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New Convex and Spherical Structures of Bare Boron Clusters

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New stable structures of bare boron clusters can easily be obtained and constructed with the help of an "Aufbau Principle" suggested by a systematic *ab initio* HF-SCF and direct CI study. It is concluded that boron cluster formation can be established by elemental units of pentagonal and hexagonal pyramids. New convex and small spherical clusters different from the classical known forms of boron crystal structures are obtained by a combination of both basic units. Convex structures simulate boron surfaces which can be considered as segments of open or closed spheres. Both convex clusters B_{16} and B_{46} have energies close to those of their conjugate quasi-planar clusters, which are relatively stable and can be considered to act as a calibration mark. The closed spherical clusters B_{12}, B_{22}, B_{32}, and B_{42} are less stable than the corresponding conjugated quasi-planar structures. As a consequence, highly stable spherical boron clusters can systematically be predicted when their conjugate quasi-planar clusters are determined and energies are compared. © 1997 Academic Press

I. INTRODUCTION

Investigations on the evolution of the bulk and the transition between individual atoms and condensed matter, like thin films, liquids, and solids, were fundamental tasks of the past decade (1). The question of whether species in the cluster phase can reproduce structures and properties of the bulk or show different behavior is still not answered. Starting with alkali metal clusters of group 1, e.g., lithium and sodium, which represent the simplest atoms with one valence electron and with very similar valence electron shells (2, 3), charged metal clusters of the same atomic group also were investigated systematically using *ab initio* quantum chemical methods (4, 5), including their properties and the relationship between the electronic and geometrical structures as well.

The detection of unusually high intensity in the mass spectral distribution of neutral sodium clusters and the corresponding Knight's shell model (6), as well as the detection of the fullerenes (7) marked the beginning of a new era of cluster research. Very small clusters are mostly composed of surface atoms with only few atoms in the interior. Consequently, it is very desirable to investigate the relationship between the electronic and geometric structures and their influence on cluster formation. Stability, fragmentation, and dissociation of clusters, energy barriers of reactions with other species, and energy transitions between the states are additional indications and measures of cluster properties, which could enhance the production of new materials for useful technological purposes.

In nature boron occurs in amorphous and crystalline forms. Best known crystals are the α- and β-rhombohedral as well as the alpha-tetragonal boron, all composed of icosahedral unit cells of B_{12} (8). The α-rh boron, also called low-temperature or red boron, was observed to have a high level of crystal purity. The icosahedra in α-rh boron are bound to each other by three-center bonds located in alternating parallel planes. The high-temperature polyhedron β-rh boron has a structure composed of a central B_{12} icosahedron surrounded by 12 pentagonal pyramids B_6. In the polyhedra of $B_{12}(B_6)_{12}$ the 12 bonds are shared by boron atoms of the central icosahedron with the central atoms of the 12 hexagonal pyramids. The spherical B_{84} units are bonded to each other through intermediary B_{12} subunits in planes parallel to the basal plane of the hexagonal cell. Nevertheless, there exist some boron polymorphs and allotropes which are still unknown (9).

From the theoretical point of view, different boron cluster sizes larger or equal to B_{12} were investigated by Kato *et al.* (10) and Kawai *et al.* (11) employing different *ab initio* methods. Tang and co-workers *et al.* (12.13) calculated the B_{14} cluster by applying the *ab initio* Hartree–Fock method. Recently, Ricca and Bauschlicher (14) investigated the cationic small boron clusters B_n^+ up to ($n = 14$) using density functional methods. Experimentally, a series of studies on the mass spectra of boron clusters were reported by Anderson and co-workers (15). La Placa *et al.* extended the mass spectra up to 52 and found similar intensities (16).

In the current work the neutral boron clusters B_n for $n = 12, 16, 22, 32, 42$, and 46 are presented applying *ab initio* quantum chemical methods. All electron calculations were determined using the Hartree–Fock self-consistent-field approach (HF-SCF). The present investigation concerns such clusters of the first element of group 13 (17), which are composed of trivalent boron atoms, characterized by its

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high melting point and hardness close to diamond. Due to the sp^2 hybridization and to the strong directed chemical bonds, the boron clusters have properties very different from those known in the alkali metal clusters (18). In contrast to the tetragonal structures of the alkali–metal clusters, the boron clusters prefer to form convex or quasi-planar surfaces (19, 20), composed of pentagonal and hexagonal pyramids different from the well known forms of the crystals, the α- and β-rhombohedral boron, described above.

II. COMPUTATIONAL METHODS

Based on the analytical conjugated gradient method (21), all calculations as well as the optimization procedure were carried out employing restricted *ab initio* Hartree–Fock theory throughout to determine the ground state energies of the boron clusters. Some symmetry restrictions were made and minimal STO-3G basis sets were employed to enable all-electron calculations and the optimization of large cluster sizes. We already applied the extended basis set 3-21G for some clusters such as B_{16} and B_{22}, but this basis set was too large for optimization of larger cluster sizes.

