Cubic C8 – An Aromatic Carbon Cluster?

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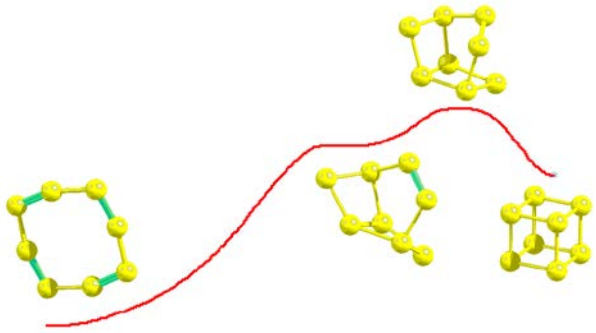
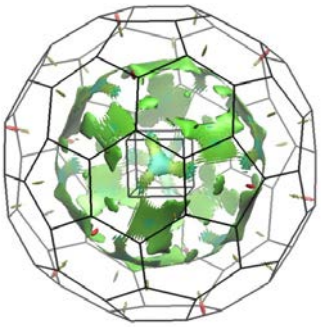
The cubic C_8 unit is represents the proposed primitive cell of the high-density carbon allotrope first described in 1978. Cubic C_8 and its isomers have been the subject of several theoretical studies.[1,2,3,] This cluster obeys Hirsch's $2(N+1)^2$ rule of spherical aromaticity. According to our high-level calculations O_h-symmetrical C_8 is a relatively stable strained cluster. The bond length is quite independent of the calculation level but unusually sensitive to the basis set used and varies between 1.47 and 1.51 Å. The lowest frequency normal vibration calculated with different levels of Møller–Plesset perturbation theory is degenerate and inconsistent with the results of coupled-cluster calculations.

The calculated electron affinity of cubic C_8 is 69 kcal/mol and ionization potential over 226 kcal/mol. The singlet-triplet gap is 17 kcal/mol, both the triplet and the cation radical are Jahn-Teller species with D_{2h} and D_{4h} symmetry, respectively. The cubic cluster is 100 kcal/mol more strained than the global minimum (C_{4h}-symmetrical ring) and can transform to it with a 62 kcal/mol barrier.



Rearrangement pathway



Non-covalent interaction in C8@C80

The exothermic reaction of C_8 with $^3O_2$ has a low barrier; 7 kcal/mol. The product is a triplet peroxide (energy gain 13 kcal/mol in comparison to separated molecules). The next step of the oxidation sequence is formation of dioxetane cycle, breaking of the propellane bond (to form a molecule familiar as to 9,10-dioxa-perdehydro-basketane) and further fragmentation. The barrier of this process is around 24 kcal/mol and is followed by spin-crossing from the triplet to the singlet state.

The cubic C_8 cluster can be encapsulated in C_{60} and C_{80} fullerenes (Russian doll structures), accompanied by strong electron transfer from C8 to fullerenes.

UV-spectra predicted by TDDFT and CASPT2 approaches are rather similar and exhibit peaks near 6.0, 7.9, 8.5, and 9.0 eV.

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[3] Manaa, M. R. *J. Mol. Struct. (Theochem)* **2001**, 549, 23-26.