

In Search of the Smallest Boroxol-Type Heterocyclic Ring System: Planar Hexagonal B3S3+ Cluster with Double $6\pi/2\sigma$ Aromaticity

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Abstract

Boroxol (B3O3) rings and relevant hexagonal B3S3 structural blocks are ubiquitous in boron oxide/sulfide glasses, crystals, and high temperature liquids. However, the isolation of an ultimate heterocyclic B3O3 or B3S3 cluster in the free-standing form, with as few as six atoms, has been unsuccessful so far. We report on computational design of the simplest case of such a system: highly symmetric D3h B3S3+ (1A1?) cluster. It is the well-defined global minimum on the potential energy surface, following global searches and electronic structure calculations at the B3LYP and single-point CCSD(T) levels. Chemical bonding analysis reveals an ideal system with skeleton Lewis B3S3 single bonds and unique double $6\pi/2\sigma$ aromaticity, which underlies its stability. The cluster turns out to be an inorganic analog of the 3,5-dehydrophenyl cation, a typical double π/σ aromatic system. It offers an example for chemical analogy between boron-based heterocyclic clusters and aromatic hydrocarbons. Double π/σ aromaticity is also a new concept in heterocyclic boron clusters. Prior systems such as borazine, boroxine, and boronyl boroxine only deal with π aromaticity as in benzene.

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