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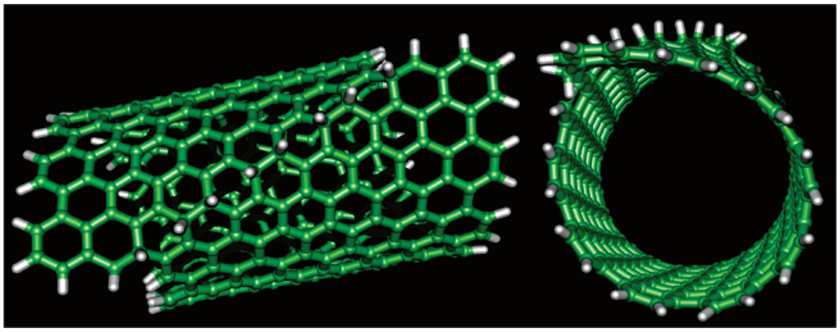
The Regioselectivity of Addition to Carbon Nanotube Segments

Jason L. Ormsby and Benjamin T. King*

Department of Chemistry, University of Nevada, Reno, Nevada 89577

king@chem.unr.edu

Received January 2, 2007



Calculations (AM1) demonstrate that Clar's valence bond model predicts the long-range reactivity patterns of hydrogenation of carbon nanotube (CNT) segments. CNT segments behave as other polycyclic aromatic hydrocarbons—hydrogenation of double bonds is energetically preferred over hydrogenation of aromatic sextets. The frontier molecular orbitals of CNT segments have greatest amplitude at the double bonds, suggesting that Clar's model also predicts kinetic reactivity.

Introduction

The covalent addition chemistry of carbon nanotubes (CNTs) determines their suitability for many applications. Oxygen reactivity may limit their use in molecular electronics,[1] nitric acid oxidation is used in their purification,[2] hydrogenation is the basis for their proposed use as a hydrogen storage medium,[3] and selective functionalization is required for their use in fantastic nanomachines.[4] We demonstrate herein that Clar's valence bond model[5] can be used to predict the preferred patterns—the regiochemistry—of addition reactions to CNT segments.

Experimental work, which has been recently reviewed,[6] has given some insight into the synthetic chemistry of CNTs. Most reactions have analogues in the chemistry of olefins and arenes, such as halogenation,[7] hydrogenation, [2 + 1] cycloadditions, etc., and are often performed under forcing conditions. The products, which invariably are complex mixtures, have been characterized by elemental analysis, vibrational spectroscopy, electron microscopy, or NMR spectroscopy. While the identity of the functionality and stoichiometry can be determined, the patterns of reactivity are largely unknown. Several computational studies[8] have dealt with CNT reactivity, often focusing on the role of sterics. In a noteworthy paper, Bettinger[9] alludes to an underlying electronic phenomenon controlling CNT reactivity.

Clar's valence bond (VB) model,[5] where valence π-electrons are represented using the maximum number of aromatic sextets and the minimum number of double bonds, is the foundation of our approach. We have recently developed rules for generating optimal Clar VB structures for CNTs.[10] Two findings are relevant. First, the criterion for conductivity of a (m,n) CNT,

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10.1021/jo0700070 CCC: $37.00 © 2007 American Chemical Society
Published on Web 02/23/2007

