homo-charged [20]. Gilli and Gilli [21] have illustrated the conditions that more likely give covalent short hydrogen bonds. This often depends on the resonance between two electronic configurations, for example a neutral and a charge transfer (ionic) one. Notably, a "charge transfer" electronic configuration does not imply at all a larger ionicity of the HB bond.

Given this illustration, it might become clear that finding features of covalent bonding between the B_2 and B_{12} units in γ-B is not in contradiction with a charged electronic configuration, as postulated by Oganov et al. [1]. In a theoretical work by the group of Martin Pendas *et al*. [22], a probabilistic interpretation was developed based on the electron distribution function. They showed how some bonds can be at the same time strongly covalent and strongly ionic. For example, carbon monoxide (CO) is a molecule with a formal triple bond (hence strongly covalent) but also with a strong bond polarity due to the different electronegativity of C and O [23].

The definition of covalency and the deformation density approach used by Zarechnaya *et al.* [2] might require some careful attention. Covalency is not the presence of "interstitial charge density" between two atoms, but it is a substantial *electron sharing* between two atoms. While electron distribution is easily measurable, electron sharing is not. Indeed, covalency might produce charge accumulation in a bond, measurable by larger amount of deformation density or larger charge concentration (more negative Laplcian, $\nabla^2\rho(\mathbf{r})$), but this is not always the case [24]. Analysis of the deformation density should be taken with a grain of salts, because it is quite well known that the difference between a total and a reference electron density might lead to ambiguities and misinterpretations. It is well known since the early '80s that F_2 and H_2O_2 molecules lack of charge accumulation in the F-F or O-O bonds [25,26], but there is no doubt on the covalent character. This apparent contradiction is just an artifact due to the non-spherical ground state of the isolated F or O atoms. Using sphericized atomic densities as reference leads to charge lacking in the bonding regions because of the large average number of electrons subtracted in the bonding region if localized lone pairs are not explicitly considered. A similar problem (but of opposite sign) would affect Boron, which is electron poor as isolated atom in the ground state ($^2P_{1/2}$), which was very likely used as reference for the deformation density plots reported in [2] and [4] or the independent atom model used for benchmark in [1]. This does not mean of course that those deformation densities are wrong, but simply that the charge accumulation is larger than what actually produced by the covalence of the bonds.

It would also be important discussing the features of chemical bonding in B forms, in view of the known hardness and bulk moduli, see also the discussion reported in other articles of this issue.[27] For example, the bonding scheme depicted by H&M, apart for computing charges in contrast to quantum mechanical calculations in the solid state, would also hamper a proper estimation of the material hardness. In fact, they associate strong 2c2e bonds only to three interactions: B_{ap}-B_{ap} (extra cage, along crystallographic a), B_{eq1}-B_{db} (extra cage along b) and B_{db}-B_{db} (intra-dumbbell along a). However, B_{eq1}-B_{db} and B_{db}-B_{db} would not be particularly effective for the hardness, given the necessarily softer bending of B_{eq1}-B_{db}-B_{db} angle which would make the compressibility not so small along the b direction. In addition, no strong extra-cage bond would be located along the c direction. In this interpretation, γ-B would not be so different from α-B, which strong 2c2e bonds are also mainly elongated in one direction. On the contrary, if all the radial *exo* bonds of a B_{12} unit are taken as strong 2c2e, a three-dimensional network of strong bond is recognized, in agreement with the measured hardness and at variance from α-B. Of course the realm of γ-B is probably a mixture of configurations, easily understood by the uneven distribution of radial B-B distances and closed shell or three center B-B bonds. The weaker extra-cage bonds in α-B were also classified by H&M as 3c2e, in agreement with ref. [12], but they should also deserve more careful attention. Because of symmetry they cannot be polar, but it seems they could also fall in a closed shell regime.