In the present work the convex and spherical boron clusters are constructed and the geometrical and electronic structures of the B_n for $n = 12$, 16, 22, 32, 42, and 46 are investigated. The optimized energies of the quasi-planar clusters (20) should act as a calibration mark only. Nevertheless, we have presented two conjugate quasi-planar structures of the spherical B_{12} and B_{32} clusters to demonstrate the existence of different local minima of lower energy on the quasi-planar potential surfaces. The starting geometries for the optimizing procedure were constructed according to the basic units of the pentagonal and hexagonal pyramids. Most of the *ab initio* Hartree–Fock self-consistent field calculations were converged after an average of 20 iteration steps, considering some symmetry restrictions as mentioned above. The final optimized structures were not far from the starting geometries and the energy lowering obtained by the optimization procedure in general is not extremely large. All computations of the boron clusters were carried out using the program package GAMESS-UK (22).

III. RESULTS AND DISCUSSION

According to the “Aufbau Principle” proposed in Refs. (19, 23) there exist two basic units, the pentagonal and hexagonal pyramids, which can form different structures. A combination of hexagonal pyramidal units produces quasi-planar surfaces. Including pentagonal pyramidal units definitely leads to three-dimensional (3D) structures. In other words, spherical clusters can be constructed only by a combination of pentagonal and hexagonal pyramids. The transition from 2D to 3D structures occurs only by including the pentagonal pyramidal unit. Analogous to the quasi-planar structures, which can easily be constructed starting from a hexagonal pyramid by adding atoms consecutively to form a new hexagonal pyramid, convex or spherical clusters can be built by starting from a pentagonal pyramid and adding atoms consecutively to form new hexagonal pyramids. This procedure can be continued to form either further hexagonal or further pentagonal pyramids. The closure of the surface depends on the number of the created hexagonal and pentagonal pyramids. Starting from a hexagonal pyramid and proceeding by creating only further hexagonal pyramids yields a quasi-planar surface. As soon as one pentagonal pyramid is installed the surface begins to bend.

Two sets of clusters were constructed and determined using the optimization procedure within a given point group symmetry at the HF-SCF level of theory. The first set contains two examples of boron clusters representing new convex structures different than those reported in (19, 23), which consist of hexagonal pyramids only. The second set contains the smallest spherical boron clusters composed either of pentagonal pyramids or of a combination of pentagonal and hexagonal pyramids, substantially different from the compact and the open three-dimensional boron clusters mentioned in (19, 23).

A. *The Convex Clusters*

Fortunately, inclusion of the pentagonal pyramids as mentioned above enables cluster formation of new convex structures containing at least one pentagonal pyramid and permits a structure transformation from 2D to 3D clusters. The first isomer of the B_{16} cluster has a convex structure of C_{5v} symmetry (see Fig. 1) and the ground state ^1A_g. The corresponding electronic configuration of the upper MOs is given in Table 1. A side perspective of the B_{16}–C_{5v} cluster shows the clusters as segments of a spherical surface. It contains a combination of dovetailed pentagonal and hexagonal pyramids. This topology consists of one pentagonal pyramid surrounded by five hexagonal pyramids. The axial bond length of the pentagonal pyramid is around 1.65 Å, and the equatorial bond length is 1.71 Å. The bond lengths between the pentagon and the peripheral atoms are 2.11 and 1.61 Å, while the distance between the outermost peripheral atoms of the cluster is 1.54 Å. The conjugate quasi-planar B_{16}–C_{2h} cluster (20) contains four hexagonal pyramids with top and bottom characters. The SCF energy difference between both isomers is of about 0.0072 a.u. (see Ref. (20)).

The largest B_{46} cluster considered in this work can easily be obtained from the previous B_{16} clusters. By adding 30 atoms around the outermost peripheral atoms of the convex cluster of B_{16} and by keeping the same point group, we obtain the convex B_{46} cluster Fig. 2. The structure of the B_{46} cluster was optimized in C_{5v} symmetry. The corresponding ground state and the electronic configuration

