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Boron hydride analogues of the fullerenes

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The BH moiety is isoelectronic with C. We have studied the stability of the $(BH)_{60}$ analogue of the C_{60} fullerene as well as the dual-structure $(BH)_{32}$ icosahedron, both of them being putative structures, by performing local-density-functional electronic calculations. To aid in our analysis, we have also studied other homologues of these systems. We find that the latter, i.e., the dual structure, is the more stable although the former is as stable as one of the latter's lower homologues. Boron hydrides, it seems, naturally form the dual structures used in algorithmic optimization of complex fullerene systems. Fully relaxed geometries are reported as well as electron affinities and effective Hubbard U parameters. These systems form very stable anions and we conclude that a search for BH analogues of the C_{60} alkali-metal supeconductors might prove very fruitful.

I. INTRODUCTION

Recently, Lipscomb and Massa[1] (LM) have noted a correspondence between the carbon fullerenes and their cagelike boron-hydride (BH) analogues. Their mapping is a geometric one. There is also another more direct mapping, based upon the isoelectronic nature of the (BH) moiety compared with C. A great deal of attention has been paid to the fullerenes and LM have suggested that it might be possible to find boron-hydride analogues by laser ablation of the appropriate "graphitic" metal borides in a hydrogen atmosphere. Such cagelike boron hydrides may have useful unusual properties and a search for such systems could prove worthwhile. For example, carbon is not alone in forming fullerene structures; recently, indium has been shown to do so also.[2]

Prompted by these ideas, we embarked on a stability analysis of *two* classes of cagelike boron hydrides, and their component parts, using *ab initio* local-density-functional theory, which has been used quite extensively and with high accuracy for the fullerene systems. In the class that LM discussed, the correspondence is based upon symmetry and sphericity. A boron atom is placed at the center of each of the faces of a fullerene. Faces generated by the boron skeleton would then have carbon atoms at their centers. This is very much related to the dual-lattice concept used in translationally invariant systems. By such a mapping, C_{60} is transformed to a B_{32} system, there being 32 faces to a C_{60} molecule. A whole host of fullerenes and their BH analogues are depicted graphically in LM's paper. We show the $B_{32}H_{32}$ molecule in Fig. 1. The hydrogen atoms which satisfy surface dangling bonds reside outside the boron cage. The calculations, as we report below, show that each boron-hydrogen bond is directed radially. The second class, based upon the conceptual similarity of bonding in C_2H_4 and B_2H_6, is discussed more fully below.

Last, we have investigated the electron affinity of these clusters; first, because doubly charged anions are often experimentally observed, and second, because the question of stability of the charged fullerene analogues is thought to be important to the understanding of superconductivity in the crystalline alkali-metal C_{60} systems.

A. Cagelike (dual) structures (Ref. 30)

The mapping that LM describes is based upon the Descartes-Euler formula[3] for polyhedra:

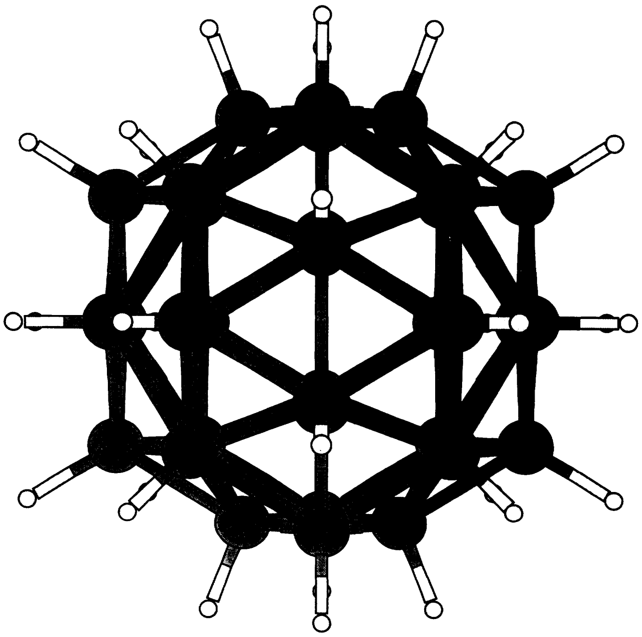

FIG. 1. $B_{32}H_{32}$ cagelike structure.

$$N+F=E+2\ , \tag{1}$$

where N is the number of vertices (i.e., skeletal atoms), F is the number of faces, and E is the number of edges (i.e., nearest-neighbor bonds). Whereas C_{60} has carbon atoms that are threefold coordinated, resulting in a "soccer-ball" shape with pentagonal and hexagonal faces, the B_{32} analogue has boron atoms that are fivefold and sixfold skeletally coordinated and the faces now are all triangular. This is related to the transformation that takes a hexagonal (i.e., graphitic) lattice to its dual analogue, the triangular lattice. Upon wrapping such lattices upon themselves to form a closed icosahedral object, topological defects (disclinations) are required, leading to the presence of some fivefold faces in one case, and some fivefold coordination in the other.