It should not escape attention, however, that the model based on $(B_{12})^{2-}(B_2)^{2+}$ is strongly distorted in the crystal structure, with deviations of *exo* B-B bonds from the expected radial directions and a large variance of bond distances, as reported in Table 1. The trend in QTAIM charges (experimental or theoretical) is also not completely consistent with that electronic configuration, see Table 2. Therefore, it is quite likely that some degree of mixing takes place between $(B_{12})^{+2/3}(B_2)^{-2/3}$ and $(B_{12})^{2-}(B_2)^{2+}$ electronic configurations. This would better justify the QTAIM charges and the observed ranges of bond distances, but it would not change the large polarity between some interactions in the solid. This feature is not in contrast and actually in agreement with the covalent network that is responsible of the structural and mechanical properties.
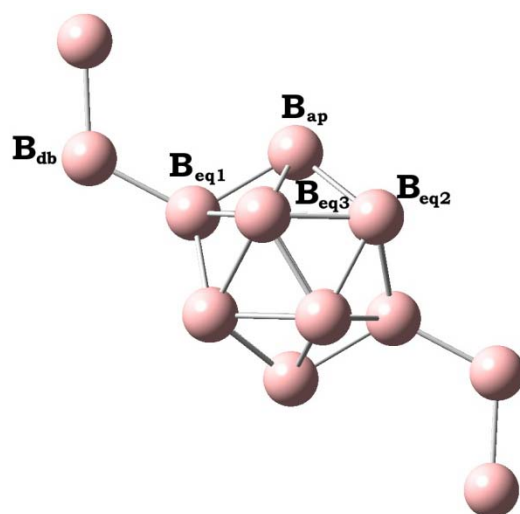
Figure 1. A schematic view of the B_{12} and B_2 sub units in γ-B, within the *pseudo* C_{2h} (2/m) symmetry of this fragment. All B atom of the B_{12} cage have a radial exo-bond toward another B_{12} unit (not shown in this picture) but B_{eq1} which is instead connected to a dumbbell Boron atom, B_{db}.
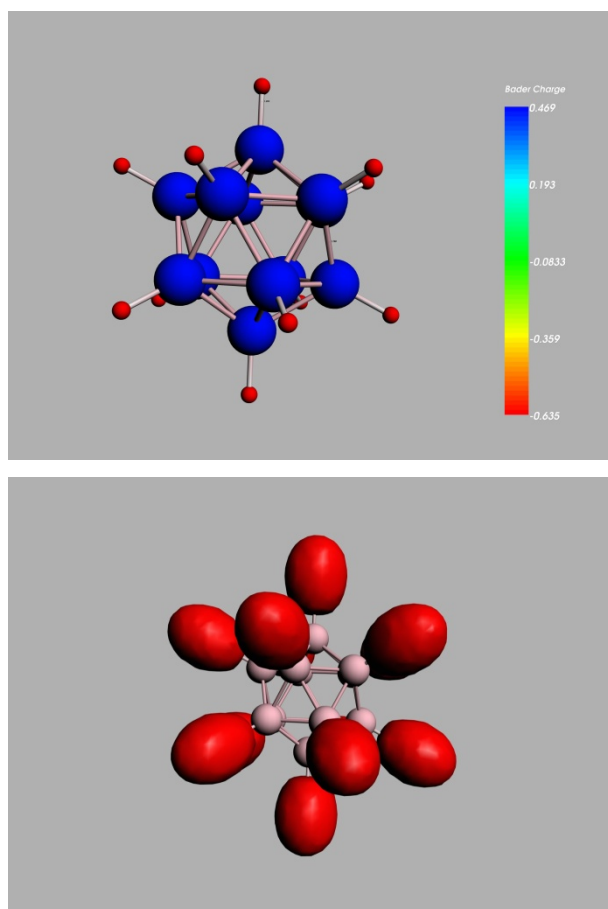
Figure 2. Top: the structure of $[B_{12}H_{12}]^{2-}$ with atoms colored according to QTAIM charges (q(B) = +0.45; q(H) = -0.6) from BLYP/QZ4P calculations; bottom: the electron localization function (isosurface at η = 0.9), showing the high localization inside B-H bonds.
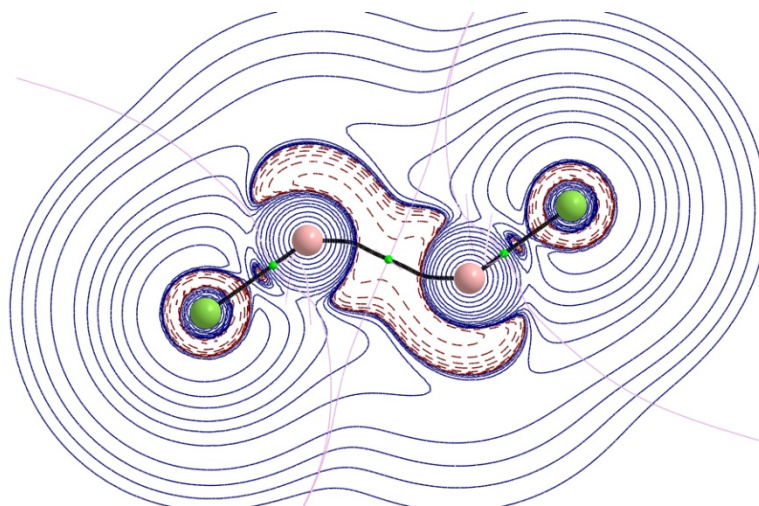
Figure 3. The Laplacian distribution of B_2F_2. The molecular graph is superimposed.