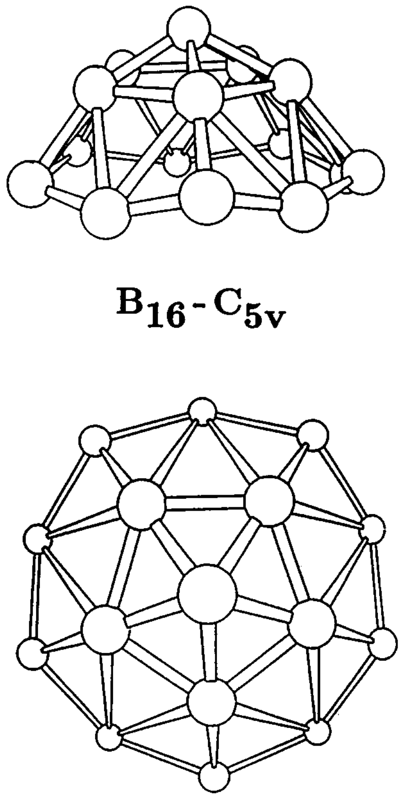


FIG. 1. Final structures of the neutral boron clusters B_{16} with the side perspective, optimized at the HF-SCF level, and obtained with the 3-21G basis set. The convex cluster is indicated with the point group symmetry.

are given in Table 1. The side perspective of the convex B_{46} cluster (see Fig. 2) shows a form like a crown. This cluster consists of 6 pentagonal and 25 hexagonal pyramids. One can easily recognize the central pentagonal pyramid surrounded by hexagonal pyramids, as well as the five peripheral pentagonal ones. The axial bond lengths of the central pentagonal pyramid are around 1.83 Å and the equatorial bond lengths are 1.78 Å. The average axial bond length of the peripheral pentagonal pyramids is around 1.68 Å, and that of the equatorial bond lengths is 1.72 Å. The distance between the outermost peripheral atoms of the cluster is 1.55 Å. The average bond length of the hexagonal pyramids is 1.70 Å.

The structure of the quasi-planar B_{46}–C_i cluster (20) contains 24 hexagonal pyramids with top and bottom characters and can also easily be obtained starting at the B_{16}–C_{2h} cluster and adding further atoms consecutively forming a new hexagonal pyramid. The apices of the hexagonal pyramids lie above or below the cluster plane with different height s of maximum 0.4 Å and the bond length of all hexagonal pyramids lies between 1.50 and 1.90 Å. The final optimized SCF energies of both B_{46} isomers have a difference of about 0.0097 a.u. (20). It is well known that different topologies have different energies. In the case of the convex and quasi-planar structures of each B_{16} and B_{46} cluster the corresponding HF-SCF energies are also different but nearly close and the energy difference is relatively small. This is of course an accidental case but nevertheless the energies of the quasi-planar clusters can help as reference energies and act as a calibration mark.

B. The Spherical Clusters

The fact that the convex clusters are considered to be segments of a sphere leads to the assumption of the existence of spherical boron clusters with different sizes similar to the phenomenon of fullerenes. In carbon clusters, series of spheres were found, all having highly symmetric sets of

TABLE 1
SCF Energies of Selected B_n Clusters Optimized at STO-3G and 3-21G

Cluster[a]	Sym., St.[b]	E(STO-3G)[c]	$E_{b/n}$[d]	$E(3-21G)$[c]	$E_{b/n}$[d]	Electronic configurations
B_{12}	$I_h, {}^3T$	– 291.53103	3.95	– 293.78512	2.51	$(...)(a_g)^2(g_u)^8(t_{1u})^6(t_{2u})^2$
	$D_{5d}, {}^3A_{2g}$	– 291.53910	3.97	– 293.83200	2.62	
	$C_{3v}, {}^1A_1$	– 291.91042	4.81	– 294.07897	3.18	See Ref. (23), Table III
B_{16}	$C_{5v}, {}^1A_g$	– 389.27280	4.91	– 392.14403	3.25	$(...)(a_2)^2(e_2)^4(e_1)^4(a_1)^2$
B_{22}	$D_{5d}, {}^3A_g$	– 535.07009	4.69	– 538.97759	2.98	$(...)(a_{1u})^2(e_{1u})^4(e_{2u})^2$
B_{32}	$I_h, {}^1A_g$	– 777.96010	4.42	—	—	$(...)(h)^{10}(t)^6(t)^6(g)^0$
	$C_{2v}, {}^1A_1$	– 778.35602	4.75	—	—	$(...)(a_2)^2(b_2)^2(a_2)^2(b_1)^2$
B_{42}	$D_{5h}, {}^1A_g$	– 1021.29613	4.56	—	—	$(...)(a_2'')^2(e_2'')^4(e_1'')^4(e_2')^4$
B_{46}	$C_{5v}, {}^1A_1$	– 1119.51438	5.12	—	—	$(...)(e_1)^4(e_1)^4(a_1)^2(a_1)^2$
B–atom	C_1–${}^2P$	– 24.14899	—	– 24.43031	—	

[a] For geometries of the boron clusters, cf. Figs. 1 to 6.

[b] Symmetry and state of the boron clustes, see text.

[c] HF-SCf energies of the boron clusters in a.u. (Hartree).

[d] The corresponding binding energy per atom in eV.

