

Prediction of a Family of Cage-shaped Boric Acid Clusters

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Equilibrium geometries, energies, and vibrational frequencies of cage-shaped boric acid clusters including the onion-like structure have been calculated at the HF/6-31G and B3LYP/6-31G(d) levels of theory. A family of cage-shaped boric acid clusters becomes evident according to our calculations. Each member of the family is formed by strong O–H···O hydrogen bonds. Higher cage-shaped boric acid clusters are more stable. The calculated stabilization energies for the cage-shaped boric acid clusters appear to steadily increase with the number of boric acid molecules (n) and are nearly linear in n . Similarities between cage-shaped boric acid clusters and fullerenes are also discussed.

I. Introduction

Boric acid, also called boracic or orthoboric acid, is a commercially important compound often used as an antiseptic, insecticide, flame retardant, solid lubricant, and food preservative. It is also used in adhesives, detergents, in the manufacture of glass and paper, and to lower the fusion point in welding. In contrast with its wide applications, the structures of boric acid are little known, even though its layered structure with hydrogen bonding within the layers was one of the first molecular crystal structures to be examined using X-ray diffraction techniques.¹ It is well-known that element carbon can be bonded with three other carbon atoms to form many wonderful structures such as balls and nanotubes.^{2,3} Similarly, the boric acid molecule also can be bonded with three other boric acid molecules via hydrogen bonding, so it might be expected to easily form some unique structures other than the layered structure like that of graphite. Recently, nano- or microscale boric acid structures have been experimentally reported.⁴ These boric acid structures were either nanotubes, nanotips, nanorods, microtubes, or microtips. For the fullerene-like boric acid clusters, there are no experimental reports up to now. A previous study, based on the computer-aided molecular design approach, suggests the existence of cage-shaped boric acid clusters.⁵ However, there remain a number of important and fundamental unsettled issues: (1) We know that fullerenes are a large family of highly symmetrical carbon-cage molecules. In theory, an infinite number of fullerenes can exist. For boric acid clusters, is there also a family of hollow cage structures with different shapes and sizes? (2) How important are cooperative effects with increasing boric acid cluster size? (3) Ugarte discovered in 1991 that fullerenes can adopt multilayered configurations where one is encapsulated inside each other, like onion layers.⁶ Again, a natural question is: Are there onion-like structures for boric acid clusters? To answer these questions, in this letter, we systematically report ab initio (Hartree–Fock, HF) and density functional theory (DFT)-based quantum chemical studies on the

stabilities, structures, and H-bonding patterns of cage-shaped boric acid clusters including the onion-like structure.

II. Computational Methods

Using the *Gaussian 03* program package,⁷ structures were fully optimized and characterized by frequency computations and wave function stability checks at the HF/6-31G level of theory initially and then refined at the B3LYP/6-31G(d) theory level. At the B3LYP/6-31G(d) level, the number of basis functions for the onion-like boric acid cluster is 2112, and it is also a considerable one for other cage-shaped boric clusters. To reduce the computational requirements, we constrained symmetry in optimization. The cage-shaped boric acid clusters (H₃BO₃)₈, (H₃BO₃)₁₆, and (H₃BO₃)₂₄ were optimized in *O*, *D*₄, and *D*₆ symmetries, respectively, and the onion-like (H₃BO₃)₈@(H₃BO₃)₂₄ cluster in *D*₂ symmetry. All of these structures were confirmed as true minima on the potential energy surface by the presence of only real frequencies after the corresponding harmonic vibrational analysis.

The determination of accurate hydrogen-bond energies is hindered by the so-called basis set superposition error (BSSE).^{8,9} One of the widely used methods to correct for the BSSE is the counterpoise method.^{8,9} Though some authors have provided both formal and numerical proofs that counterpoise correction yields accurate interaction energy, a number of recent papers have still raised doubts on the efficacy of this procedure.¹⁰ This is particularly true when the size of the molecular cluster is large because one cannot employ very large basis sets to carry out these calculations, so we do not correct for the BSSE for the systems reported in the present study. On the other hand, the BSSE is negligible in comparison with the larger stabilization energy. It should have no significant effect on the results.

III. Results and Discussion

The optimized cage-shaped structures for boric acid clusters having between 8 and 32 boric acid molecules are shown in Figure 1. Table 1 summarizes the structural features and the energy values for these clusters.

