

## Models for Acetylene-Bridged Buckminsterfullerenes

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Molecules capable of reversible chemical reductions (addition of electrons) are generally quite important technologically because the variable electronic states give rise to enhanced catalytic, (semi)conductive, nonlinear optical, and/or magnetic properties. Nevertheless, only few molecules can undergo multiple redox steps, with the metal dithiolenes and phthalocyanines being among the earliest and best-known examples. Redox changes of only a few integral charge steps can normally be achieved even in these remarkable materials.

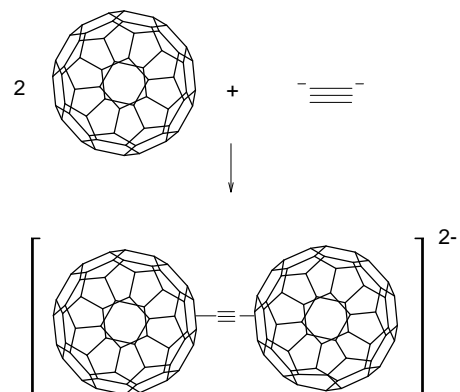
This highlights the dramatic discovery that buckminsterfulleren,  $C_{60}$ , can undergo six (6) successive reductions reversibly! [1] The cyclic voltammogram of  $C_{60}$  provides stunning proof of this ability to pump up to six electrons into an all carbon structure – especially remarkable given the relatively small size of  $C_{60}$ . The electron affinity of  $C_{60}$  is high, putting it more or less in the range of the halogens. This caught our attention several years ago, and some quantum mechanical work was directed toward understanding the Jahn-Teller distortions of  $C_{60}^-$  [2].

The utility of the high electron affinity of  $C_{60}$  was shown when polythiophene was doped with  $C_{60}$  to form polymer photovoltaics[3]. The high electron affinity promoted photo-induced electron transfer from the polythiophene to the  $C_{60}$  in 100% quantum efficiency. While the overall device was disappointing (less than 1% due to poor mobility), this demonstration provided the impetus for much additional work. Yet – it seems that the underlying paucity of a wide pallet of good electron accepting molecules, especially those capable of existing in multiple charge states, is needed for this field to advance. Toward this end we report the results from quantum chemical modeling of the species associated with the reaction scheme outlined in the Figure above.

The structure of the product may be different than the one drawn with respect to inter- $C_{60}$  bonding. At least five structures are plausible. One is an apex bonded acetylide containing sp hybridized carbons as shown. But, the acetylide could be sp<sup>2</sup> hybridized and bridge fullerene double bonds, forming cyclopropene rings. Since there are fullerene bonds connecting two six-membered rings (designated 6,6) as well as fullerene bonds connecting a five and a six membered ring (designated 5,6), this adds two more possibilities. Additionally, in the 5,6 or 6,6 modes, the actual fullerene

carbon-carbon could rupture, giving open-5,6 or open-6,6 structures.

These possible structures are being modeled at several levels of theory for various bonding patterns, charges and spin states. Results will be compared with



recent experimental results on C<sub>122</sub> [5,6].

## REFERENCES

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