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# Clar Valence Bond Representation of $\pi$-Bonding in Carbon Nanotubes

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The application of the Clar aromatic sextet valence bond (VB) model to extended, defect-free single-walled carbon nanotubes (CNTs) with roll-up vectors ($m$, $n$) provides a real space model of their electronic structure. If $m - n = 3k$, where $k$ is an integer, then all $\pi$-electrons can be represented by aromatic sextets, and the CNT is fully benzenoid; the converse is also true. Since $m - n = 3k$ is known to be a necessary criterion for conductivity in CNTs, only fully benzenoid CNTs are metallic, and only potentially metallic CNTs are fully benzenoid. This behavior contrasts with that of planar polycyclic aromatic hydrocarbons, in which the fully benzenoid structures are known to have large HOMO−LUMO gaps. For CNTs that are not fully benzenoid, e.g., $m - n = 3k + l$, where $l = 1$ or 2 and $k$ is an integer, a seam of double bonds wraps about an otherwise benzenoid CNT at the chiral angle − 60° or the chiral angle, respectively. Nucleus-independent chemical shift calculations on hydrogen-terminated CNT segments support this, and show that the magnetic manifestation of aromatic sextets is not due to electron correlation. The resonance hybrid of the Clar VB structures corresponds to patterns occasionally observed in scanning tunneling microscopy images of CNTs.

## Introduction

The electronic properties of single-walled carbon nanotubes[1,2] (CNTs) have been the subject of intense study, both theoretical[3] and experimental.[4,5] In particular, the relationship between electronic properties and structure in CNTs is well explained by linear combination of atomic orbital (LCAO) methods in reciprocal space.[6,7] In this paper, we present an alternative description of the bonding in defect-free CNTs based on Clar's chemically intuitive, real-space, aromatic sextet valence bond (VB) model. The model correlates both with the classification of CNTs as either metallic or semiconductive and with the calculated magnetic properties of short CNTs. It also provides a simple explanation of the dissymmetry often observed in images of CNTs obtained using scanning tunneling microscopy (STM). A recent report[8] by Matsuo, Tahara, and Nakamura describes the use of a Clar VB model to explain finite length effects[9−12] in the ($m$, $m$) armchair CNTs.

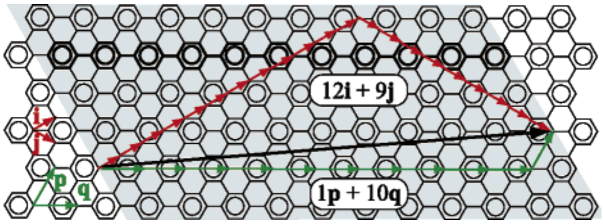

**FIGURE 1.** Roll-up vector for a (12, 9) CNT (black arrow) in the conventional basis **i**, **j** (red) and the Clar basis **p**, **q** (green). Atoms in the unit cell are bold; the parent graphene strip is gray.