Bonding in these so-called electron-deficient (i.e., the "octet rule" is not satisfied) first-row systems has been explained in terms of what have come to be called Wade's rules,[4] although it seems that Mingos[5] and Williams[6] were also nearly contemporaneous progenitors of similar concepts. The idea is that in cagelike BH systems, the skeletal boron atoms sp hybridize so that a direct covalent bond is made between the boron and the radial hydrogen atoms and the other hybrid orbital points toward the center of the cluster. The remaining two p orbitals on the skeletal boron atom then lie tangentially with respect to the pseudospherical polyhedral surface and are available for efficient bonding. Simple molecular-orbital (MO) arguments suggest that systems with the generic formula $B_nH_n^{2-}$ should be particularly stable because if a pair of electrons is associated with each BH bond, there remain $(n+1)$ electron pairs that can be accommodated in bonding skeletal MO's. For example, Longuet-Higgins and Roberts,[7] as early as the 1950's, suggested that $B_{12}H_{12}^{2-}$ would be stable but the neutral structure would not. They predicted, in particular, that the neutral structure would have an open-shell structure, whereas the anion would not. Eberhardt, Crawford, and Lipscomb[8] and Hoffmann and Lipscomb[9] used similar semitopological orbital methods to come to similar conclusions. Experimentally, many of the doubly charged cagelike systems have been observed, whereas the B_nH_n neutral structures have not.[10]

Another observation in such systems is that polyhedral structures of the electron-deficient systems often have triangular rather than square or pentagonal faces. Also, some clusters that disobey the $(n+1)$ rule are known to exist—e.g., B_4Cl_4. These observations have been put on firmer theoretical foundation via graph-theoretical and via symmetry plus angular-momentum constructs. Stone[11] showed, for example, that in these polyhedra bonding is maximized if the number of edges is maximized. Examination of Eq. (1) indicates that for a fixed number of vertices (i.e., skeletal atoms), the number of edges is maximized when the number of faces is maximized and this, in turn, occurs when all the faces are triangular. Treating the cagelike systems as perturbed spherical shells and then performing symmetry analyses, Stone further explained why neutral tetrahedral (B_4) boron structures may also sometimes be stable.

B. Fullerene (direct) structures

A more direct mapping is suggested by the similarity between ethylene (C_2H_4) and diborane (B_2H_6). These are isoelectronic molecules. We can consider the latter as being a doubly charged anion ($B_2H_4^{2-}$) that has an electronic configuration identical to that of ethylene, i.e., each boron/carbon atom is sp^2 bonded, but to which has been added two protons which exist in the middle of the π charge distribution above and below the B_2H_4 plane. In other words, every time a π bond is found in a carbon system, replace it with two hydrogen atoms in the boron-hydride analog. Such bonds are known as "banana" bonds because electron density contours show high density starting at the boron atom, reaching up toward the hydrogen atom and then extending back down to the next skeletal atom, one banana being below the plane, the other above. Since C_{60} has single and double bonds (it is not completely resonance stabilized due to frustration), and since there are thirty of the latter, a possible structure that might be stable is $B_{60}H_{60}$. Here, around the perimeter of each hexagonal face, where in C_{60} there are three alternating double bonds, we placed three pairs of hydrogen atoms—three outside and three inside the icosahedron. Such a structure is depicted in Fig. 2.

In the next section, we briefly discuss our calculational method as well as the other molecules we considered to aid in our stability analysis. Section III gives numerical results, that is, geometries, energies, electron affinities, and effective Hubbard U parameters. Finally, Sec. IV presents our conclusions.

II. METHOD OF ANALYSIS

The electronic-structure method used here was developed by Pederson and Jackson and has been dis-

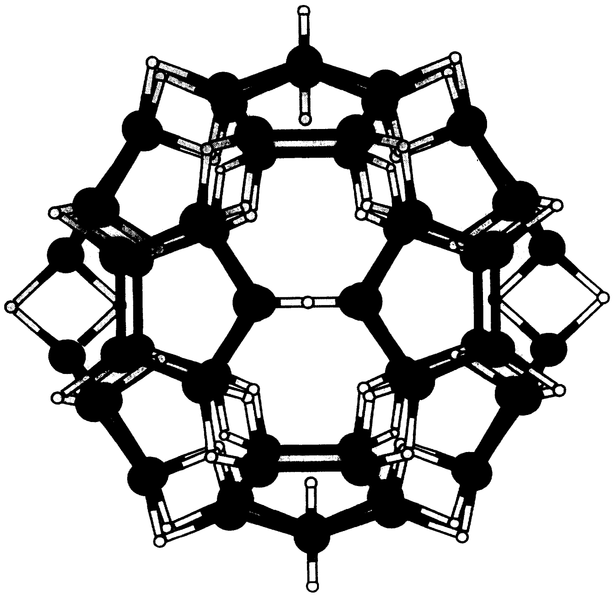

FIG. 2. $B_{60}H_{60}$ direct structure.