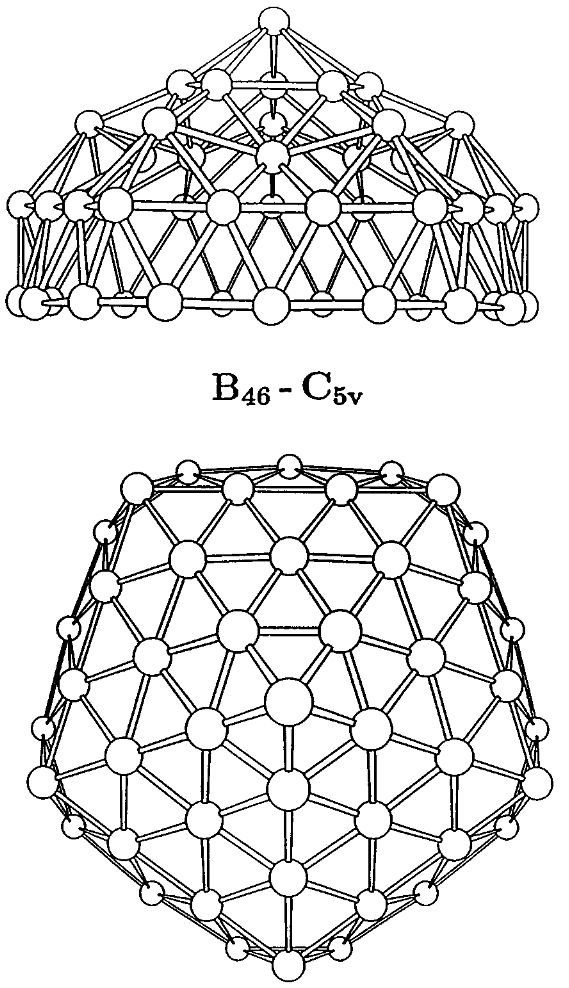


FIG. 2. Final structures of the neutral boron clusters B_{46} with the side perspective, optimized at the HF-SCF level, and obtained with the 3-21G basis set. The convex cluster is indicated with the point group symmetry.

truncated icosahedra composed of pentagonal and hexagonal rings. The proposed boron quasi-planar surfaces (20) are similar to that of those of graphite, where the hexagonal rings are replaced by hexagonal pyramids. The closure of the quasi-planar surfaces of boron into spherical polyhedra obeys the same rules as in graphitic surfaces, which can be closed into hollow cages of fullerenes. The transition from 2D to 3D structures simply requires the elimination of some hexagonal vertices from the planar surfaces to form pentagonal rings or pyramids and enables the transformation to 3D structures.

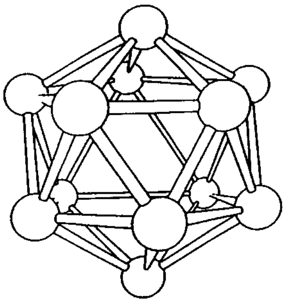
However, a pattern of pentagonal and hexagonal pyramids makes a significant contribution to cluster formation, removes the ambiguity of the cluster growth, and diminishes the route of approaching stable hollow boron spheres resembling the buckyball C_{60}, a hollow cage composed only of pentagons and hexagons. Due to the sp^2 hybridization the predicted spherical boron structures should be highly stable and might have an appearance similar to that of the fullerenes. Nevertheless, the investigation of either highly symmetric 3D or less symmetric 2D species implies that limitation of the symmetry, and the corresponding degrees of freedom, permits us to select structures which can be computed and evaluated. Indeed, the spherical boron clusters should be the conjugate form of the fullerenes proposed by Tang *et al.* (13), where the pentagonal and hexagonal faces are centered by atoms which form pyramids. The strategy of search for stable spheres can be realized within a procedure which first begins with the construction of the polyhedral spheres, as well as their conjugated quasi-planar species using the Aufbau pattern, and then by applying the optimization procedure using the gradient methods and finally by determining and comparing their energies.

We have learned from the open three-dimensional clusters (19, 23) that they are mostly composed of pentagonal pyramids and energetically about 0.18 a.u. less stable than the convex or the quasi-planar clusters composed of hexagonal pyramids. For example, the B_{14}–D_{6d} cluster, which can be obtained from the B_{13}–C_s cluster by adding one atom closing the sphere, contains two parallel hexagonal pyramids and is unstable. As soon as the optimization procedure is applied the spherical cluster B_{14}–D_{6d} dissociates into two species of hexagonal pyramids. However, there are different factors contributing to the instability of 3D clusters. Besides the Jahn–Teller effect, the angle between the overlapping sp^2 hybrid orbitals plays a very important role. The tension in the small spherical species seems to be relatively high, which causes instability in clusters. In addition, the outward pointing π_p hybrids slightly interact within the polyhedra and less with themselves, contributing a minimal overlap. In contrast to the quasi-planar species, where the π_p hybrids interact with each other, the electron cloud which arises stabilizes the cluster very strongly. Besides the icosahedron we have introduced in this section three highly symmetric spherical models constructed from pentagonal and hexagonal subunits.

