WHAT (EXACTLY) IS ON THE EDGES OF GRAPHENE LAYERS IN CARBON: THE UNFOLDING STORY

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Introduction

Knowledge of the chemical details of edge termination of a graphene sheet continues to be important in all applications of carbon materials (e.g., gasification reactivity, substituent effects in liquid-phase adsorption of aromatic compounds, and perhaps even enhanced gas adsorption potentials). The most recent evidence for this insufficiently recognized fact is the dramatic effect of "simple annealing of SWNT-based p-FETs in a vacuum" (1) on the behavior of carbon nanotubes as inter- and intramolecular logic gates. Perhaps surprisingly, this subject has been discussed in the literature only sporadically, most notably by C. A. Coulson and S. E. Stein. Today, when molecular-scale manipulation of the electronic properties of carbons is attracting much scientific attention and even becoming commercially viable, it is very important to be as specific as possible about the surface chemistry of edge carbon atoms. The common assumptions, that either all edge sites are saturated with heteroatoms or that the free edge sites are conventional (and thus very reactive) free radicals (2), do not appear to be justified (3). Modern quantum chemistry is increasingly providing the tools to confirm this. In this presentation we scrutinize the (relatively scant) literature and discuss our recent Gaussian98 (4) results to argue in favor of the following edge structures: ortho-benzyne at the armchair sites and carbene or m-benzyne at the zigzag sites. Unfortunately, we cannot be more specific in the case of zigzag sites. There is a very rich benzyne and carbene literature today, mostly theoretical but also experimental, so organic chemists will hopefully be comfortable with this proposal; and yet, many carbon scientists may be at least surprised.

The distribution of electron density at these sites is important because it can lead to quantitative indices of carbon atom (re)activity, and the litmus test here is to account for the reactivity differences between zigzag and armchair sites.

Overview of Theoretical Results

The distinction between armchair and zigzag sites is of both fundamental and practical importance; the ultimate goal is to be able to explain the experimental finding (5) that the latter are usually more reactive than the former.

The existence of unpaired σ electrons on armchair sites raises the possibility of the formation of a triple bond. Such a structure has indeed been proposed by Coulson (6), but it has been largely ignored in recent modeling studies of carbon electronic structure and reactivity. The fate of the unpaired σ electron on the zigzag sites is much more controversial (see Figure 1). Here again the most useful literature source is Coulson (6), who proposed the existence of a "divalent state based on s^2p^2" hybridization. Use of the same model chemistry for the armchair sites – B3LYP/3-21G*//B3LYP/6-31G(d) – does not lead, however, to equally successful geometry optimization. Indeed, the results are very sensitive to the exact location of radical sites in the cluster shown below. However, the presence of preadsorbed oxygen does help to stabilize the zigzag structure, by analogy with the stability of 4-oxycyclohexa-2,5-dienylidene. The existence of the "in-plane σ pair," the somewhat vague concept dating from the pioneering works of S. Mrozowski and P. L. Walker, is also discussed.

Implications for Carbon Reactivity

The most fundamental definition of reactivity is

$$R = (1/(1-X))(dX/dt) = \{\text{Site reactivity}\}\{\text{Number of reactive sites}\}$$

where X is carbon conversion. In our previous studies (7), as a first approximation, we equated site reactivity with $\Sigma(FV)_i$, where FV is the free valence index from simple Hückel molecular orbital theory. Subsequently, we estimated site reactivity using a Monte Carlo technique (8). Now, we are in a position to use a (unique?) set of fundamental reactivity indices, such as electron density (in the case of adsorption) and bond strength (in the case of desorption), to determine the above two reactivity parameters simultaneously; in such an approach, the number of reactive sites is automatically determined by the threshold level of site reactivity.

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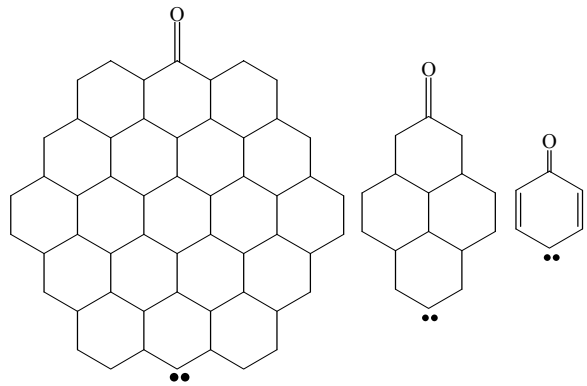

Figure 1. Model carbene structures for zigzag carbon atoms in different-size graphene layers of carbon materials.