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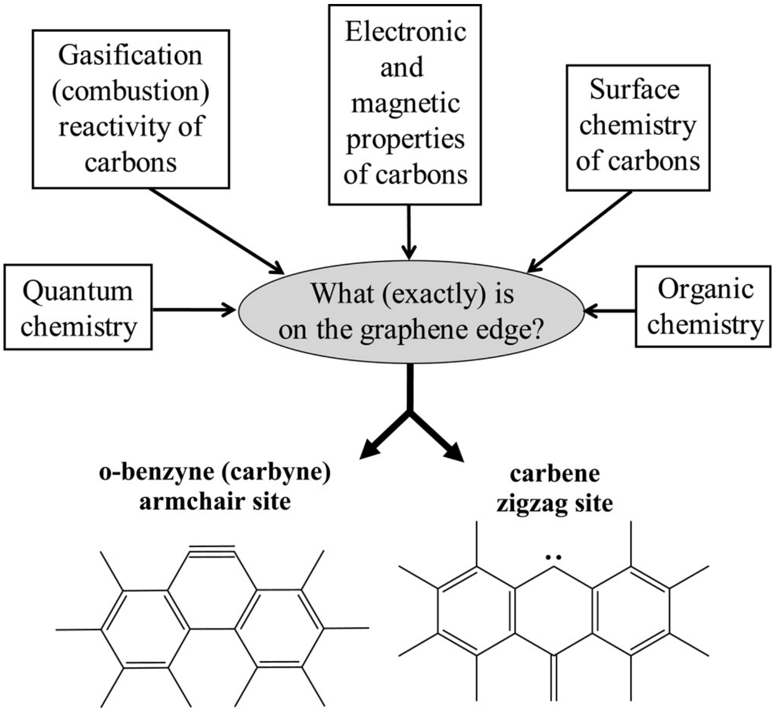

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On the Chemical Nature of Graphene Edges: Origin of Stability and Potential for Magnetism in Carbon Materials

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Abstract: Heretofore disconnected experimental observations are combined with a theoretical study to develop a model of the chemical composition of the edges of graphene sheets in both flat and curved sp^2-hybridized carbon materials. It is proposed that under ambient conditions a significant fraction of the oxygen-free edge sites are neither H-terminated nor unadulterated σ free radicals, as universally assumed. The zigzag sites are carbene-like, with the triplet ground state being most common. The armchair sites are carbyne-like, with the singlet ground state being most common. This proposal is not only consistent with the key electronic properties and surface (re)activity behavior of carbons, but it can also explain the recently documented and heretofore puzzling ferromagnetic properties of some impurity-free carbon materials.

1. Introduction

The chemical properties of sp^2-hybridized carbon materials[1]—including the classical graphitizable and turbostratic carbons as well as the novel nanotubes, and perhaps even the "polymerized" fullerenes—are crucially dependent on the nature and abundance of edge sites. This is especially true for the so-called "nanographites"[2−8] where the concentration of edge (or defect) sites at the periphery of either flat or rolled graphene sheets may be quite high in comparison to the basal plane sites. (A more appropriate term is "nanocarbons",[1] because neither graphite's crystallites nor its porosity is of nanometer size.) Yet the exact nature of the edge sites has been both neglected and misunderstood; indeed, its "chemical" and "physical" interpretations are far from being reconciled.

Here we offer a concrete proposal[9−11] which turns out to be consistent with a remarkable array of heretofore disconnected aspects of the chemistry and physics of carbon, including the controversial magnetic properties of some carbon materials. It also turns out to be quite similar to the largely unrecognized proposal made (primarily based on intuition) by none other than Coulson,[12] almost half a century ago: "[I]f the third valence is not used, the atom may ... pair with a neighboring edge atom to form a partially triple bond ... or revert to a divalent state based on s^2p^2." In the terminology of modern organic chemistry, the free armchair sites are of the *o*-benzyne (or carbyne) type, while the free zigzag sites are of the carbene type.