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TABLE 1: Total Stabilization Energies (ΔE), Stabilization Energies per Monomer ($\Delta E/n$), Average Distances $R(\text{O}-\text{H})$, and Dihedral Angles $\angle(\text{H}-\text{O}-\text{B}-\text{O})$ for All Optimized Boric Acid Clusters Calculated at HF/6-31G and B3LYP/6-31G(d) Levels of Theory

cluster	ΔE (kcal/mol)	$\Delta E/n$ (kcal/mol)	$R(\text{O}-\text{H})$ (\AA)	$\angle(\text{H}-\text{O}-\text{B}-\text{O})$ ($^\circ$)
B3LYP/6-31G(d)				
(H_3BO_3) ₈	145.35	18.17	0.9850	16.26
(H_3BO_3) ₁₆	331.50	20.72	0.9866 ± 0.0014	11.86 ± 5.11
(H_3BO_3) ₂₄	518.48	21.60	0.9879 ± 0.0021	9.50 ± 4.53
(H_3BO_3) ₈ @(H_3BO_3) ₂₄	662.13	20.69	0.9822 ± 0.0067	9.81 ± 7.70
HF/6-31G				
(H_3BO_3) ₈	136.46	17.06	0.9607	10.99
(H_3BO_3) ₁₆	344.84	21.55	0.9647 ± 0.0027	8.28 ± 5.21
(H_3BO_3) ₂₄	558.25	23.26	0.9681 ± 0.0022	7.20 ± 4.10
(H_3BO_3) ₈ @(H_3BO_3) ₂₄	675.90	21.12	0.9605 ± 0.0080	7.05 ± 5.92

As can be seen from Figure 1, a large family of cage-shaped boric acid clusters become evident though other higher cage-shaped boric acid clusters are not included because of computation limit. It is intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds that result in the formation of cage-shaped boric acid clusters. From inspection of Table 1, geometrical parameters obtained at the HF/6-31G and B3LYP/6-31G(d) levels include average distances $R(\text{O}-\text{H})$ and dihedral angles $\angle(\text{H}-\text{O}-\text{B}-\text{O})$. Compared to the monomer, the $\text{O}-\text{H}$ bond becomes longer by 0.005–0.023 \AA at the HF/6-31G level. This is an indication of a weakening of the $\text{O}-\text{H}$ bond due to intermolecular interactions in the clusters. Similar conclusions are drawn from the B3LYP results: an increase of 0.008–0.023 \AA is observed for the $\text{O}-\text{H}$ bond length. At the same time, for the cage structures, we can notice that average distances $R(\text{O}-\text{H})$ steadily increase as a consequence of cooperative enhancement and increasing hydrogen bond strength with larger cluster size. The onion-like (H_3BO_3)₈@(H_3BO_3)₂₄ shows its exception because it is not a pure cage structure. On the other hand, the boric acid monomers were significantly distorted from planarity upon cluster formation. Investigating the atom dihedral angles $\angle(\text{H}-\text{O}-\text{B}-\text{O})$ of boric acid monomers in the cage-shaped structure of the boric acid cluster, we found the largest deviation of about 17° from the planar structure. Deformation of boric acid monomers leads to the formation of more intermolecular hydrogen bonds and improves the stabilization energy. Obviously, the dihedral angle $\angle(\text{H}-\text{O}-\text{B}-\text{O})$ becomes smaller when the cage size becomes larger.

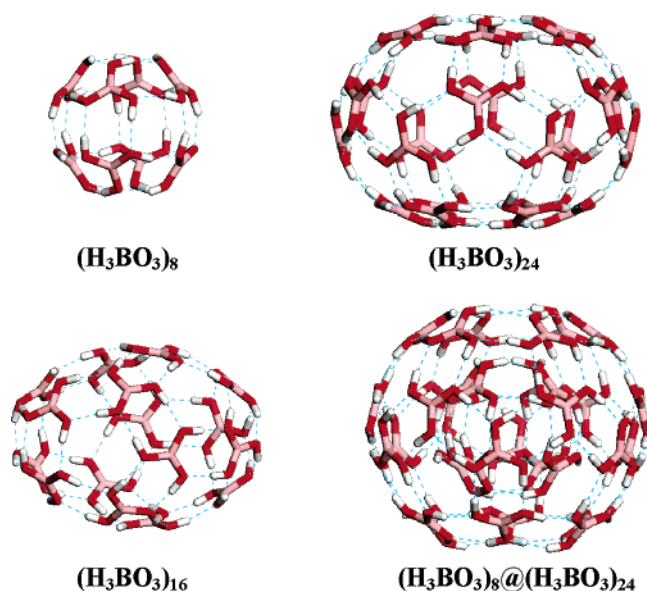
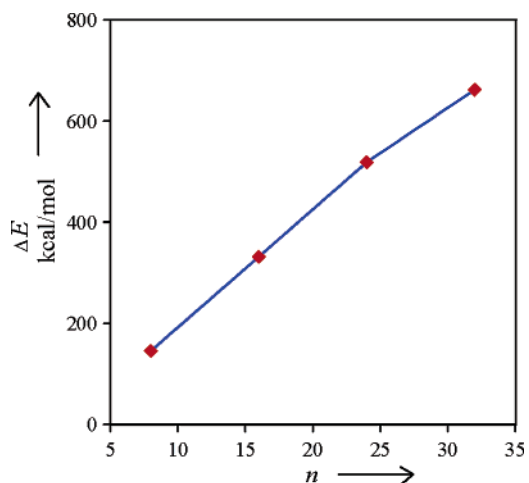
**Figure 1.** Optimized structures of cage-shaped boric acid clusters. The dashed blue lines indicate hydrogen bonds.

