Final Technical Report

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I. Personnel

The research group consists of a research assistant professor (Dr. Andrzej Sygula from Jagiellonian University), a post-doc (Dr. Zbigniew Marcinow from Akademia Rolnicza), a part-time technician (Renata Sygula, an M.S. level chemist) and a graduate student, Mark Clayton from the University of Kentucky. Dr. Sygula and Mark Clayton are supported fully from DOE funds, and Renata Sygula is supported partially by DOE funds. Dr. Marcinow is also working on the DOE project, and his salary support comes from university sources.

II. Summary of Technical Accomplishments

Accomplishments have been excellent resulting in a number of publications listed below in Part II. Highlights of selected achievements will be briefly outlined here.

Under earlier DOE funding we reported the first example of an aromatic hydrocarbon with a carbon framework represented on the buckminsterfullerene surface (a "buckybowl") that-unlike corannulene—does not undergo rapid bowl-to-bowl inversion. As such cyclopentanocorannulene (1) represented the first example of a "locked bowl." (As noted in the press: "Researchers 'Lock' Bowl-Shaped Geometry of Corannulene," Chemical and Engineering News, April 19, 1993). Under the most recent program we have been able to stereoselectively
deutereogenate 2 enabling us to measure the bowl-to-bowl inversion process by following the appearance of convex hydrogens in the NMR spectra at various temperatures. This is the first time a bowl-to-bowl inversion barrier has been measured for a hydrocarbon on the C$_{60}$ surface larger than corannulene; $\Delta G^\#$ was determined to be 27.8 kcal/mol, as compared to ca, 10-11 kcal/mol for corannulene. Hence at ambient temperature, the system is, for all intents and purposes, locked.

In 1994 we prepared the first C$_{30}$ semibuckminsterfullerene, 4. However the most difficult step in its synthesis was preparation of the key intermediate, tetraketone 3. We have now developed a new route to 3 (below) involving benzeneseleninic anhydride oxidation that represents a significant improvement in the overall process making 4 more accessible.

One of our major goals has been to make additional buckybowls and we were successful in preparing a new C$_{32}$ H$_{12}$ (below). This structure represents only the second example of a buckybowl synthesis beyond C$_{30}$, the other being
a C_{36} recently prepared by the Scott group. This success of this methodology has also allowed us to develop some likely routes to even larger buckybowls as discussed in the accompanying proposal.

We have also developed a synthetic route to the octamethyl derivative 5. While the carbon framework of 5 is represented on the C_{60} surface, it is, of course, planar. However, we are interested in the use of 5 as an intermediate for a very large scale, non-pyrolytic synthesis of buckybowl 4 (see accompanying proposal). While the synthesis is somewhat tedious, it does represent a route whereby large amounts of 5 could be prepared. Making “connections” between each of four pairs of methyls would lead to 4. The crystal structure of 5 was also determined and, as one would expect, there is a considerable twisting of the structure due to crowding of the methyls.

Most recently we have reported the first crystallographically characterized transition metal buckybowl compound (6). We have found metal complexes
and metal compounds of buckybowls very difficult to prepare and so we were quite pleased to be able to isolate 6. (This work was also noted by the press: "Metal-Buckybowl Structure Dishes Out a Surprise," *Chemical and Engineering News*, February 2, 1998, p. 25)