Figure 1 illustrates why it has been so difficult to arrive at this conclusion. The evidence is necessarily circumstantial, although compelling, as presented and discussed in section 3. The essential clues are dispersed among different scientific "disciplines", and it has been a challenge, thus far, to unify them. As summarized schematically in Figure 2,[13−16] in any given sp^2-hybridized carbon material the individual graphene layers contain some or all of these functionalities, depending on the material's origin, thermal history, and any chemical posttreatment. Here we focus our attention on the *free* edge sites, the

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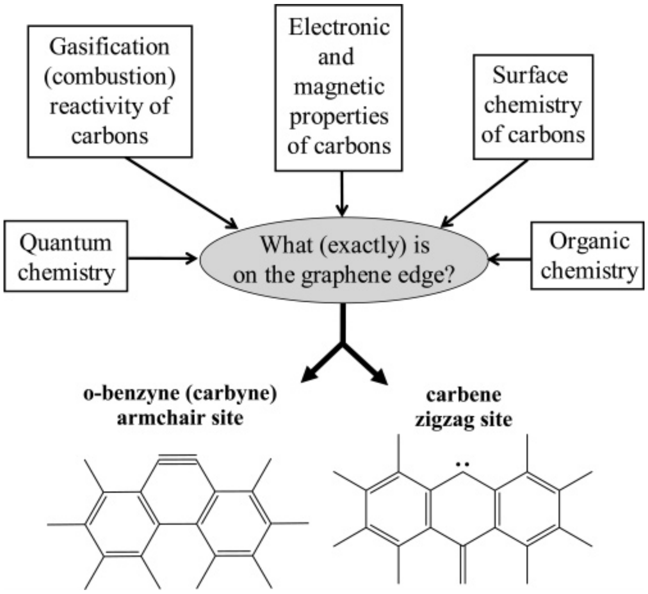

Figure 1. Proposal for the chemical nature of free edge sites in sp^2-hybridized carbons, based on current understanding of chemistry and physics of carbon materials.

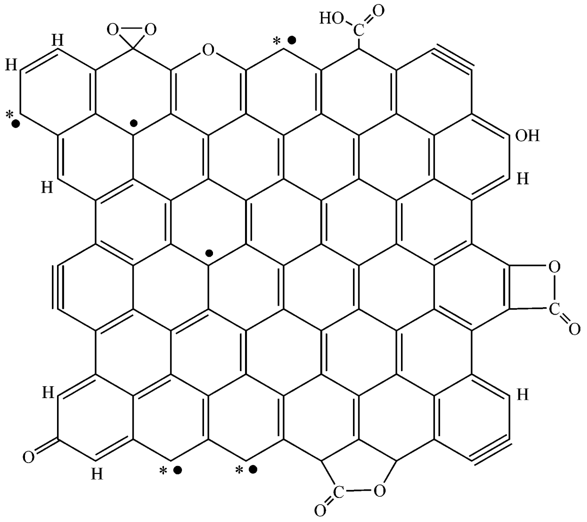

Figure 2. Schematic representation of the main chemical features in a graphene sheet, with its typical surface functionalities, and including the free edge sites. The pairing of σ (*) and π (●) electrons at the zigzag sites and the presence of triple bonds at the armchair sites is indicated. The abundance of aromatic sextets and the degree of π electron delocalization depends on size, shape. and connectivity of the graphenes, as well as on their edge termination.

evidence for their existence, and their chemical identification. The still controversial aspects of some of the surface functional groups shown in Figure 2 (e.g., nondissociatively adsorbed molecular O_2 on a zigzag site) will be discussed elsewhere.

2. Computational Analysis

All the results were obtained using Gaussian98 and Gaussian03 programs.[17] The initial structures were prepared using ChemDraw and Chem3D software (CambridgeSoft, version 7.0), and the initial geometry optimization was carried out using the default MM2 force field parameters in Chem3D. Both for the geometry optimizations and the thermochemical calculations, density functional theory (DFT) at the B3LYP/6-31G(d) level was used throughout as a reasonable compromise that minimizes spin contamination, includes configurational interaction, and accomplishes the calculations at acceptable computational expense.