cussed in detail elsewhere.[12] Briefly, it is based upon the local-density-functional approximation (LDA) and has been used effectively to study the fullerenes.[13] The method builds electron correlation into the energy of the system. The basis functions we chose are of "double-zeta" quality. Both the hydrogen and boron atoms have s and p functions. The hydrogen basis consists of one contracted set of s Gaussians plus one bare s and one bare p. The boron basis consists of two contracted and three bare s functions, plus one contracted and three bare p functions. A similar basis has been used for C_{60} studies and proved reliable.[13] Integrals are evaluated using an efficient variational mesh. Forces, with Pulay corrections,[14,15] are also calculated within the code and the geometries we will give are fully relaxed, that is, all forces are effectively zero (~ 0.005 eV/Å). Conjugate-gradient techniques are used to minimize the energy with respect to nuclear geometry.

To aid in our analysis, we will consider several small boron-hydride molecules. The first molecules are the B_4H_4 tetrahedron and the $B_{12}H_{12}$ icosahedron (Fig. 3). The former is the simplest cagelike system we can imagine and the latter is the smallest possible icosahedron (its dual carbon analogue is C_{20}, an icosahedron with five-sided faces). Their energies will be compared with the $B_{32}H_{32}$ structure. The second three molecules will be BH_3, diborane, and the BH direct analogue of benzene, i.e., $(B_6H_6)(H_2)_3$. We write the latter this way to show that we place two hydrogen atoms in each of the three Kekule-structure double bonds in benzene. These ethylene and benzene analogues are graphically depicted in Fig. 4. Diborane exists in nature, whereas the benzene analogue does not. We consider these secondary molecules because, using the concept of chemical additivity of covalent bond energies (which works so well for carbon- and hydrogen-containing compounds), we can separate BH single-bond, BB single-bond, and B_2H_2 banana-bond energies. The energy of $B_{60}H_{60}$ may then be compared with its planar analogue (just as C_{60} bond strengths have been compared with those in graphite and benzene) as well as with $B_{32}H_{32}$, its dual analogue.

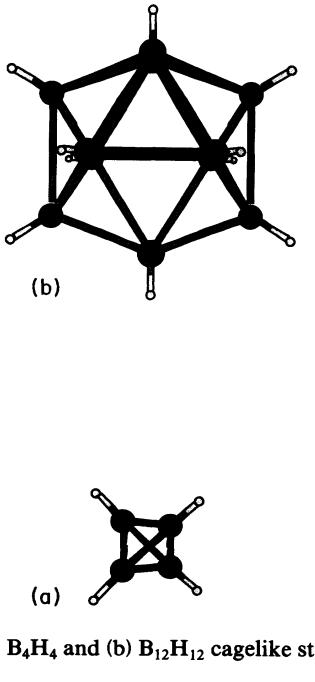

FIG. 3. (a) B_4H_4 and (b) $B_{12}H_{12}$ cagelike structures.

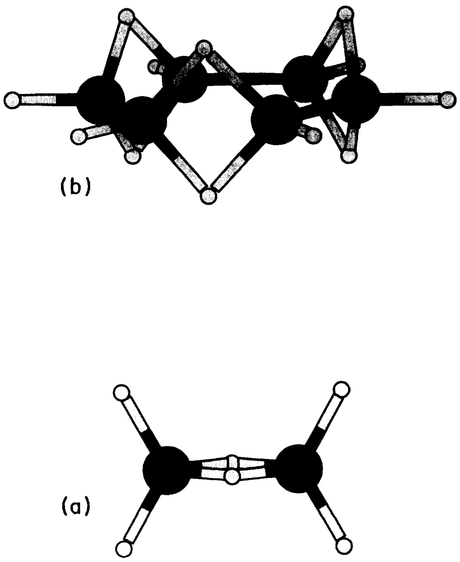

FIG. 4. (a) B_2H_6 and (b) $B_6H_6(H_2)_3$ direct structures.