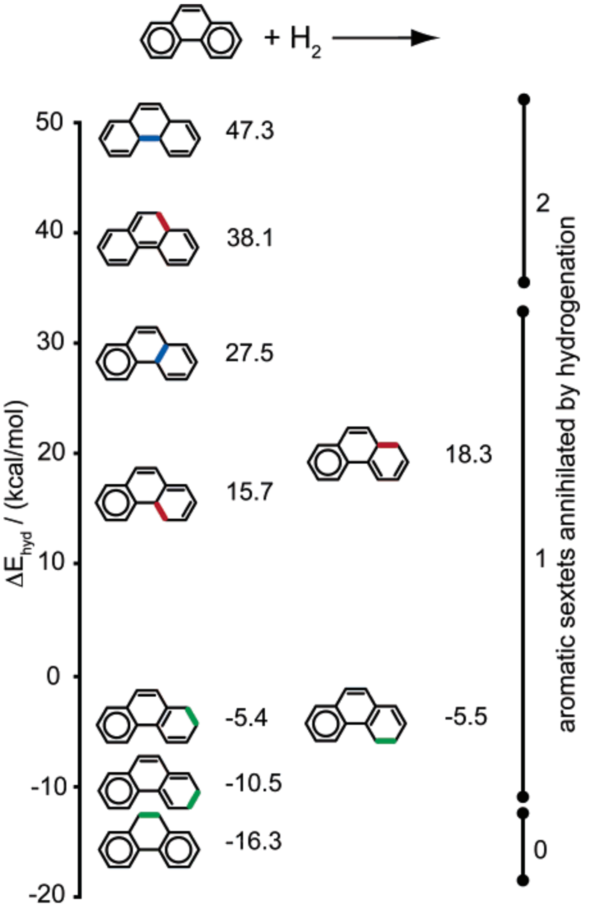

FIGURE 1. Clar VB representations of every possible α,β-hydrogenation of phenanthrene with corresponding electronic energies of hydrogenation (B3LYP/6-31G*). Hydrogenated bonds are colored according to the number of adjacent hydrogens (0 = blue, 1 = red, 2 = green).

where the characteristic index ($m - n$) modolo 3 equals 0, is equivalent to the fully benzenoid criterion, where only aromatic sextets are necessary to complete the π-VB structure. Second, in semiconductive CNTs, where the characteristic index ($m - n$) modolo 3 equals 1 or 2, a seam of double bonds wraps around the CNT at the chiral angle or the chiral angle − 60°, respectively.

Results and Discussion

Clar developed his model to rationalize trends in PAH reactivity[5]—aromatic sextets are less reactive than double bonds. It is therefore not surprising that the thermodynamics of hydrogenation of PAHs correlate with Clar's model. Consider phenanthrene, as in Figure 1. Hydrogenation is most favorable across the double bond at position 9,10, where no aromatic sextets are annihilated; it is next most favorable where a single aromatic sextet is annihilated; it is least favorable where two aromatic sextets are annihilated.

Similarly, the energies of hydrogenation (B3LYP/6-31G*) of every α,β-dihydro isomer of tetracene, triphenylene, coronene, benzo[*ghi*]perylene, dibenzo[*g*,*p*]chrysene, benzo[*e*]pyrene, and pyrene correlate ($R^2 = 0.64$) with the number of aromatic sextets annihilated (Figure 2). Sterics and strain clearly play a role; internal bonds (blue), which bear no H atoms, are most difficult to hydrogenate; terminal bonds (red), which bear one H atom, are next to most difficult; and external bonds (green), which bear two hydrogen atoms, are easiest.[11] This trend is also manifest in phenanthrene (Figure 1). Clar's model predicts the thermodynamically favored sites of hydrogenation.

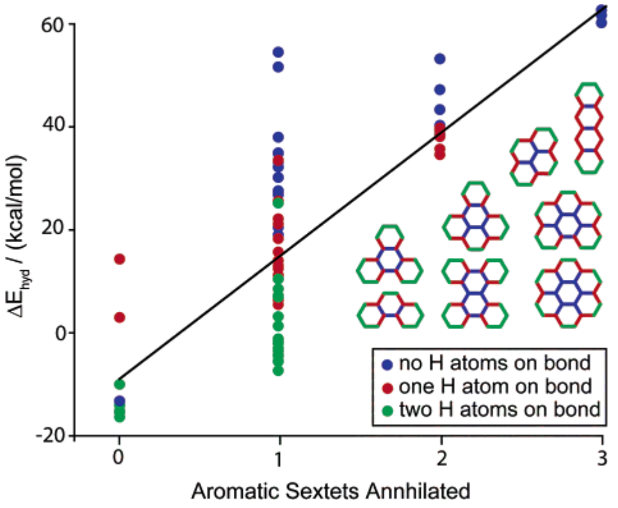

FIGURE 2. Correlation between aromatic sextets annihilated and ΔE_{hyd}.