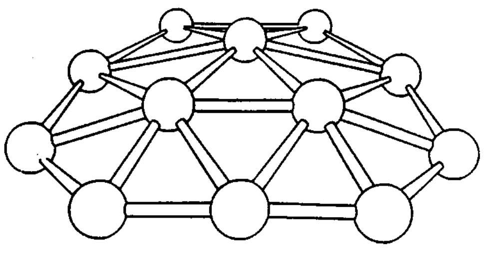
B.1. The icosahedron B_{12}. Besides the platonic body of the icosahedral structure there is another nuclear arrangement of B_{12}, which is a highly symmetric cube-octahedron. In many crystals the icosahedron builds the basic unit of the α- and β-rhombohedral (8) boron crystals, which are the well known forms in the boron-rich phases. The elementary cell of the crystal lattice is built up by more or less regular icosahedra which are connected by various intericosahedral bonds or by single boron atoms. The presence of icosahedral clusters is not so surprising as in the case of boron-rich phases. They are characterized by covalent bonds in view of the electron deficiency of boron and of the efficient manner for distributing electrons providing the ideal compact icosahedral cage. The polyhedral structure of the icosahedron, which can easily be achieved by a slight transition of a cube-octahedron, as reported by Matkovich and Economy (24), consists of 12 vertices, 30 edges, and 20 trigonal faces. The icosahedron can also be described as being composed of 12 dovetailed penatgonal pyramids.

One should notice that the construction of the buckminster fullerene C_{60} was done by truncation of the icosahedron, in such a way that each of the 12 vertices converts into a nonabutting pentagon and each of the 20 trigonal faces into 20 abutting hexagons (25). The point group symmetry of the regular icosahedron contains a large number of symmetry elements, namely: an inversion center, 6 fivefold axes, 10 threefold axes, 15 twofold axes, and 15 mirror planes. The most exceptional feature of this polyhedron is the presence of the fivefold axes.

The electronic structure of a regular icosahedron B_{12}–I_h (Fig. 3) was studied by Longuet-Higgins and Roberts (26) in the 1950s. The icosahedron of the B_{12} cluster, optimized in the D_{5d} point group symmetry, has a bond length of 1.67 Å so that the diameter of the icosahedral sphere is about 3.3 Å. The main configuration of the valence electrons $(a_g)^2(t_{1u})^6(h_g)^{10}(a_g)^2(g_u)^8(t_{1u})^6(t_{2u})^2$ corresponds to the orbital energies − 1.08, − 0.84, − 0.58, − 0.42, − 0.37, − 0.20, + 0.09 a.u., respectively, computed with the STO-3G basis set, as mentioned above. The triply degenerate HOMOs (t_{2u}) are occupied by two valence electrons only. Due to the partial occupation of the degenerate HOMOs the Jahn–Teller distortion follows, causing a symmetry lowering of the cluster geometry, and transfers the point symmetry I_h into D_{5d}. Of course the symmetry lowering into D_{5d} leads to an energy lowering of 0.0081 a.u. only. This artificial degeneracy is removed after using the larger basis set 3-21G. Therefore, the energy lowering increases to 0.047 a.u., (see Table 1). The optimized B_{12}–D_{5d} cluster has $^3A_{2g}$ as a ground state and the average bond length of the slightly distorted B_{12}–D_{5d} cluster is about 1.68 Å.



B_{12} - I_h



B_{12} - C_{3v}

FIG. 3. The structure of the icosahedral boron cluster B_{12}, optimized at the HF-SCF level, and obtained with the 3-21G basis set. The icosahedron and its conjugate quasi-planar cluster are indicated with the point group symmetry.

As mentioned above, we would like to demonstrate the existence of at least one quasi-planar cluster, which consists of different elements compared to the isolated icosahedron. The conjugate convex B_{12}–C_{3v} cluster (Fig. 3) is more stable than isomers B_{12}–I_h and B_{12}–D_{5d}. The HF-SCF energy of the convex structure lies below the corresponding energies of the 3D species by more than 0.37 a.u. at the STO-3G basis, and reduces to 0.24 a.u. for the 3-21G basis (Table 1). The convex cluster has three hexagonal pyramids with an average bond length of 1.76 Å. The B_{12} cluster calculated by Kato *et al.* (10) confirms the 2D character of the quasi-planar clusters, but is still slightly higher energetically than that of the current work.

