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Comment on "Theoretical Investigation of the Formation Mechanism of Metallofullerene Y@C_{82}"

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A recent study[1] by Gan and Wang characterized a formation mechanism for the metallofullerene Y@C_{82}, and the energetically favorable path was determined to be a reaction $C_{76} + YC_6 \rightarrow Y@C_{82}$. The YC_6 reactant was portrayed as a six-membered ring of carbon coordinated to an yttrium atom in η^6 fashion, with C_{6v} or near-C_{6v} point group symmetry. However, what is the stability of this proposed reactant relative to other YC_6 isomers? Will the YC_6 exist in the proposed form with a sufficient lifetime to perform its proposed role in the mechanism? Using the B3LYP/LANL2DZ method[2,3] of the previous study, this isomer of YC_6 is compared to two other YC_6 isomers from a previous study[4] by Strout and Hall. These two other isomers are shown in Figures 1 and 2. Figure 1 shows a planar isomer in which the yttrium atom is coordinated to a six-membered carbon ring in η2 fashion. Figure 2 shows the so-called "fan isomer" is which the yttrium atom is coordinated to a linear chain of six carbons in such a way as to have Y-C bonding distances with all six carbon atoms.

The first major result is that the geometry optimization of a C_{6v} isomer was unsuccessful due to gradients that suggest that the six Y-C distances should be non-identical. The stationary point most similar to the previous authors' C_{6v} isomer was found in C_{2v} symmetry and is shown in Figure 3. Even this structure is not quite a local minimum, having a single imaginary frequency of 135i. The molecules in Figures 1 and 2 are local minima at the B3LYP/LANL2DZ level of theory. Table 1 shows the relative energies of these three stationary points. The fan isomer is the lowest in energy, followed by the planar η^2 ring isomer, with the nonplanar isomer lying much higher in energy. Given this energy ordering of the isomers, it is plausible to envision a reaction path whereby the yttrium atom of the nonplanar isomer slides down to its position on the planar ring, followed by insertion of the yttrium into the ring to form a fan isomer. If the barrier between nonplanar ring isomer and planar ring isomer is a high one, then the nonplanar ring isomer may be stable enough to perform its proposed role in the formation of Y@C_{82}. However, that would have to be demonstrated to be the case in order for the nonplanar YC_6 to be a plausible reactant in a Y@C_{82} reaction mechanism.

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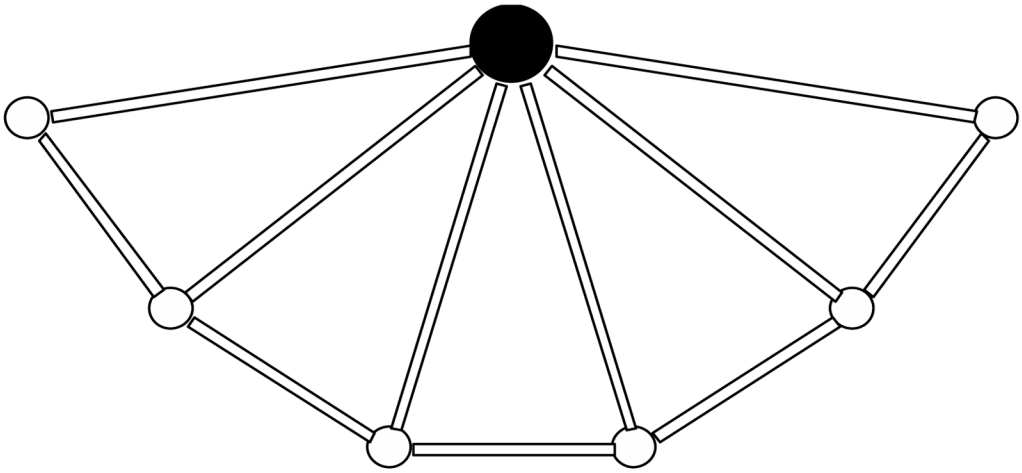

Figure 1.
Fan isomer of YC_6 (C_{2v} point group symmetry).