DFT or ab initio calculations are, at the time of writing, too demanding for these large CNT segments considered here. Fortunately, the AM1 model chemistry successfully describes hydrogenation reactions; the AM1 results for the 69 reactions in Figure 2 correlate well with the B3LYP/6-31G* results ($R^2 = 0.96$, slope = 1.21) (see Supporting Information). Since we are interested in trends in reactivity, not high accuracy, the AM1 model chemistry is satisfactory.

Does Clar's model also apply to hydrogenation of CNT segments? To test this hypothesis, a set of CNT segments with fundamentally different Clar structures was selected (Figure 3), which is equivalent to choosing CNTs with different characteristic indices, $R = (m - n)$ modolo 3. Both (12,7) CNTs ($R = 2$) and (12,8) CNTs ($R = 1$) have a seam of double bonds wrapping at the chiral angle or chiral angle − 60°, respectively. (12,9) CNTs ($R = 0$) have only aromatic sextets. The length was chosen to accommodate full aromatic sextets. The diameter was made as similar as possible, and all CNT segments were terminated with H atoms.

Hydrogenation of the double bond seam was calculated for the (12,7) and (12,8) CNT segments. The (12,9) CNT segment, whose Clar structure has no double bonds, was hydrogenated analogously to the (12,7) CNT segment. These reactions are shown in Figure 3. Consistent with the Clar model, hydrogenation of the fully benzenoid (12,9) CNT segment was significantly less energetic (by ~8 (kcal/mol)/mol H_2) than hydrogenation of the double bond containing (12,7) and (12,8) CNT segments.

Every permutation of seam hydrogenation was considered. Not surprisingly, the hydrogenation of the terminal bonds was easier than the internal bonds, likely because the terminal carbons can more closely approach a tetrahedral geometry; this trend was also observed in the small molecule PAH hydrogenations (Figure 2). The hydrogenation becomes increasingly

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[11] No effort was made to deconvolute sterics, strain, and electronics.

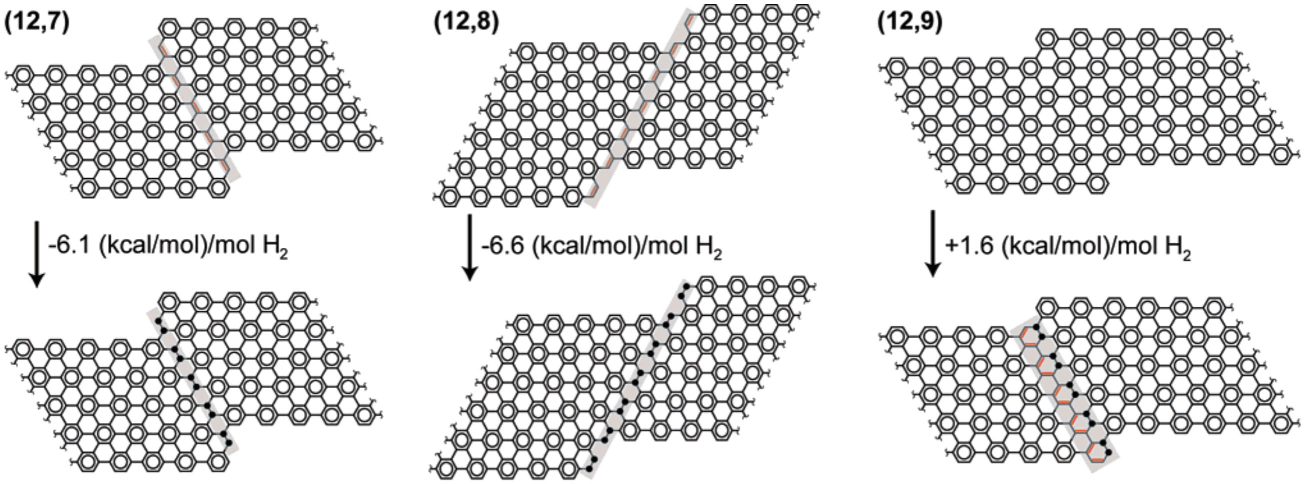

FIGURE 3. From left to right, hydrogenation of equivalent vectors of (12,7), (12,8), and (12,9) CNT segments (planar representations).

