Published in final edited form as:

J Phys Chem A. 2006 March 30; 110(12): 4285–4286. doi:10.1021/jp053586q.

Comment on “Theoretical Investigation of the Formation Mechanism of Metallofullerene Y@C₈₂”

Douglas L. Strout

Department of Physical Sciences, Alabama State University, Montgomery, AL 36101

A recent study¹ by Gan and Wang characterized a formation mechanism for the metallofullerene Y@C₈₂, and the energetically favorable path was determined to be a reaction C₇₆ + YC₆ → Y@C₈₂. The YC₆ reactant was portrayed as a six-membered ring of carbon coordinated to an yttrium atom in η⁶ fashion, with C_{6v} or near-C_{6v} point group symmetry. However, what is the stability of this proposed reactant relative to other YC₆ isomers? Will the YC₆ 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 YC₆ is compared to two other YC₆ isomers from a previous study⁴ 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” in 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 η² 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@C₈₂. However, that would have to be demonstrated to be the case in order for the nonplanar YC₆ to be a plausible reactant in a Y@C₈₂ reaction mechanism.

Acknowledgements

The Alabama Supercomputer Authority is gratefully acknowledged for a grant of computer time on the SGI Altix operated in Huntsville, AL. This work is also supported by the National Institutes of Health (NIH/NCMHD grant 1P20MD000547-01). The taxpayers of the state of Alabama in particular and the United States in general are also gratefully acknowledged.

References

1. Gan LH, Wang CR. *J Phys Chem A* 2005;109:3980. [PubMed: 16833719]
2. Becke AD. *J Chem Phys* 1993;98:5648. Lee C, Yang W, Parr RG. *Phys Rev B* 1988;37:785.
3. Hay PJ, Wadt WR. *J Chem Phys* 1985;82:299.
4. Strout DL, Hall MB. *J Phys Chem* 1996;100:18007.

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