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COMMENT

Comment on “B₃₈: an all-boron fullerene analogue” by J. Lv, Y. Wang, L. Zhu and Y. Ma, *Nanoscale*, 2014, 6, 11692

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In a recent paper (*Nanoscale*, 2014, 6, 11692), based on the results computed using DFT and MP2 methods, the all-boron fullerene **I** was reported to be the global minimum of the cluster B₃₈ and much more stable than the quasi-planar **II**. In this comment, we showed that at higher level of theory CCSD(T), both structures **I** and quasi-planar **II** are almost degenerate in energy and the B₃₈ can be considered as a transition size between 2D and 3D boron clusters. While the MP2 method favours the 3D structure **I**, the CCSD method tends to overestimate the relative stability of the 2D structure **II**.

In a recent paper, Ma and co-authors¹ reported theoretical results on the boron cluster B₃₈. They showed that B₃₈ is an all-boron fullerene containing 4 hexagonal holes and 56 triangles. Since the clusters B₃₀² and B₃₆³ were recently found to have bowl-like structures that contain pentagonal and hexagonal holes, respectively, the existence of a three-dimensional fullerene as the most stable isomer of B₃₈ is interesting. However, the computed results¹ should be reconsidered since the MP2 method was known to give unrealistic results for boron clusters.^{4,5} In this comment, we show that both isomers, including caged-like structure **I** and quasi-planar structure **II**, are almost degenerate in energy (cf. Figure 1), and the B₃₈ can be considered as a transition size between 2D and 3D boron clusters.

Ma and co-workers¹ performed a search for the local minima of B₃₈ using a particle swarm optimization algorithm. Based on relative energies (REs) calculated using the methods PBE/6-311G(d), PBE0/6-311G(d) and MP2/6-311G(d)//PBE0/6-311G(d), these authors concluded that the 3D fullerene **I** is the most stable isomer of the B₃₈. While both isomers **I** and **II** are almost degenerate in energy at the PBE/6-311G(d) level, **I** is much more stable than **II** when the MP2 method was used. It is however known that the MP2 method tends to overestimate relative stability for 3D structures of boron clusters, whereas the DFT functionals such as PBE, TPSSh, PBE0 can produce more realistic RE values that are comparable with those obtained at CCSD(T) level.^{4,5} Thus a re-examination of structural stability of the B₃₈ isomers is necessary.

The lowest-lying isomers reported by Ma *et al.*¹ are thus re-optimized by using the DFT functionals TPSSh,⁶ PBE and PBE0^{7,8} in conjunction with the 6-311+G(d) basis set that are implemented in Gaussian 09 package.⁹ Our PBE and PBE0 energy values agree well with Ma *et al.*¹ that the fullerene **I** is more stable than the form **II**. However, the functional TPSSh gives a reversed ordering of energy where the form **II** is now 0.34 eV more stable than **I**.

To confirm the relative stability of both isomers, their single point electronic energies are calculated by using the MP2,¹⁰ CCSD¹¹ and CCSD(T)¹² methods with TPSSh/6-311+G(d) and PBE0/6-311+G(d) geometries. These calculations are performed using the Molpro 09 package.¹³ At the higher level CCSD(T)/6-311G(d), both structures are almost degenerate in energy with a tiny energy gap (Fig. 1). Structure **I** is slightly more stable than structure **II** when the TPSSh/6-311+G(d) geometries are used. The quasi-planar structure **II** becomes somewhat more stable when the PBE0/6-311+G(d) geometries are used.

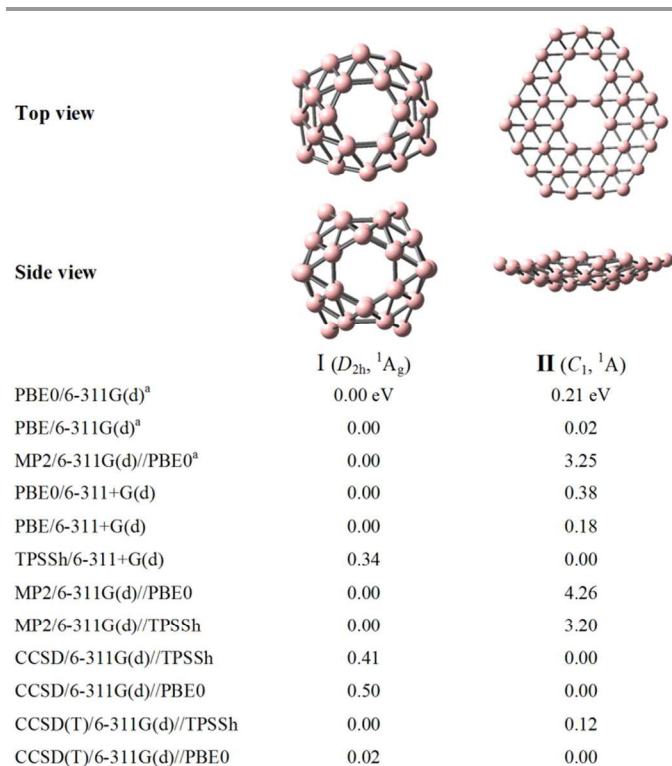


Fig.1 Shapes and relative energies (eV) of isomer I and II obtained at various computational methods. a) The values obtained at ref. 1.

It is more important to note that the MP2 method was confirmed to overestimate the relative stability of three-dimensional fullerene **I** and provides unrealistic computed results for boron clusters. At the MP2/6-311G(d), the 3D structure **I** is much more stable than the structure **II** with energy gap of 3.20 - 4.26 eV. Oppositely, the CCSD method tends to favour the planar structure **II**. Our CCSD results show that **II** is more stable than **I** with relative energy of 0.41 – 0.50 eV.

In conclusion, we re-examined the relative stability of the isomers B_{38} using the different quantum chemical methods, including DFT, MP2, CCSD and CCSD(T). At the highest level considered CCSD(T), we found that the B_{38} is not completely a 3D fullerene, and both isomers **I** and **II** are almost degenerate in energy and likely coexist in the energy landscape of B_{38} . This size can be considered as a transition size between 2D and 3D boron clusters since the cluster B_{36}^3 is quasi-planar structure, whereas the $B_{40}^{14,15}$ was recently found to be a stable fullerene. While the MP2 method favours the 3D structure **I**, the CCSD method overestimates the stability of the quasi-planar structure **II**.

These findings not only give more insight into the structural characteristics of the boron cluster B_{38} , but they also provide a benchmark for the computational methods for this intriguing system.

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Notes and references

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