Models for Acetylene-Bridged Buckminsterfullerenes

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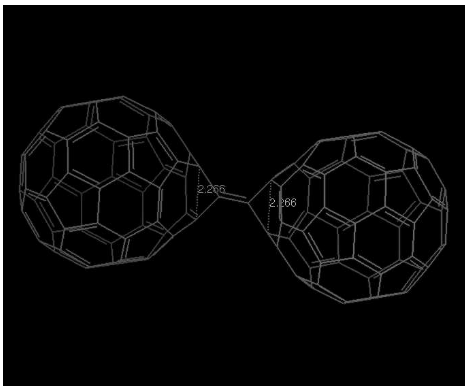
Molecules capable of reversible chemical reductions (addition of electrons) are generally quite important technologically because the variable electronic states give rise to enhanced catalytic, (semi)conductive, nonlinear optical, and/or magnetic properties. Nevertheless, only few molecules can undergo 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-Tellar 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.

The structure of the product may be different than the one drawn with respect to inter-C60 bonding. At least five structures are plausible. One is an apex bonded acetylide containing sp hybridized carbons as shown. But, the acetylide could be sp2 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 semi-empirical (AM1) and density functional (DFT) levels of theory for various bonding patterns, charges and spin states. The figure below shows a 5,6 bridged species (calculated using the B3LYP hybrid functional) where the CC distance on the buckyball has been distorted to 2.26 Å (from 1.44 Å) Complete results will be compared with recent experimental studies on C122 [5,6].



REFERENCES

[1] D. Dubois, G. Moninot, W. Kutner, M. T. Jones and K. M. Kadish, _J. Phys. Chem_. 1992, ***96***, 7137-7145
[2] D. Dudis, unpublished computational results (1995).
[3] N. S. Saracifti, A. Smilowitz, A. Heeger and F. Wudl, _Science_ 1992, ***258***, 1474.
[5] N. Dragoe, S. Tanibayashi, K. Nakahara, S. Nakao, H. Shimotani, L. Xiao, K. Kitazawa, Y. Achiba, K. Kikuchi and K. Nojma, _J. Chem. Soc. Chem. Commun._, ***1999***, 85-86.
[6] T. S. Fabre, W. D. Treleaven, T. D. McCarley, C. L. Newton, R. M. Landry, M. C. Saraiva and R. M. Strongin, _J. Org. Chem_., 1998, ***63***, 3522-3523.