VB models are simple and effective tools for predicting

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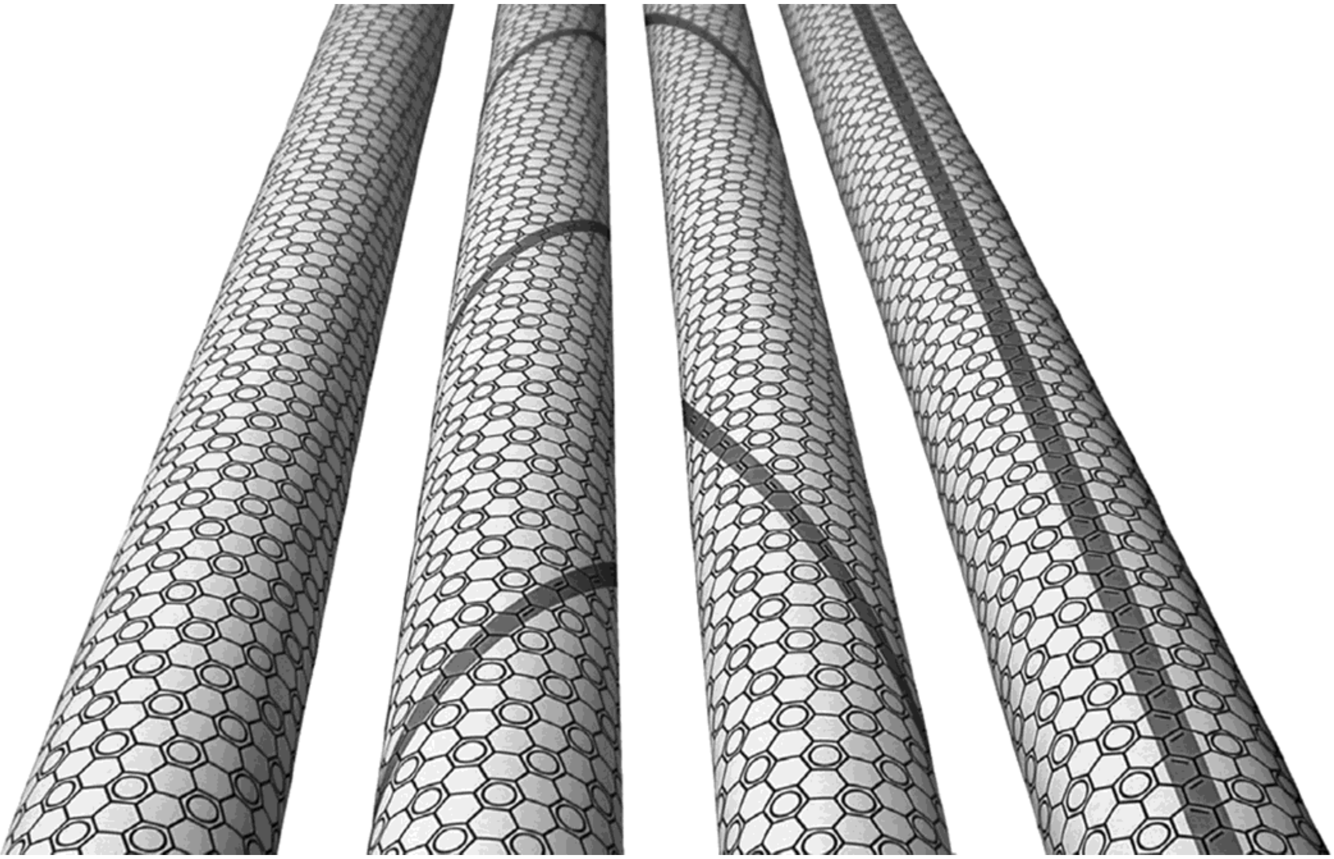

**FIGURE 2.** Clar VB representation of (12, 9), (12, 8), (12, 7), and (19, 0) CNTs, with $R(m, n) = 0$, 1, 2, and 1, left to right.

properties and reactivity. The Clar VB model[13,14] employs both conventional two-electron $\pi$-bonds, represented by lines, and aromatic sextets (six-electron $\pi$-cycles), represented by circles. By preparing and studying several hundred polycyclic aromatic hydrocarbons (PAHs), Clar convincingly demonstrated that the VB structures with the most aromatic sextets best model chemical reactivity,[13] and that structures possessing only aromatic sextets, called *fully benzenoid*, are found to be especially unreactive and have large HOMO−LUMO gaps.[15] A prodigious review on this subject has recently appeared.[16] However, the physical basis for the Clar representation remains somewhat unclear.[16,17]

A CNT is conventionally described by its roll-up vector[18] $m\mathbf{i} + n\mathbf{j}$, whose ends connect when a hypothetical graphene sheet is rolled to form the CNT (Figure 1).[1] Theory predicts that the value of $R(m, n) = m - n$ modulo 3 largely determines the conductivity of defect-free CNTs:[3,6] if $R(m, n) = 0$, the CNT is metallic; otherwise, the CNT is semiconductive. This is supported by measurements.[2,4,5]

## Computational Methods

Idealized CNT geometries were generated in a two-step process. An idealized carbon-only CNT with nearly identical C−C bond lengths (±0.001 Å) was generated using Tubegen.[19] Unwanted carbon atoms were deleted and hydrogen atoms placed at idealized locations using Ghemical.[20] Optimizations were performed using Gaussian 03[21] at the PM3 or B3LYP/6-31G(d) levels of theory. Due to the size of the molecules considered, vibrational analyses were not feasible. Nucleus-independent chemical shift (NICS) calculations[15,22] were performed with Gaussian 03[21] using the GIAO approximation at the level of theory and geometry noted.