Table 1 also lists the stabilization energies and stabilization energies per monomer for cage-shaped boric acid clusters including the onion-like structure. As is evident from Table 1, the larger cage-shaped boric acid clusters have larger stabilization energies and larger stabilization energies per monomer, which is inconsistent with the conclusion from $\text{O}-\text{H}$ bond analysis. This can be explained on the basis of a more favorable geometry of hydrogen bonds. The smaller hydrogen bond angles cause a large amount of strain energy within the clusters. Mainly due to this strain energy, cage-shaped boric acid clusters are thermodynamically less stable than planar boric acid clusters. Higher cage-shaped boric acid clusters, smaller curvature and less strain, are more stable. In fact, the calculated stabilization energies for the cage-shaped boric acid clusters appear to steadily increase with the number of boric acid molecules (n) and are nearly linear in n (see Figure 2). For fullerenes, it is the highly pyramidalized sp^2 carbon atoms in cage-shaped fullerene that cause a large amount of strain energy within the molecule. Fullerenes are thermodynamically less stable than graphite. Higher fullerenes are more stable, too. The calculated binding energies for the fullerenes also appear to steadily increase with the number of carbon atoms (n) and also are nearly linear in n .^{11–13} The cage-shaped boric acid clusters behave most like the well-studied fullerenes. It must be pointed out that the onion-like (H_3BO_3)₈@(H_3BO_3)₂₄ shows its exception again. Its stabilization energy value is less than the sum of cage-shaped (H_3BO_3)₈ and (H_3BO_3)₂₄ stabilization energy values. Carbon onions are easily obtained, for instance, by electron-beam irradiation of carbon soot particles.¹⁴ Several theoretical results seem to indicate that the multilayered spheric fullerenes are the most stable form of carbon groups. Why not for the onion-like (H_3BO_3)₈@(H_3BO_3)₂₄? Looking at the optimized structures of

**Figure 2.** Stabilization energies for boric acid clusters calculated at the B3LYP/6-31G(d) level.

(H₃BO₃)₈, (H₃BO₃)₂₄, and (H₃BO₃)₈@(H₃BO₃)₂₄ in Figure 1, we find that the larger (H₃BO₃)₂₄ has been deformed after enclosing the smaller (H₃BO₃)₈ cluster. It is the smaller outer shell that leads to the stabilization energy value of onion-like (H₃BO₃)₈@(H₃BO₃)₂₄ to be less than the sum of cage-shaped (H₃BO₃)₈ and (H₃BO₃)₂₄ stabilization energy values. Similar results have been found for carbon onions, for example, it has reported that only C₆₀ and C₇₀ are stabilized in C₂₄₀ cage and other higher fullerenes (C₇₆, C₈₀, ...) are destabilized in C₂₄₀ cage.¹⁵

IV. Conclusions

Hartree–Fock and density functional theory calculations have been performed to investigate the family of cage-shaped boric acid clusters including the onion-like structure. Each member of the family is formed by strong O–H···O hydrogen bonds. Higher cage-shaped boric acid clusters are more stable. The calculated stabilization energies for the cage-shaped boric acid clusters appear to steadily increase with the number of boric acid molecules (*n*) and are nearly linear in *n*. Similarities are observed between cage-shaped boric acid clusters and fullerenes. We hope our results may very well spur further work on the structures of boric acid, both experimental and theoretical. Further investigations on their unique properties and potential applications are now in progress in our laboratory.

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Supporting Information Available: Cartesian coordinates and absolute energies for all optimized structures at the HF/6-31G, and B3LYP/6-31G(d) levels of theory, complete citations

for *Gaussian 03*. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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