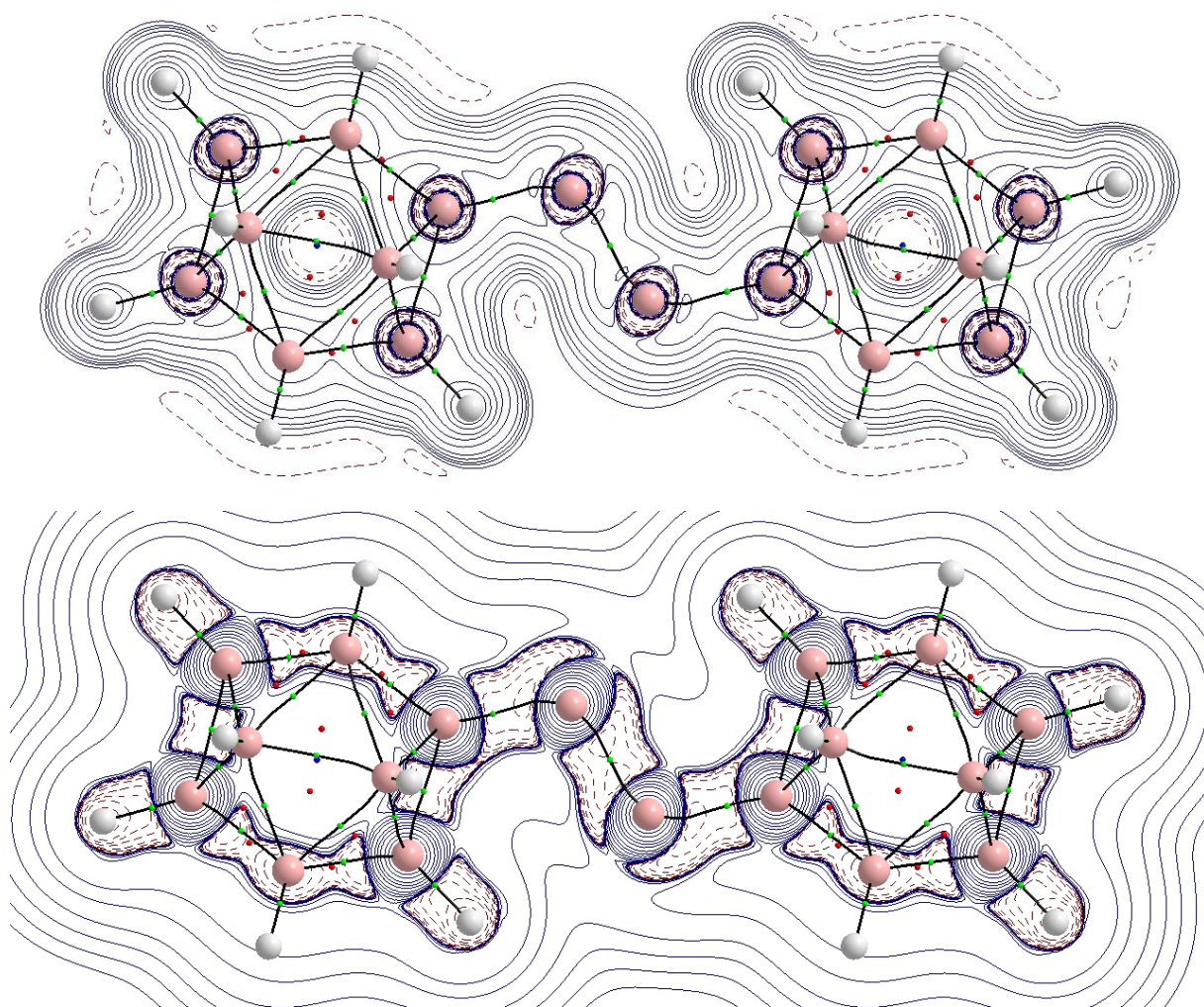**Figure 4**. Top: Electronic Energy Density in $[B_{12}H_{11})B_2(B_{12}H_{11})]^{2-}$; bottom: Laplacian of the electron density distribution. The molecular graph is superimposed, note in particular the curvature of the B-B bond paths of the B_2 dumbbell.