## Results and Discussion

By applying the Clar VB model to CNTs, we find that three variations exist, one for each possible value of $R(m, n)$ (Figure 2). If $R(m, n) = 0$, then the CNT is fully benzenoid[23] and potentially metallic. This behavior con-

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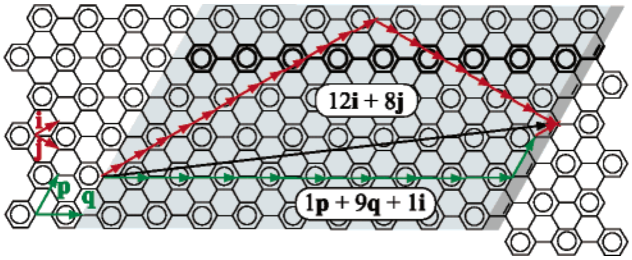

**FIGURE 3.** Roll-up vector for a (12, 8) CNT (black arrow) in the conventional basis **i**, **j** (red) and the Clar basis **p**, **q** (green). Atoms in the unit cell are bold; the parent graphene strip is gray.

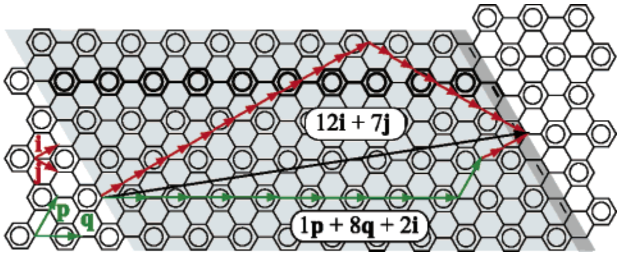

**FIGURE 4.** Roll-up vector for a (12, 7) CNT (black arrow) in the conventional basis **i**, **j** (red) and the Clar basis **p**, **q** (green). Atoms in the unit cell are bold; the parent graphene strip is gray.

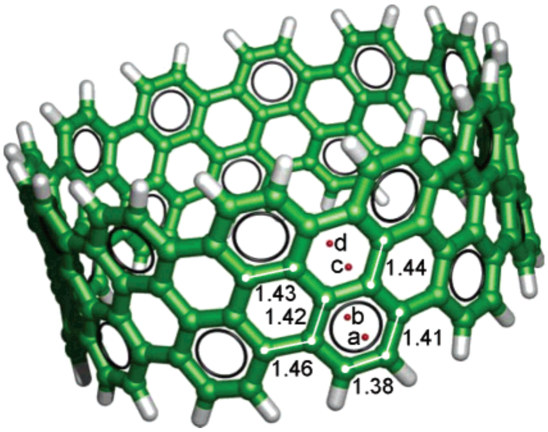

**FIGURE 5.** Calculated structure showing the Clar VB representation, NICS dummy atoms, and bond lengths (Å).

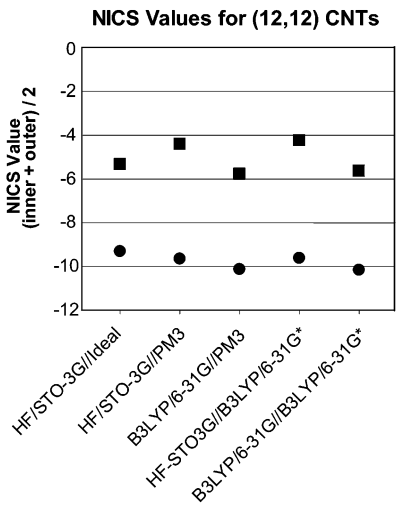

**FIGURE 6.** Comparison of NICS values obtained at different levels of theory for varying geometries. Circles are hexagons containing aromatic sextets, and squares are empty hexagons.

trasts with that of planar PAHs, in which the fully benzenoid structures are known to have large HOMO−LUMO gaps.[15] If $R(m, n) = 1$, then a row of double bonds wraps about an otherwise fully benzenoid CNT at the chiral angle − 60°, parallel to the unit vector **p** (Figure 3). If $R(m, n) = 2$, then a seam of double bonds wraps about the otherwise fully benzenoid CNT at the chiral angle, parallel to the vector $\mathbf{p} - \mathbf{q}$ (Figure 4).