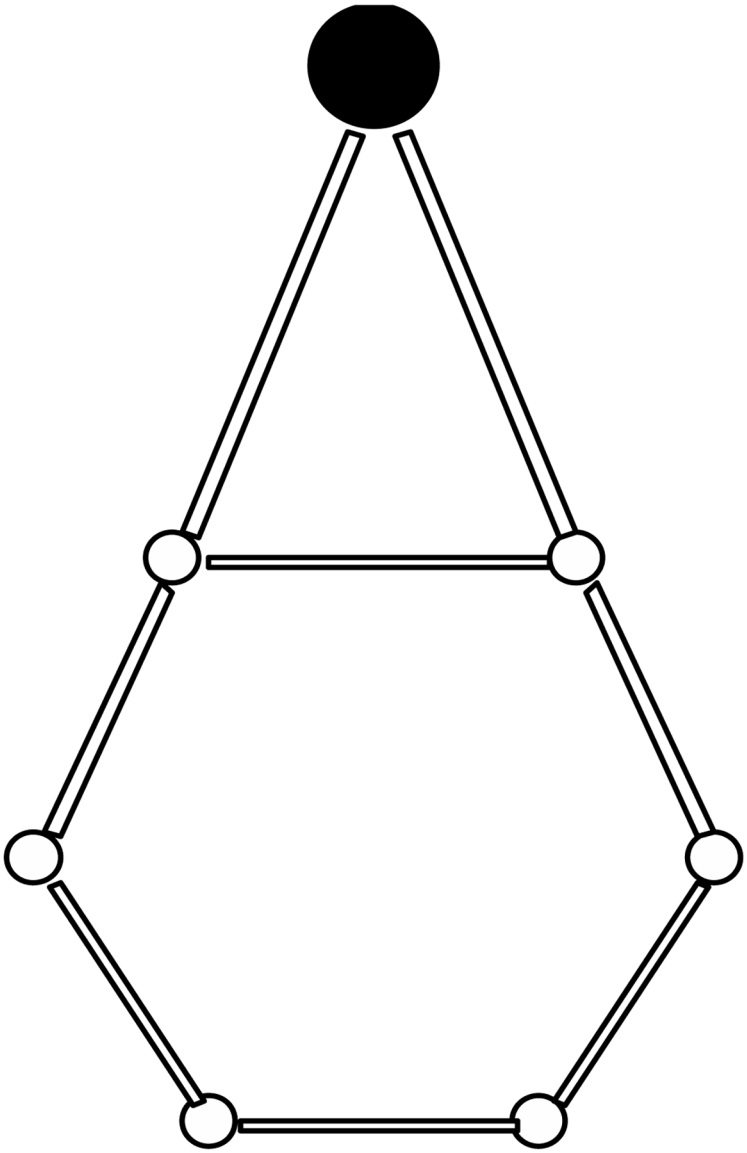

Figure 2.
Planar ring isomer of YC_6 (C_{2v} point group symmetry).

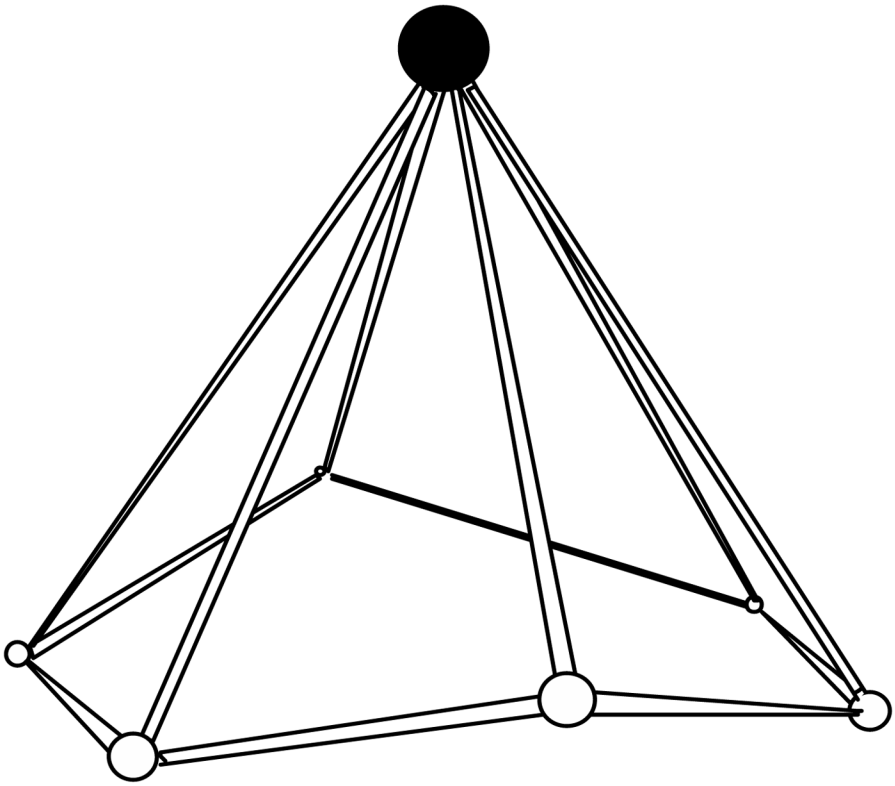

Figure 3.
Nonplanar ring isomer of YC_6 (C_{2v} point group symmetry). This structure resulted from unsuccessful attempts to optimize the structure with C_{6v} symmetry.

TABLE 1

Relative energies of three isomers of YC_6 (calculated with B3LYP/LANL2DZ method, energies in kcal/mol).

Isomer	Energy
Fan isomer (Figure 1)	0.0
Planar ring isomer (Figure 2)	+19.3
Nonplanar ring isomer (Figure 3)	+63.1