III. RESULTS

A. Geometries

Table I collects bond lengths for each of the systems considered. The banana-bond systems are grouped first, followed by the cagelike systems. We see that for the former, BH and BB covalent bonds (those we would typically call single bonds) are reasonably system independent, being approximately 1.21 and 1.71 Å, respectively. The BH, BB, and HH distances within banana bonds are also quite system insensitive, being 1.33, 1.76–1.85, and 1.93–2.00 Å respectively. Note that in contrast to carbon chemistry, where double bonds are shorter than single bonds (1.35 versus 1.54 Å),[16] the BB distance in the banana bond (i.e., the double-bond analogue) is slightly larger than that of the single bond. In other words, transferability is rather good in these systems. The B_2H_6 geometry is very close to that reported in many other literature references.[17] In B_6H_{12} the banana-bond hydrogens actually lie slightly outside the pseudohexagonal boron skeleton and the radial H to nearest banana H distance is, for geometric (i.e., accidental) reasons, very similar to the intra-banana-bond HH distance and is 1.95 Å. In either case, these are nonbonded interactions. In $B_{60}H_{60}$ the HH axis within a banana bond lies axially symmetrically but the outer hydrogen atom lies slightly nearer the boron pseudosphere than the inner one of the pair. The distance between the inner hydrogen atoms on one banana bond and that on the neighboring banana bond (i.e., the "meta" position) is only slightly larger than that between the pair of hydrogen atoms within the banana bond. The former is 2.06 Å. This may seem strange, but the point to note is that the inner hydrogen atoms point radially towards the center of the cluster, that is, the curvature of the cluster plays a significant role in bringing these inner meta hydrogen atoms together. Nevertheless, as in B_6H_{12}, both these types of HH distances are nonbonded. The radius of the boron cage in $B_{60}H_{60}$ of 4.38 Å is to be compared with the LDA radius of C_{60}, which is near 3.51 Å.[12,13] The reason for the larger radius of the former is due to the larger mean BB distance of 1.78 Å compared with the mean CC distance of 1.42 Å.

Turning to the cagelike systems, the transferability of the BB and BH bond lengths is not quite as good as in the banana-bonded systems. The BH bond lengths vary from 1.13 to 1.21 Å, while the BB bonds vary from 1.67 to 1.81 Å. The cagelike tetrahedral B_4H_4 system has similar geometry to that optimized by Morrison[18] in his intermediate-neglect-of-differential-overlap calculations. A face-centered B_4H_4 cluster is also given for comparison; this tetrahedral system is far less stable than the cagelike form and has much greater BB and BH bond lengths. Interestingly, the hydrogen atoms reside inside the cage of this high-energy structure; starting with the

TABLE I. Geometries and atomization energies.

System	Bond type	Bond length (Å)	Atomization energy per molecule (eV)
BH_3	BH (covalent)	1.212	12.95
B_2H_6	BB (banana)	1.757	28.63
	BH (banana)	1.331	
	BH (covalent)	1.207	
	HH (banana)	2.000	
B_6H_{12}	BB (banana)	1.772	70.18
	BB (covalent)	1.707	
	BH (banana)	1.334	
	BH (covalent)	1.218	
	HH (banana)	1.933	
$B_{60}H_{60}$	BB (banana)	1.851	529.2
	BB (covalent)	1.721	
	BH (banana, in)	1.322	
	BH (banana, out)	1.353	
	HH (banana)	1.931	
	center-B	4.380	
	center-H (inside)	3.337	
	center-H (outside)	5.269	
B_4H_4 (face-centered)	BB (face)	2.395	19.85
	BH (face)	1.604	
	center-B	1.467	
	center-H	1.301	
B_4H_4 (cagelike)	BB (cagelike)	1.673	33.46
	BH (cagelike)	1.199	
	center-B	1.024	
	center-H	2.224	
$B_{12}H_{12}$	BB (cagelike)	1.760	112.5
	BH (cagelike)	1.210	
	center-B	1.694	
	center-H	2.904	
$B_{32}H_{32}$	BB (cagelike fivefold)	1.725	297.3
	BB (cagelike sixfold)	1.815	
	BH (cagelike sixfold)	1.126	
	BH (cagelike fivefold)	1.200	
	center-B (fivefold)	2.790	
	center-B (sixfold)	2.543	
	center-H (fivefold)	3.990	
	center-H (sixfold)	3.669	

