

Qualifying Exam Question from Dr. Prakash

In April 2002, J. B. Lambert and coworkers reported the preparation and characterization of stable antiaromatic pentamethylcyclopentadienyl cation. After the paper was published the interpretation of the structure was refuted in C & E News (Prakash and Olah), *Angew. Chem. Int. Ed.* (Bertrand, Muller) and *Chem. Commun.* (Cowley). Succinctly discuss this major screw-up in modern science.

J. B. Lambert et al. *Angew. Chem. Int. Ed.*, **2002**, *41*(8), 1429.

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In his claim to have made a stable pentamethylcyclopentadienyl cation, Lambert must have ignored what the crystal structure showed (Figure 1). Instead, he was too intent on applying computational numbers to what he wanted to see. The pyramidalization of carbon's C4 and C5 appears to clearly be sp^3 hybridized rather than try hard to explain it as a weak sp^2 under crystal packing forces. In his own words: "the major differences between our calculations and observations are an observed lengthening of C4-C5 by 0.15 angstroms and pyramidalization of C4 and C5."¹ There were many indications in his data that he instead made the known *trans*-1,2,3,4,5-pentamethylcyclopent-1-enyl cation.

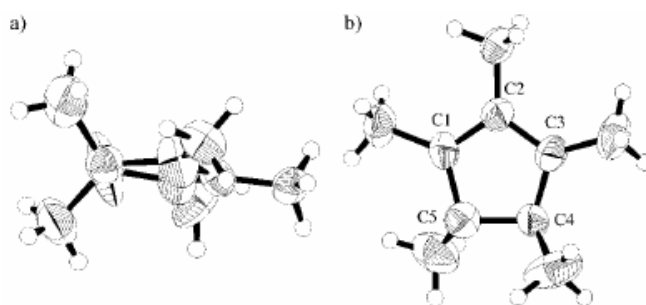


Figure 1. Crystal structure of *trans*-1,2,3,4,5-pentamethylcyclopent-1-enyl cation; a.) edge view, and b.) top view.

As noted by Bertrand *et al.*,² the observed bond length for C4-C5 was 1.51 angstroms was 11% longer than the calculated one, 1.36 angstroms. Also, the pyramidalization of C4 and C5 was not predicted by the calculations. Lambert tried to explain the differences by crystal packing between the anion and cation, causing a distortion that would pyramidalize those carbons. Bertrand was not convinced by this explanation, primarily because the dihedral angle observed for the methyl groups attached to C4 and C5 were in the *trans* position of a saturated fragment. Also, the C4-C5 bond length was in agreement for the single-bonded saturated fragment. The ^{13}C NMR data also showed that the chemical shift for the C4 and C5 carbons was ($\delta = 60$

ppm) where one would expect to find the C4 and C5 sp^3 carbon atoms of the pentamethylcyclopentenyl cation. Lambert did work with Bertrand to correct his errors.

Muller also had problems with the claim, and commented on the X-ray structure and NMR.³ By his calculations with tetramethylethylene, the energetically unfavorable pyramidalization of the double bonded C4-C5 fragment should only extend the bond length by 0.04 angstroms. Also, the ^{13}C NMR signals would have been shifted downfield, rather than unusual upfield signal Lambert reported.

Cowley *et al.* intentionally made pentamethylcyclopentenyl cation as the tetrakis(pentafluorophenyl)borate salt, Lambert's unintentional product.⁴ The X-ray data and computational model they obtained were in excellent accord with their desired product.

Probably more amazing than Lambert's claim was the fact that the very obvious errors were missed not just by him and his co-workers, but also by the editors and referees of *Angewandte Chemie*, as well as *Chemical and Engineering News*. Lambert did retract his claim and as noted worked with Bertrand to correct his mistakes. The lesson to learn from this event is that it is better to not rely on the computational models more than the physical data. If there are obvious variations from what is expected, then the most likely explanation just might be the simplest. The C4-C5 bond was longer than it could be as a double bond, therefore it must have become saturated. The *trans* orientation of the methyl groups on the C4 and C5 carbons suggest that the C4 and C5 carbons were sp^3 -hybridized. The NMR data also suggests that C4 and C5 were also sp^3 -hybridized. Therefore the product must be pentamethylcyclopentenyl rather than the pentamethylcyclopentadienyl.

REFERENCES

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- ¹ Lambert, J. B.; Lin, L.; Rassolov, V.; *Angew. Chem. Int. Ed.*, **2002**, *41*(8), 1429.
- ² Otto, M.; Scheschkewitz, D.; Kato, T.; Midland, M. M.; Lambert, J. B.; Bertrand, G.; *Angew. Chem. Int. Ed.*, **2002**, *41*(13), 2275.
- ³ Muller, T.; *Angew. Chem. Int. Ed.*, **2002**, *41*(13), 2276.
- ⁴ Jones, J. N.; Cowley, A. H.; Macdonald, C. L. B.; *Chem. Commun.*, **2002**, 1520.