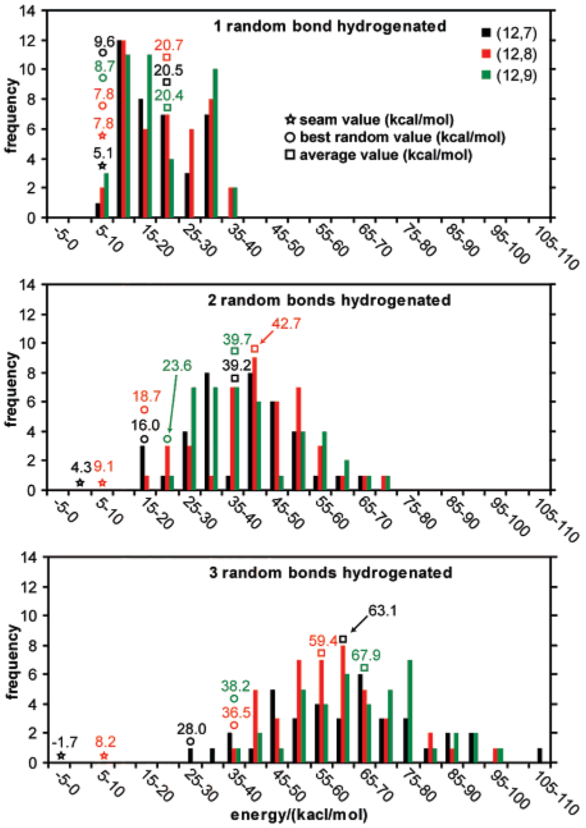

FIGURE 4. Distribution of ΔH_{hyd} for random bonds.

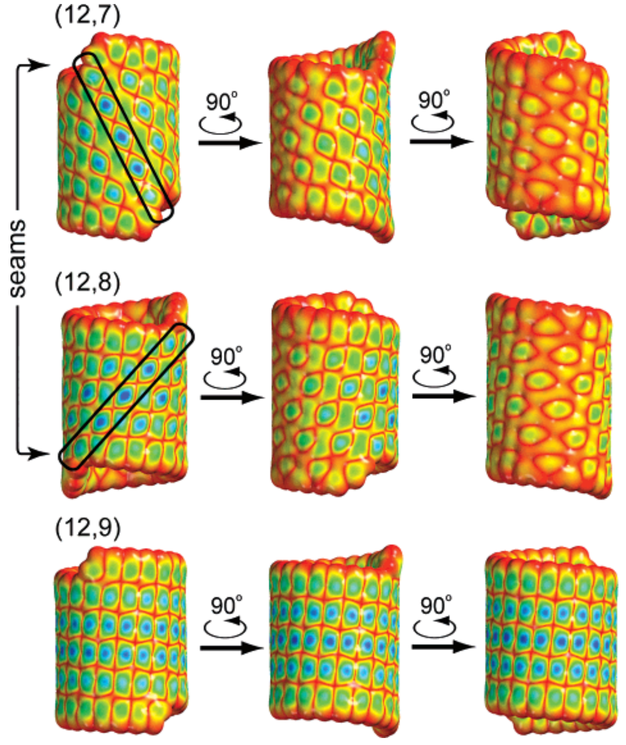

FIGURE 5. Top to bottom, the HOMO (AM1) plotted on the isodensity surface for (12,7), (12,8), and (12,9) CNT segments. The locations of the double bond seam are indicated.

exergonic as the reaction progresses because the tube adopts a tear-shaped profile, relieving strain of the tetracoordinate carbons. Once hydrogenation of the seam of double bonds begins, the pattern should propagate.