First, consider fully benzenoid CNTs, which are necessarily derived from fully benzenoid graphite (Figure 1). We introduce the Clar basis (**p**, **q**), which, unlike the conventional basis (**i**, **j**), reflects the translational symmetry of fully benzenoid graphite. Any roll-up vector $r\mathbf{p} + s\mathbf{q}$, where $r$ and $s$ are integers, will generate a fully benzenoid CNT. Changing from the Clar basis to the conventional basis determines which CNTs are fully benzenoid: $s = (m + 2n)/3$ and $r = (m - n)/3$. A similar pattern, but in a different context, has been observed.[24]

Since $r$ is an integer, the expression $r = (m - n)/3$ is identical to the criterion for conductivity in CNTs. Similarly, only those CNTs where $(m - n)/3$ = integer can be expressed in the Clar basis. Fully benzenoid is equivalent to $(m - n)/3$, a necessary criterion for metallic CNTs.

A unit cell that fully contains the Clar VB structure can be chosen parallel to the unit vector **q**, and generates the CNT by action of a screw axis operator. This Clar unit cell is preferable to the conventional translational unit cell[1] because it is smaller and fully represents the Clar VB structure. A similar cell has previously been described using reciprocal space.[25] Since each of the unit vectors **p** and **q** spans exactly one aromatic sextet, the unit cell of a fully benzenoid CNT contains exactly $r + s = (2m + n)/3$ aromatic sextets.

These ideas provide a physical picture for the value of $r = (m - n)/3$: it is the degree of helicity of a fully benzenoid CNT constructed from *p*-polyphenylene strips wrapped around a hypothetical cylinder. If $r = 0$, the CNT is not helical; if $r = 1$, the CNT consists of a single right-hand helix of *p*-polyphenylene; if $r = 2$, the CNT consists of a double right-hand helix, etc. The (12, 9) CNT (Figure 2) is a single helix. Achiral CNTs with $R(m,n) = 0$ and $r \neq 0$ can be described as either a left- or right-handed helix.

If $R(m, n) = 1$, the CNT is not fully benzenoid, but a best Clar VB structure, which has the smallest ratio of double bonds to aromatic sextets, can be constructed (Figure 3). Since the termini of the roll-up vector must be identical, a seam containing double bonds must exist

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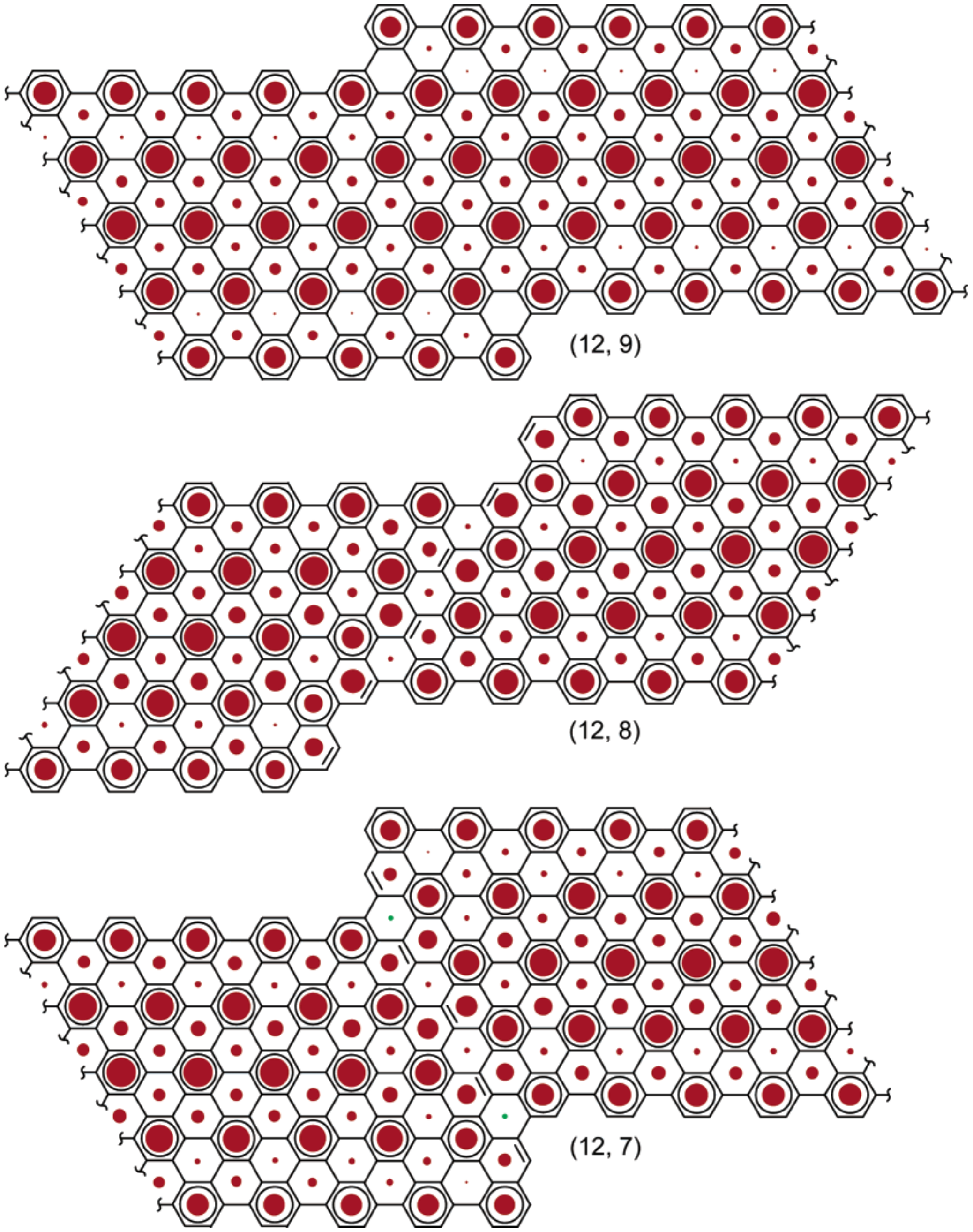