face-centered hydrogen atoms outside the boron cage, the energy of the system follows a downhill path all the way to the final hydrogenic location inside the cage. The boron skeletal radius here is significantly larger than that of the cagelike form. Turning now to $B_{32}H_{32}$, this cluster has two types of boron and hydrogen atoms; the BB distance of the fivefold (skeletally) -coordinated boron atoms is approximately 0.1 Å shorter than that of the sixfold ones. The same observation was made by Brown and Lipscomb[19] who studied a range of cagelike boron hydrides using the semiempirical partial-retention-of-diatomic-differential-overlap (PRRDO) scheme. The BH bond lengths also differ depending upon the boron atom to which the hydrogen atoms are attached; here, the sixfold bond to hydrogen is appreciably shorter than the fivefold bond. This seems to be a robust property of fivefold borons because in $B_{12}H_{12}$ the BH distance (there is only one such, by symmetry) is very similar to the analogous one in $B_{32}H_{32}$. Agreement of the geometry of $B_{12}H_{12}$ with published x-ray-diffraction results[20] is good for the BB bond length (1.77±0.06 Å) but worse than one might like for that of the BH (1.07±0.06 Å). Relaxing the nuclear positions of the doubly charged $B_{12}H_{12}$ anion by LDA changes bond lengths by less than 0.005 Å. The experimental results are for ionic salts of $B_{12}H_{12}$ and we might expect the resolution of hydrogen to be difficult. Perhaps, therefore, the BH bond-length discrepancy is understandable. Our bond lengths, however, are in close agreement with the PRRDO calculations of Brown and Lipscomb.[19] Last, the radius of the boron cage in $B_{32}H_{32}$ is significantly smaller than that of either $B_{60}H_{60}$ or C_{60}; this is due primarily to its low skeletal atom number count.

B. Energies

LDA, in general, does rather poorly at describing absolute cohesive (i.e., atomization) energies;[21] nevertheless, these are given in Table I. The conventional wisdom is that the approximation is somewhat better at dealing with condensed phases or molecules than with individual atoms. There is a certain amount of overcounting that occurs by virtue of LDA including, in the exchange-correlation term, interactions of the electron with itself. Hydrogen, therefore, is treated rather poorly but when spin-polarized calculations are performed, the agreement with experiment improves significantly. Using our basis, for example, the spin-polarized energies of H and B are −0.478 75 and −24.348 36 Hartrees, respectively. The energy of the combined infinitely separately BH unit is thus −24.827 11 Hartrees.

In our analysis of the stabilities of these systems, we will concentrate more on relative cohesive energies that we expect LDA to predict well. We will discuss energies per BH unit (see Table II) or with respect to bond-counting arguments. LM's $B_{32}H_{32}$ structure is indeed more stable than $B_{60}H_{60}$ by 0.47 eV per BH unit. However, $B_{60}H_{60}$ is itself more stable than the cagelike B_4H_4 by 0.46 eV in the same units. But the most stable structure studied is $B_{12}H_{12}$, which is even more stable than $B_{32}H_{32}$ by 0.08 eV/BH. Early analyses predicting the instability of neutral $B_{12}H_{12}$ were predicated on the idea that non-closed shell structures would be inherently unstable, that is, these analyses based their conclusions on symmetry and electron-count arguments rather than on actual energies.[7] In accord with such analyses, we, too, find an open-shell structure for the neutral system and would expect a Jahn-Teller distortion if such a system were to be isolated. (The algorithms used here actually ascribe a fractional occupancy to each of these degenerate states so as to preserve spherical symmetry). All of the systems in Table II are very stable with respect to the infinitely separated atoms by a margin which is easily outside any possible LDA error in absolute cohesive energies. But we should note here that a large cohesive energy is not necessarily synonymous with observability; as we have said, the B_nH_n neutral structures have not been isolated. The two larger neutral cagelike systems studied here are, after all, open-shell systems (although, interestingly, the B_4H_4 is not) and reactivity may be an issue. Table II also gives the LDA cohesive energy per carbon for C_{60}, which is of very similar magnitude to the BH analogues.

TABLE II. Cohesive energies.

System	Cohesive energy/(BH) (eV)
B_4H_4 (face-centered)	−4.96
B_4H_4 (cagelike)	−8.36
$B_{12}H_{12}$	−9.37
$B_{32}H_{32}$	−9.29
$B_{60}H_{60}$	−8.82
C_{60}	−8.50
$B_{12}H_{12}{}^{2-}$	−9.98
$B_{32}H_{32}{}^{2-}$	−9.44
$B_{60}H_{60}{}^{2-}$	−8.86

We have already discussed that the face-centered form of B_4H_4 is significantly less stable than the cagelike form, the former being 3.4 eV higher in energy per BH unit than the latter. It seems that cagelike forms with radial hydrogens attached to each boron, as predicted so long ago, are indeed very stable systems. The cagelike stability per BH unit maximizes near 12 skeletal atoms, with the stability of the banana-bonded sixty-atom skeleton lying midway between the four- and thirty-two-boron cagelike forms. It remains to be seen, but assuming monotonic energy versus atom number behavior, it may well be that stability will continue to decrease as the curvature of the cagelike skeleton tends to zero. This monotonic behavior is not always a good approximation in cluster chemistry, but it has been observed by Bicerano, Marynick, and Lipscomb[22] in their PRRDO calculations of $B_nH_n{}^{2-}$ anions. They varied n from 9 to 24 and found not only that $n=12$ was very stable (as we do) but that for n greater than 12 the stability, barring minor fluctuations, monotonically decreases.