Table 1: Bond distance ranges in γ-Boron (at ambient pressure): a comparison between the H&M and the $(B_{12}^{2-})(B_2^{2+})$ schemes

	Distances single crystal [2]	Distances ab initio [1]	Bond type H&M scheme [ref. 4]	Bond type B_{12}^{2-} B_2^{2+} scheme
B-B within B_{12} (B_{eq1}-B_{eq2}; B_{eq2}-B_{eq3}, B_{ap}-B_{eq1}, B_{ap}-B_{eq2} B_{ap}-B_{eq3}; B_{eq3}-B_{eq3})	1.73-1.88	1.77-1.81	Multi center, multi-electron	Multi center, multi-electron
Inter-B_{12} radial B-B (B_{ap}-B_{ap})	1.72	1.66	*2c2e*	*2c2e*
Inter-B_{12} radial B-B (B_{eq2}-B_{eq3})	**1.83**	**1.82**	**3c2e**	**2c2e**
B_{12} cage - B_2 dumbbell (B_{eq1}-B_{db})	1.61	1.67	*2c2e*	*2c2e*
B_{12} cage - B_2 dumbbell (B_{eq2}-B_{db}; B_{eq3}-B_{db})	**1.98-2.1**	**1.90-2.05**	**3c2e**	**Closed shell**
Intra-dumbbell (B_{db}-B_{db})	1.66	1.73	*2c2e*	*2c2e*

Table 2: Atomic charges in γ-B based on electron counting schemes and on QTAIM

Atom	Site Multiplicity	QTAIM DFT [ref. 1]	QTAIM expt [ref.6]	$B_{12}^{2/3} B_2^{-2/3}$ scheme [ref. 4]	$B_{12}^{2-} B_2^{2+}$ scheme
B_{ap}	4	+0.03	+0.06	-1/6	-1/6
B_{eq1}	4	+0.06	-0.14	-1/6	-1/6
B_{eq2}	8	-0.17	-0.19	+1/6	-1/6
B_{eq3}	8	+0.00	+0.00	+1/6	-1/6
B_{db}	4	+0.24	+0.41	-1/3	+1

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