**FIGURE 7.** Planar representations of short (12, 9), (12, 8), and (12, 7) CNTs shown with the Clar VB structures. Filled circles represent the magnitude of the average of the NICS values inside and outside the CNT, with the radius normalized to the largest value. Red is negative, and green is positive.

in the otherwise fully benzenoid graphene sheet, and the roll-up vector must cross at least one double bond. Therefore, a roll-up vector which crosses exactly one double bond provides the best Clar VB structure. The existence of a seam of double bonds parallel to the unit vector **p** satisfies this condition when $R(m, n) = 1$. The unit cell contains $(2n + m - 1)/3$ aromatic sextets and one double bond.

Likewise, if $R(m, n) = 2$, then again the CNT is not fully benzenoid, and a best Clar VB structure can be constructed (Figure 4). In this case, the seam of single bonds is parallel to the vector $\mathbf{p} - \mathbf{q}$. The unit cell contains $(2m + n - 1)/3$ aromatic sextets and one double bond.

One exception exists. For an achiral $(m, 0)$ CNT with $R(m, 0) = 1$, the rule generates an enatiomeric pair of chiral Clar VB structures, each having a seam 60° offset from the CNT axis. This is unsatisfactory, since VB representations of achiral structures should be achiral. However, in this case only, a representation having an achiral quinoidal seam parallel to the CNT axis (Figure 2) has the same double bond:aromatic sextet ratio as the chiral representations. The unit cell contains $(2m - 2)/3$ aromatic sextets and two double bonds.

To support the application of the Clar VB model to CNTs, calculations (GIAO/B3LYP/6-31G//B3LYP/6-31G-(d)) were performed on a short, H-terminated, fully benzenoid (12, 12) CNT (point group $D_{12}$) containing two

Clar VB unit cells (Figure 5). Calculations of the NICS values provided insight to the degree of aromaticity of the different hexagons, with more negative values suggesting greater aromaticity.[15,26] The NICS values calculated at ±1.00 Å along the normal to the least-squares plane through the centroid of the unique hexagons are as follows (ppm): sextet, average −10.6, out (a) −9.6, in (b) −11.6; empty, average −3.6, out (c) −2.1, in (d) −5.1. These values and bond lengths are consistent with the Clar VB representation.

To determine if structural distortions, such as bond length alternation, are responsible for the trends in aromaticity, NICS values were calculated at three geometries: idealized, PM3, B3LYP/6-31G(d). The resulting values are qualitatively insensitive to geometry (Figure 6). This demonstrates that the magnetic properties of CNTs are topological in origin and not the result of structural parameters such as bond length differences.