We can get a sense of what the planar limit might be for the banana-bonded systems by imagining, as we did above, that the $B_{60}H_{60}$ system is composed of single BB bonds and BH_2B double bonds (i.e., BB banana bonds). It is possible to "decompose" the bonding in BH_3, B_2H_6, and B_6H_{12} to get at individual bond energies. These are given in Table III and compared with those of similar quality basis-set LDA calculations on hydrocarbons and C_{60}.[13] The banana bond, which includes two hydrogens, is seen to be very strong. BH and BB single bonds are weaker than their carbon analogues. The correct number of single and double BB bonds in $B_{60}H_{60}$ are obtained by considering B_6H_{12} and B_2H_6 alone with no atomic reference. The energy of 30 double and 60 single BB bonds of which the $B_{60}H_{60}$ system is conceptually composed is simply given as the energy of twenty B_6H_{12} molecules minus the energy of thirty B_2H_6 molecules. The energy due to BH single bonds vanishes in this difference, there being 120 BH covalent bonds in the 20 molecules of one and the 30 molecules of the other. This analysis shows that $B_{60}H_{60}$ is 0.25 eV less stable per skeletal boron than the simple (planar geometry) bond-count analysis would predict. This number is of similar magnitude to that quoted per carbon atom for C_{60} relative to graphite where 0.3–0.4 eV is often given.[23] Thus, the energy due to curvature and inclusion of disclinations makes $B_{60}H_{60}$ less stable than its planar analogues. A similar detailed analysis for the cagelike forms is lacking but it seems likely that as these tend to the planar limit, they will become less stable and a crossover in stability of the cagelike versus banana-bond structures as a function of skeletal radius may be observed.

C. Electron affinities and states near the Fermi level

The ability of fullerene structures to accept electrons has been shown to be fundamental to understanding bonding in the alkali-metal compounds of these systems. For example, in K_3C_{60} the bonding is ionic, with the C_{60} accepting three electrons, one from each of the potassium atoms. The resulting Madelung energy stabilizes the small negative (repulsive) electron affinity of the triply charged fullerene.[24] It is of interest to see what happens in the BH systems.

Table IV gives electron affinities and Hubbard U parameters. The latter is a measure of how rapidly the energy of the system changes (parabolically) with the addition of electronic charge. The C_{60} values are quoted from similar quality LDA calculations.[13] Table V shows the degeneracy of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of the neutral structures, the LDA gap, and the electron population of these states as a function of charge on the molecule.

TABLE III. Bond energies.

Bond type	Bond energy (eV)
BH (covalent)	4.31
BB (covalent)	3.38
BB (banana)	11.37
CH (single)	5.02
CC (single)	4.36
CC (double)	7.42
CC (C_{60} average)	5.67

TABLE IV. Electron affinities.

System	Electron affinity (eV)		U (eV/esu^2)
B_4H_4	first	1.07	
	second	−4.67	5.74
$B_{12}H_{12}$	first	5.98	
	second	1.40	4.62
	third	−8.04	
	sum	−0.66	
$B_{32}H_{32}$	first	4.22	
	second	0.63	3.78
	third	−3.60	
	sum	+1.25	
$B_{60}H_{60}$	first	2.27	
	second	−0.11	2.38
	third	−2.64	
	sum	−0.48	
C_{60}	first	3.00	
	second	−0.02	3.02
	third	−3.08	
	sum	−0.10	

Consider first the di-anions. Note that both of the larger cagelike structures have sequential attractive interactions with the addition of electrons, thus showing that Wade's rules are obeyed, i.e., $B_nH_n^{2-}$ systems are exceptionally stable. Even the $B_{60}H_{60}$ system has a doubly charged anion more stable overall than the neutral one. The B_4H_4 system, however, does not form the stable di-anion. This is due partly to the neutral system being closed shell (see Table V) and also perhaps to the very large curvature and the concomitant large Coulomb repulsion upon addition of electrons. Table II lists cohesive energies of the di-anions with respect to the separated atom and separated electron limit. It is perhaps this table which illustrates how very stable the

TABLE V. Orbital occupation.

