# A Chemical Theory of Graphite

S. E. Stein and R. L. Brown
Chemical Kinetics Division
National Bureau of Standards
Gaithersburg, Maryland 20899

## Introduction

Graphite and many other carbonaceous materials consist primarily of polynuclear aromatic hydrocarbons. The inability to isolate such compounds for individual study has resulted in their reactions being described in very general, phenomenological terms. Reactivity is believed to involve active sites whose chemical nature is speculative.

Because we believe that reactions of carbonaceous materials are likely to follow straightforward organic mechanisms, we have been applying semi-empirical pi-electron theories to very large polyaromatic species. Several of these theories are well-suited for this purpose since they are computationally simple and have been quite successful for polybenzenoid structures. By using these theories to develop structure/reactivity relations, we hope to devise models for reactions of carbonaceous materials.

## Theories Based on Kekule Structure Counts

### Structure-Resonance Theory

This theory is the simplest and could be applied to the largest structures.[1] Using this method we have examined graphitic molecules containing as many as 16,000 C-atoms.[2,3] Most trends predicted by SRT are consistent and reasonable. Local properties such as bond orders and aromaticity indices converge properly to graphitic limits and appear to be qualitatively correct. Unfortunately, overall molecular properties such as ionization potentials do not converge with increasing size, and others converge to different values depending on edge structure.

### Perturbation Molecular Orbital (PMO) Theory

Mathematically related to SRT, this theory always yields reasonable convergence limits.[4] It predicts electron localization energies, a key factor determining the likelihood of free-radical attack at a specified position in the molecule.

## Molecular Orbital (MO) Theories

### Huckel Molecular Orbital (HMO) Theory

Although the oldest of the pi-electron theories, it is still considered to be fundamentally correct for benzenoid polyaromatic molecules. It yields energies of all occupied energy levels along with the electron densities associated with each level. The least stable (i.e., highest) occupied orbital is often considered to be the one through which chemical reaction occurs. The largest molecules we have examined so far by this theory contained 1500 C-atoms.

### Self-Consistent Field (SCF) Theories

Although more complex and time-consuming than HMO calculations, SCF theories are generally considered to be more accurate. Most of our recent work has been on the development of efficient computer codes to adapt the Pople version of these methods to very large molecules.[5,6]

All of the simpler theories we examined required constructing the so-called bond matrix which describes how the carbon atoms are connected. The key to their extension to large molecules was the use of a unique numbering system for the carbon atoms which resulted in a narrow banded bond matrix whose eigenvalues and inverse could be easily determined.[2] If, however, one is interested in the electron densities associated with the energy levels, or requires their use in iterative calculations as in SCF methods, then computational problems rapidly become enormous for molecules of even modest size. In these cases, the only way to study large molecules is to require them to have the maximum symmetry. Then, group theoretical methods can be applied to greatly simplify the computational problem. Another advantage of using symmetrical structures is that they are easily formed into homologous series, each series consisting of a progression of increasingly large molecules. Using this approach we have been able to use the SCF method on molecules containing up to 1000 C-atoms. For complete convergence of this iterative method, such molecules required three to six days on a high speed computer. To our knowledge, the largest molecule to which this method had previously been applied was kekulene which contains 42 C atoms.[7]

## MO Theory Results

So far, our results with the MO theories are usually in qualitative agreement with simpler theories. One critical difference, however, is that these methods, in accord with intuition, indicate that resonance energies per C-atom approach a unique value with increasing molecular size, independent of edge type. For the simplest theory used in previous studies, different limiting values were approached which depended on edge type.

For the highest occupied orbital, both HMO and SCF predict a large probability for the electron to be concentrated at the perimeters of large hexagonal molecules having an anthracene-like edge structure. This is in contrast to similar molecules with phenanthrene-like edges. For these the electron distribution in the highest orbital is very uniform over the whole molecule. In the anthracene-type structures this concentration of electron probability at the edge of the molecule is not limited to only the highest level. It is evident in orbitals whose energies lie as much as 0.8 eV below the highest level.

## References

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