B.2. The B_{22} clusters. The next spherical 3D structure is the B_{22}–D_{5d} cluster shown in Fig. 4. The side perspective of this spherical B_{22} cluster shows an oblate 3D geometry similar to a discus form. It contains a combination of 12 pentagonal and 10 hexagonal pyramids. The ground state of the oblate B_{22}–D_{5d} cluster $^3A_{2g}$ corresponds to the leading electronic configuration (see Table 1) considering the last four MOs. The corresponding orbital energies of these MOs are − 0.241, − 0.231, − 0.144, and − 0.197 a.u., respectively. It is seen that the energy of the doubly occupied and degenerate open shell e_{2u} orbital lies lower than that of the closed shell orbital e_{1u}. The axial and equatorial bond lengths of the central pentagonal pyramid are 1.77 and 1.66 Å, while those of the peripheral pentagonal pyramids are 1.77 and 1.66 Å, respectively. The average of the bond length of the hexagonal pyramids is 1.85 Å.

The conjugate quasi-planar B_{22}–C_2 cluster (20) consists of eight hexagonal pyramids with parallel apices of top and bottom characters. It is about 0.143 a.u. more stable than the oblate cluster B_{22}–D_{5d}. Nevertheless, the shape of the oblate structure can be converted into a spherical one by using larger basis sets. Also the geometry of the quasi-planar cluster corresponds to a local minimum on the energy potential surface, which surely contains other energy minima lower than that mentioned above. However, the B_{22}–C_2

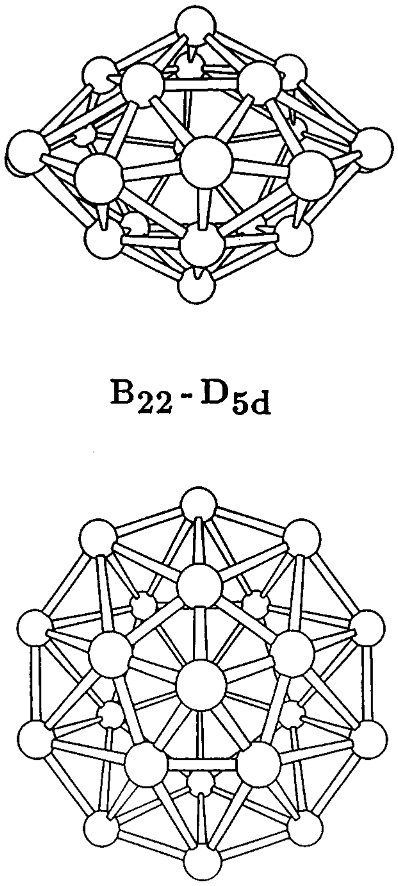


FIG. 4. Final structure of the oblate spherical boron cluster B_{22} with the side perspective, optimized at the HF-SCF level, and obtained with the STO-3G basis set. The spherical cluster is indicated with the point group symmetry.

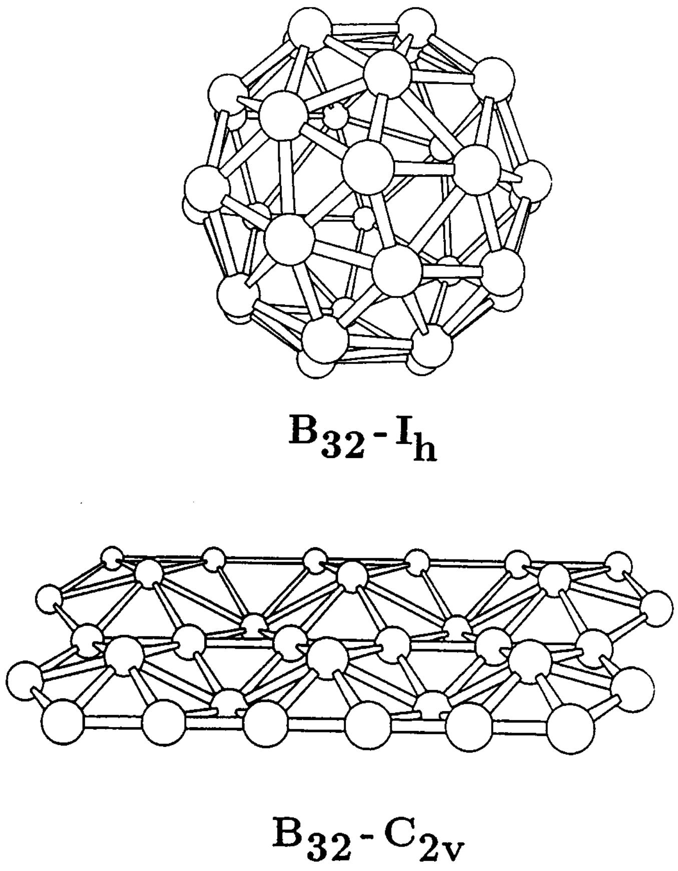


FIG. 5. Final structure of the boron sphere B_{32} and one conjugate quasi-planar cluster, both optimized at the HF-SCF level and obtained with the STO-3G basis set. The spherical cluster and its conjugate one are indicated with the point group symmetry.

cluster (20) is an example to illustrate the existence of isomers of quasi-planar structure which are more stable than the 3D structure for B_{22} clusters. The behavior of the 2D and 3D polyhedra of the B_{22} cluster shows the same relationship as in the case of the B_{12} isomers.