System	HOMO (H)/LUMO (L) degeneracy	Gap (eV)	Orbital population in charge states (0,−1,−2,−3)
B_4H_4	twofold (L) threefold (H)	3.47	0,1,2,3 6,6,6,6
$B_{12}H_{12}$	onefold (L) fourfold and fivefold (H)	0.00	0,0,0,1 16,17,18,18
$B_{32}H_{32}$	threefold (L) threefold (H)	0.73	0,0,0,1 4,5,6,6
$B_{60}H_{60}$	threefold (L) fivefold (H)	1.39	0,1,2,3 10,10,10,10
C_{60}	threefold (L) fivefold (H)	1.70	0,1,2,3 10,10,10,10

$B_{12}H_{12}^{2-}$ anion really is. The two larger cagelike di-anions are both closed shell. That neutral $B_{12}H_{12}$ is not observed experimentally may have more to do with the very much higher relative stability of the di-anion than intrinsic lack of stability of the neutral system.

We turn now to the triply charged systems. In free space these are all unbound (see Table IV); the added third electron might have a resonance but would drift off to infinity. Use of local basis-set LDA calculations, however, can give us a guide to the approximate energy that these systems might have if they were placed in an ionic environment. The three electrons that reside on the fullerene in K_3C_{60} occupy triply degenerate states, making this a high-spin symmetry Hund's rule system (see Table V). Exactly the same situation applies for $B_{60}H_{60}^{3-}$. In contrast, the electron added to the closed-shell $B_{12}H_{12}^{2-}$ system goes into an A_{1g} orbital while the last electron in $B_{32}H_{32}^{3-}$ enters a triply degenerate state. Madelung effects, in a crystal of boron-hydride anions and alkali-metal cations, would, of course, stabilize a triply charged state, the stabilization being greater for $B_{12}H_{12}$ and $B_{32}H_{32}$ than for C_{60} because of smaller lattice parameters (these two BH systems have smaller radii than the fullerene). Note that within these finite basis-set calculations, the triply charged state of $B_{32}H_{32}$ is exceptionally stable; its energy is lower than that of the neutral.

The HOMO-LUMO (Table V) gaps in C_{60} and $B_{60}H_{60}$ are of similar magnitude, being of order 1.5 eV; but the grouping of states near the Fermi level are different. There are two fivefold states within 0.21 eV of one another at the HOMO and two triply- and one fivefold-degenerate states within 0.08 eV of one another at the LUMO in $B_{60}H_{60}$. In contrast, the nearest occupied states to the HOMO in C_{60} are 1.2 eV away and the state above the LUMO is 1.0 eV higher (see Fig. 2 of Ref. 13).

The degeneracy of the HOMO states (hence the zero gap) in $B_{12}H_{12}$ was predicted by Longuet-Higgins and Roberts[7] back in 1955 to be fourfold, from which they anticipated the open-shell nature of the system. This suggestion, based upon the very simplest of Huckel-type arguments is in remarkable agreement with our LDA results, although Table V shows that we find a fivefold and fourfold set in almost perfect accidental degeneracy.

The U parameters for all these systems are positive. Many-body effects may reduce the magnitude of these values, but not into the negative regime where they might have proven useful for models of superconductivity in alkali-metal compounds.[25]

IV. CONCLUSIONS

Dual structures are encountered frequently in fullerene research as a way of determining carbon positions on surfaces of given topology.[26] A simple pair potential is used to minimize the energy of the dual system before reversion back to the real-space structure. One significance of the boron-hydride cagelike systems is that they may be thought of as representing, in their natural state, the carbon dual structures.

Our stability analysis has shown that LM's postulated 32-boron-atom cagelike form[1] is the more stable of the C_{60} analogues. However, the 12-skeletal-atom cagelike structure is even more stable. By comparing the energy of the $B_{60}H_{60}$ "direct" structure with its planar graphitic counterpart, and noticing the trend with cluster size for the cagelike forms, it may be that large BH clusters, if they could be made, might revert to the direct structure for large enough radius. In other words, there is a likely crossover in stability between these alternate structural forms with cluster radius.

There are other ways in which the direct structures might be rendered even more energetically stable, thereby moving the crossover to smaller radius. For example, we have chosen a subclass of structures in which each banana bond consists of two hydrogen atoms. But, given the near degeneracy of single and double bonds in C_{60} (i.e., there are near-degenerate Kekule or valence-bond structures in such systems), we might equally have placed a single hydrogen atom at each BB bond midpoint with hydrogen atoms being alternately above and below the plane of a given six-member ring. It is possible to do this without frustration; each five-member ring is either all up or all down. Whether the subclass we have explicitly considered is more stable than this alternative subclass (or mixtures thereof), we know that fluxionating bonds (proton tautomerism) are common in such systems[27] and we can expect energy differences to be low between the different subclasses. In other words, entropy effects may be large leading to extra stability in the direct structures.