Are the double bonds the most energetically favorable sites to hydrogenate within a given CNT segment? To address this question, ΔH_{hyd} was calculated for 366 trials for the (12,7), (12,8), and (12,9) CNT segments with one, two, or three random internal bonds hydrogenated (only bonds that would be blue according to the coloring scheme of Figures 1 and 2); there were ~40 random trials for each scenario. The distributions of ΔH_{hyd} are shown in Figure 4. In every case, the hydrogenation at an internal Clar double bond or bonds (again, bonds that would be blue by the criterion used in Figures 1 and 2) is more exothermic than at randomly selected internal bonds. The energetic preference for hydrogenation along the Clar double bonds is significant, averaging 17 (kcal/mol)/mol H_2 over random addition.

Kinetic selectivity is a more difficult computational problem than thermodynamic selectivity, but it often correlates with the amplitudes of the frontier orbitals. The HOMO (Figure 5) of

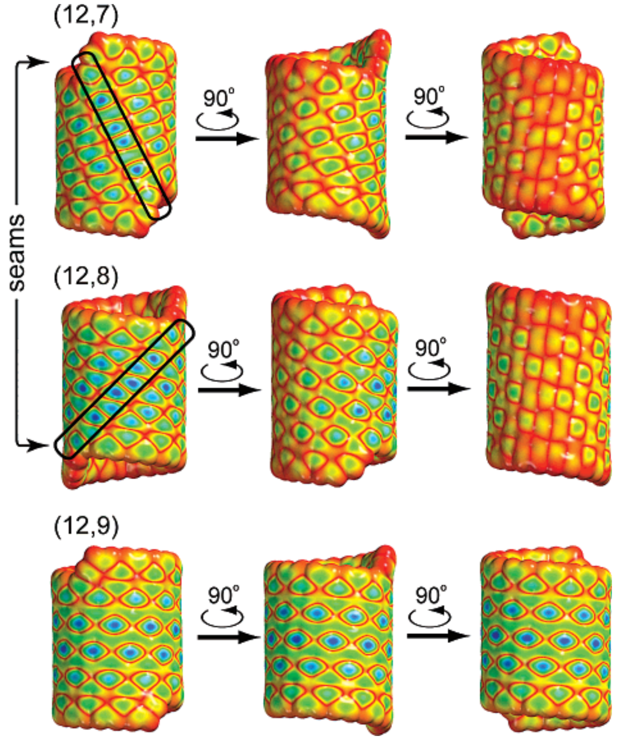

FIGURE 6. Top to bottom, the LUMO (AM1) plotted on the isodensity surface for (12,7), (12,8), and (12,9) CNT segments. The locations of the double bond seam are indicated.

the (12,7) and (12,8) CNT segments has maximum amplitude along the double bond seam; the HOMO of the (12,9) CNT is evenly distributed about the diameter. The LUMO (Figure 6) exhibits similar patterns. The LUMO of the (12,7) and (12,8) CNTs has maximum amplitude along the double bond seam; the LUMO of the (12,9) CNT is evenly distributed about the diameter. In all cases, the amplitude increases toward the middle of the CNT segment.

Conclusions

The Clar VB representations of CNT segments predict the thermodynamically favored isomers of hydrogenation. Fully benzenoid CNT segments, which compose conductive CNTs, are most resistant to addition reactions. CNT segments with double bonds, which compose semiconductive CNTs, are more susceptible to addition reactions. The frontier orbitals of a CNT segment correlate with the Clar VB description of the CNT segment. Addition to double bonds is favored over addition to aromatic sextets.

Acknowledgment. This work is dedicated to Professor Neil Bartlett on the occasion of his 75th birthday. This work was supported by the National Science Foundation (CHE-0449740). This research used resources of the National Energy Research Scientific Computing Center, supported by the Department of Energy (Contract No. DE-AC03-76SF00098). We thank John Kenyon for assistance with programming.

Supporting Information Available: Computational methods and references, correlation of AM1 and DFT results, discussion of random bond sampling, and coordinates of parent CNT segments. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0700070