Next, it was important to demonstrate that the NICS values are consistent between different levels of theory, not just between geometries of differing quality (Figure 6). This was done to justify a less expensive level of theory, since NICS calculations at high levels of theory were not feasible on the larger chiral systems shown in Figure 7. These calculations were performed on the (12, 12) CNT (Figure 5) at both the B3LYP/6-31G and HF/STO-3G theoretical levels for all three geometries, with the exception of B3LYP/6-31G//idealized, for which the NICS calculations did not converge. The results are qualitatively insensitive to the level of theory, and therefore, the Clar nature of the system is correctly described at inexpensive levels of theory.

The role of electron correlation in the Clar character of CNTs is also revealed by comparing NICS values at the different theoretical levels. The HF/STO-3G calculations, which do not account for electron correlation, provide a description of Clar character similar to that of the B3LYP/6-31G calculations, which do account for electron correlation. This demonstrates that electron correlation is not responsible for Clar behavior in these systems.

To understand the magnetic properties of chiral metallic and semiconductive CNTs, NICS calculations were performed (HF/STO-3G//PM3) on short, $C_2$ symmetric, (12, 9), (12, 8), and (12, 7) CNTs at points ±1.00 Å along the normal to the least-squares plane through the centroid of the unique hexagons. As expected, the NICS values for the fully benzenoid (12, 9) CNT are in complete accordance with the Clar model (Figure 7).

The NICS values of the (12, 8) and (12, 7) CNTs, both of which possess a seam, also correspond with the Clar model. Far from the seam, the agreement is excellent for both full and empty hexagons. Near the seam, the distinction between full and empty hexagons becomes more complex. The empty hexagons lying on the seam have NICS values very near zero, while the empty hexagons distal to the seam and sharing a double bond on an edge have intermediate NICS values.

Of course, a single VB representation from a degenerate set alone does not provide a chemically realistic structure: a closer approximation is the resonance combination of all degenerate structures. Hence, it is important to describe the degree of degeneracy of the Clar VB representation for a given CNT. Finite fully benzenoid CNTs having an integral number of Clar unit cells possess exactly one best Clar VB representation. Infinite fully benzenoid CNTs possess exactly three degenerate representations. For infinite $R(m, n) = 1$ or 2 semiconducting CNTs, the number of resonance structures is given by $m + 2n$ and $2m + n$, respectively.

The analysis of CNTs using the Clar VB model is related to edge effects in large PAHs.[27,28] The parent graphene strips of CNTs with $R(m, n) = 1$ or 2 cannot be fully benzenoid and necessarily possess double bonds. It is interesting that the nature of fully benzenoid CNTs is fundamentally different from that of fully benzenoid planar PAHs. Since they are metallic, fully benzenoid CNTs have small band gaps. Fully benzenoid planar PAHs have large HOMO−LUMO gaps.[15]

Like their degenerate Clar VB contributors, the chemically realistic net resonance hybrids have distinct structures depending on the value of $R(m, n)$. If $R(m, n) = 0$, all C−C bonds are equivalent in that their π-bonding is represented exclusively by aromatic sextets. If $R(m, n) = 1$, then the C−C bonds parallel to the basis vector $\mathbf{p}$ have enhanced double bond character. If $R(m, n) = 2$, then the C−C bonds parallel to the vector $\mathbf{p} - \mathbf{q}$ have enhanced double bond character. Some STM images[4,5,25,29] exhibit patterns consistent with this analysis; we are currently examining this correlation in more depth. These patterns have been explained in the physics literature.[7,25]

The physical basis of Clar's aromatic sextet model remains unclear.[16,17] The correspondence between the reciprocal-space treatment and real-space Clar VB treatment of CNT bonding may provide insight to this problem.

## Conclusions

The utility of the Clar VB model for predicting the properties of PAHs has been extended to include CNTs. The model is a useful representation for bonding in CNTs and generates structural categories which correspond to known electronic classifications. A definition of Clar unit cells naturally follows. The calculated NICS values of short CNTs agree with the Clar VB model. Patterns predicted by the Clar VB model have been observed in STM images.

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**Supporting Information Available:** Cut-out models, formal proofs, geometric definitions and coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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