Last, we note that complexes and ionic salts of B_nH_n systems are known and are stable. However, it seems that only salts of the doubly charged anion have been isolated. For example, $Na_2B_{12}H_{12}$ (Ref. 28) exists, as do the K (Ref. 20) and Cs (Ref. 29) analogues. Based upon our results, it is likely that salts and endohedral complexes of the alkaline-earth metals should also be stable. The endohedral complexes might be formed by laser ablation of the alkaline-earth borides in a hydrogen atmosphere.[1] Further, our stability analyses of the cagelike and direct structures above, both in the neutral and ionic states, and our survey of the electronic analogies between C_{60} and those systems studied here, suggest that a concerted experimental search for BH fullerene analogues of the K_3C_{60} superconductor might prove very worthwhile. $K_3B_{12}H_{12}$ and $K_3B_{32}H_{32}$ would be leading contenders in this search.

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[30] Throughout this manuscript, the term "cagelike" refers to the technically specific work "closo" more familiar to chemists.

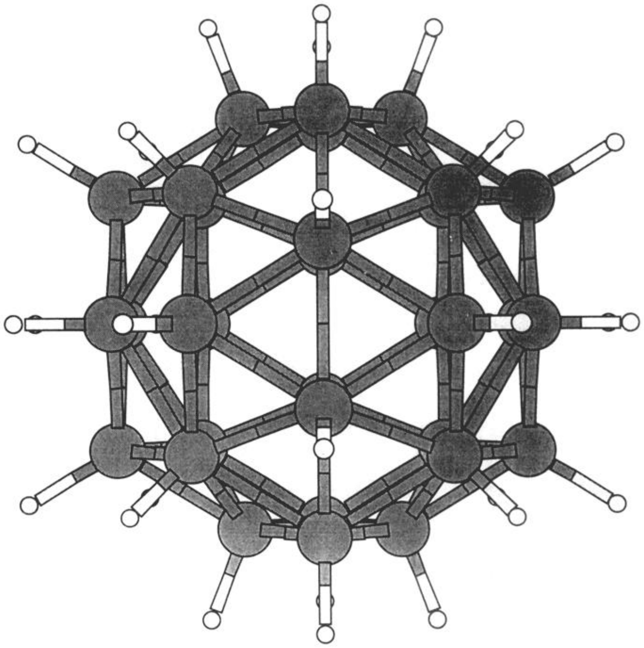

FIG. 1. $B_{32}H_{32}$ cagelike structure.

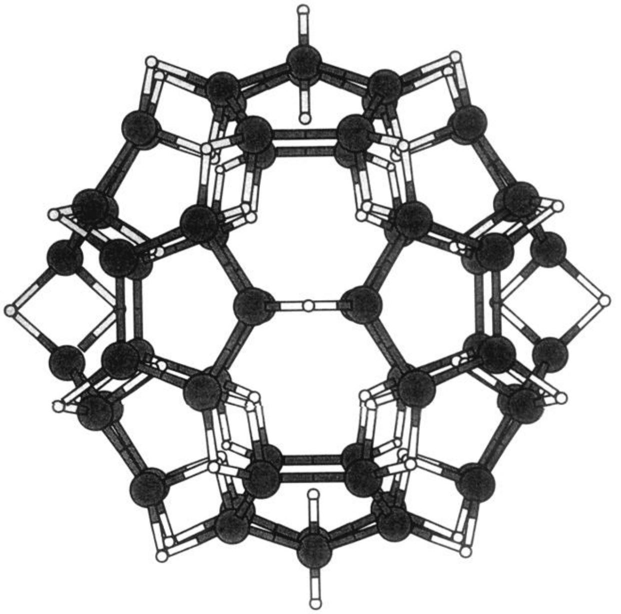

FIG. 2. $B_{60}H_{60}$ direct structure.

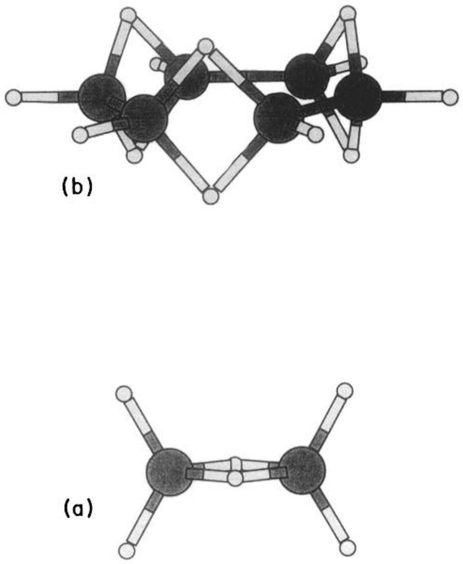

FIG. 4. (a) B_2H_6 and (b) $B_6H_6(H_2)_3$ direct structures.