B.3. The B_{32} clusters. The polyhedron B_{32} belongs to I_h point group symmetry, consists of 12 pentagonal and 20 hexagonal pyramids shown in Fig. 5. The structure of this polyhedron was computed in D_{5d} symmetry using the same standard STO-3G basis set and applying the same approach. The optimized HF-SCF energy is in agreement with the one calculated by Tang *et al.* (13) and determined at the same level of theory (see Table 1). The computed axial and equatorial bond lengths of the pentagonal pyramids are 1.66 and 1.75 Å, respectively. The corresponding diameter of the spherical polyhedron B_{32} is about 5.14 Å, due to both optimized radial parameters of the Z-Matrix computed in the D_{5d} symmetry. The low-lying ground state of the B_{32}–I_h polyhedron is ^1A_g and corresponds to the electronic configuration given in (Table 1), which includes *t*, *g*, and *h* MOs assigning three-, four-, and fivefold degeneracy, respectively.

In contrast, the conjugate B_{32}–C_{2v} cluster (see Fig. 5) is one of various isomers of quasi-planar configurations which are energetically more stable than the spherical cluster B_{32}–D_{5d}. The optimized HF-SCF energy is about 0.396 a.u. lower than that obtained for the truncated icosahedral spherical structure of the B_{32}–I_h polyhedron (Table 1). The quasi-planar B_{32}–C_{2v} cluster consists of 24 hexagonal pyramids with top and bottom characters of the apices.

The large Hartree–Fock stabilization energy of 0.396 a.u. obtained for the quasi-planar cluster B_{32}–C_{2v} in relationship with the spherical structure B_{32}–I_h can also be explained by strongly interacting outward pointing π_p hybrids. Optimal overlap between the out-of-plane π_p orbitals produces electron clouds on both sides of the cluster plane similar to graphite and causes a larger stability of the clusters besides an energy lowering.

B.4. The B_{42} clusters. Based on the same procedure, we have constructed the hollow polyhedron of B_{42} using pentagonal and hexagonal pyramidal subunits. The spherical structure of the B_{42}–D_{5h} cluster consists of 12 pentagonal, 30 hexagonal pyramids, and 120 edges. The preliminary HF-SCF energy obtained with the STO-3G basis set is given in Table 1. The alternating characters of the hexagonal and pentagonal pyramids can be seen in Fig. 6. The ground state of the spherical B_{42}–D_{5h} polyhedron (A'_1) corresponds to the electronic configuration concerning the last four MOs (see Table 1). By the generated Z-Matrix of the internal coordinates, only two radial distances were considered as variable parameters. All other parameters regarding the rotation axes, like the bond angles and the dihedral angels, were kept constant. Starting from different spherical configurations one local minimum was obtained. The obtained radial and equatorial bond lengths of the pentagonal pyramids are 1.68 and 1.72 Å, and those of the hexagonal pyramids are simultaneously the same equatorial bond lengths of the pentagonal pyramids, namely 1.72 Å. The estimated diameter of this spherical polyhedron B_{42} is around 5.98 Å.

As expected, the conjugate quasi-planar B_{42}–C_i cluster (20) is more stable than the spherical structure B_{42}–D_{5h}. The HF-SCF energy is about 0.544 a.u. lower than that of the spherical polyhedron B_{42}–D_{5h}. This can be connected to the fact that the energy of the spherical B_{42} cluster corresponds only to a saddle point and the true minimum has still not been found. The high stability of the quasi-planar cluster can also be related to the strongly interacting outward pointing π_p hybrids. The out-of-plane overlapping π_p orbitals establish electron clouds above and below the cluster plane, which produce a strong stabilization effect, as in graphite. The computed local minima of both isomers do not represent any global minima on the energy potential surface.

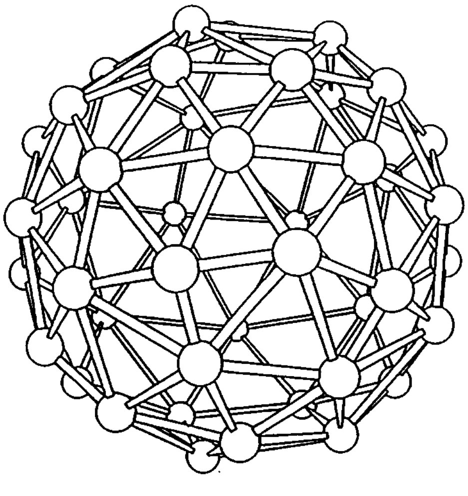


FIG. 6. Model structure of the boron sphere B_{42} obtained at the HF-SCF level with the STO-3G basis set. The spherical cluster is indicated with the point group symmetry.

C. Discussion

In the present work, we have proposed new stable convex surfaces and predicted the existence of spherical polyhedra similar to the hollow cages of fullerenes. With these convex and spherical forms we have tried to formulate new ideas suggesting the construction and simulation of novel cluster formation. All these contributions are based on results obtained with *ab initio* quantum chemical methods and on an Aufbau Principle (AP) proposed for the cluster formation of boron (23). It concludes that highly stable species of different forms and sizes can be constructed from two basic units, the pentagonal and hexagonal pyramids, either by a combination of each unit or by both together.

A combination of pentagonal pyramids produces only exclusive three-dimensional surfaces, like the icosahedron in Fig. 3 or those open 3D structures reported in Ref. (23). A combination of hexagonal pyramids results in two kind of species, the quasi-planar surfaces, as demonstrated in Figs. 3 and 5 (see also Ref. (20)). A combination of both units, the pentagonal and hexagonal pyramids, leads to the convex and spherical clusters as demonstrated in the current study, as well as to closed three-dimensional surfaces of tubular forms (27). It must be noted that the inclusion of the pentagonal pyramid transforms the 2D surface into 3D as well, leading to closed or open three-dimensional surfaces like tubules.

Obviously, highly symmetric spherical structures do not automatically have high stability. This is the case in the investigated 3D hollow B_{12}, B_{22}, and B_{32} clusters. In the solid state, each of the slightly distorted icosahedra of the α- and β-rhombohedral boron crystals interacts with the neighboring icosahedron connected through appropriate $\sigma_{s,p}$-bonds. These intericosahedral bonds stabilize all icosahedra mutually, so that the electron deficiency is compensated. In contrast, a perfect isolated icosahedron B_{12} is definitely Jahn–Teller distorted because of a partial occupation of the HOMOs. The consequence is the symmetry lowering and the transformation of the icosahedral structure into the convex one and that is the stable B_{12}–C_{3v} cluster. Besides the in-plane $\sigma_{s,p}$-bonds, of course the stabilization factor is guaranteed by the out-of-plane π_p-bonds, which compensate the electron deficiency of the system. Moreover, the conditions of stabilization and the proposed rules drawn for the alkali–metal cluster formations (2) have an opposite effect on boron clusters. Hereafter, the tendency toward higher symmetry as well as to higher compactness, expressed as the number of the nearest neighbors (see cf. Table IV of Ref. (28)), do not affect the 3D boron polyhedra. Having the largest number of bonds of the icosahedron B_{12}, which is equal to the number of edges ($N = 30$), does not lead to high stability for the cluster. Opposite to that, in the convex B_{12}–C_{3v} cluster, the breaking of six bonds toward a small number of bonds of ($N = 26$) evidently stabilizes the cluster.

The behavior of the chemical bonds of the boron cluster B_{32} are similar to that of all other investigated clusters in the present work. The presence of two different bond lengths in the highly symmetric spherical B_{32} cluster can be related to single and double bonds, characterized by localized in-plane inward-pointing hybrids $\sigma_{s,p}$ interacting between the atoms of the own system, and with delocalized out-of-plane outward-pointing π_p hybrid orbitals. These orthogonal hybrids are interacting between the atoms of the own system over the cluster surfaces but fortunately can interact with orbitals of foreign systems, analogous to the carbon clusters or graphite. At this point we can predict that the 3D species of boron clusters can either react with other systems, like small molecules or clusters, or surround such molecules like cages serving as carriers, as in the case of fullerenes. In this way the foreign chemical bonds provide new electrons and can contribute to more stability, similar to the embedded icosahedron in α- and β-rhombohedral boron crystals.

Finally, we conclude that the proposed Aufbau Principle can help to predict larger cluster formations. The combination of only hexagonal pyramids leads either to 2D surfaces of quasi-planar structures or to 3D surfaces of tubular form. The combination only of pentagonal pyramids results in 3D surfaces like the open 3D structures of Refs. (19, 23). However, the combination of pentagonal and hexagonal pyramids transforms the 2D into 3D surfaces and enables cluster formation of convex or spherical clusters. We expect the existence of graphite-like boron surfaces composed of parallel layers in quasi-planar or tubular forms. We also expect the existence of hollow spheres but with larger cluster sizes. The closure of one-layer surfaces into a spherical polyhedron fulfills the same procedure analogously to close one graphitic surface into the hollow cages of a fullerene. The transformation from the 2D to 3D structures simply requires the elimination of some hexagonal vertices from the planar surfaces to form pentagonal rings or pyramids.

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