3. Results and Discussion

Evidence from Organic Chemistry. The chemistry of carbenes[18] and benzynes[19] is a very productive area of reactive intermediates research. For example, the relative stability of *o*-benzyne-like species has been invoked recently[20] in connection with the dehydrogenation of polyaromatic hydrocarbons (PAH), while many years ago arynes had been implicated in the enhanced graphitization achieved upon co-pyrolysis of organics.[21]

The singlet/triplet energy splitting ($\Delta E_{S/T}$) of both benzynes and carbenes has long been used as a litmus test in the development of computational chemistry methods,[22] and most currently used ab initio and DFT methods correctly predict the higher stability of *o*-benzyne, e.g., 37.5 kcal/mol, vs 21.0 and 3.8 for *m*- and *p*-benzyne.[23,24] Carbenes are known to possess two nonbonding electrons and, depending on their molecular structure, may have either a triplet or a singlet electronic ground state.[25] The ground state is known to also be affected by the presence of substituents.[26−30] However, thus far there have been no suggestions that the location of the divalent carbon is *within* the aromatic system, as shown in Figure 2.

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Table 1. Summary of Relevant Theoretical and Experimental Information on Selected PAH Molecules

	energy (hartrees)	HOMO (hartrees)	ionization potential (eV)	LUMO (hartrees)	electron affinity (eV)	HOMO–LUMO gap (eV)	HOMO–LUMO gap^f (eV)
benzene	−232.2486417	−0.24632	9.25^a 9.43^b	0.0037	−1.38^a −0.54^b −1.12^e	6.80	4.452
naphthalene	−385.8927295	−0.21271	8.15^a 8.68^b 8.26^c 8.12^c	−0.03521	−0.28^a 0.65^b 0.15^d −0.19^e	4.83	2.635
azulene	−385.8381597	−0.19039	7.43^a	−0.06714	0.86^a 0.66^d	3.35	1.858
anthracene	−539.5305234	−0.19205	7.47^a 8.20^b 7.55^c	−0.05996	0.46^a 1.19^b 0.42^c 0.56^d 0.53^e	3.59	1.803
phenanthrene	−539.5386567	−0.21058	7.86^a 8.62^b 8.03^c	−0.03652	0.03^a 0.69^b 0.20^c 0.31^d	4.74	2.713
pyrene	−615.7731341	−0.19575	7.41^a 7.72^c	−0.05438	0.38^a 0.39^c 0.59^d	3.85	
coronene	−921.8978708	−0.2003	7.60^a	−0.05197		4.04	
graphite^g			4.39^b		4.39^b		

[a] Selsby et al., *Int. J. Quantum Chem.* **1990**, *37*, 539. [b] Pople, *J. Phys. Chem.* **1957**, *61*, 6; Mulliken, *Phys. Rev.* **1948**, *74*, 736. [c] Briegleb, *Angew. Chem., Int. Ed.* **1964**, *3*, 617. [d] Younkin et al. *Theor. Chim. Acta* **1976**, *41*, 157. [e] Rienstra-Kiracofe et al. *J. Phys Chem A* **2001**, *105*, 524. [f] Hoffmann, *J. Chem. Phys.* **1963**, *39*, 1397. [g] Experimental result.

To gain confidence in the selection and the sensitivity of our model chemistry and model structures, we performed a series of "blank" computational experiments. We first determined the properties of singlet and triplet methylene and silylene[31] using the same procedures outlined in section 2. We obtained the following results for $\Delta E_{S/T}$: $CH_2 = -13.7$ kcal/mol (triplet ground state), $SiH_2 = 20.1$ kcal/mol (singlet ground state). In comparison, Apeloig et al.,[31] while quoting experimental values of −9.0 and 18−21 kcal/mol, respectively, used the CASSCF level of theory with a large Gaussian basis set to obtain values of −10.7 and 18.2 kcal/mol.

We also analyzed a series of PAH molecules. The results are summarized in Table 1. (The HOMO and LUMO values were "reproducible"—e.g., between the various versions of the Gaussian software, or for independent "experiments" using different initial **Z** matrices—to within 10^{-4} hartrees; the total energies were reproducible to within 10^{-6} hartrees.) Phenanthrene is confirmed to be more stable than anthracene[32] and azulene less stable than naphthalene.[33] The calculated HOMO−LUMO gaps correlate reasonably well ($R^2 = 0.97$, including the extrapolation to zero gap for graphite) with those obtained using the extended Hückel molecular orbital (EHMO) theory,[34] which is known to be quite suitable for benzenoid aromatics. Both the HOMO vs ionization potential and the LUMO vs electron affinity correlations are reasonable, given the narrow range of values considered and the evident uncertainties in the experimental determination of electron affinities.

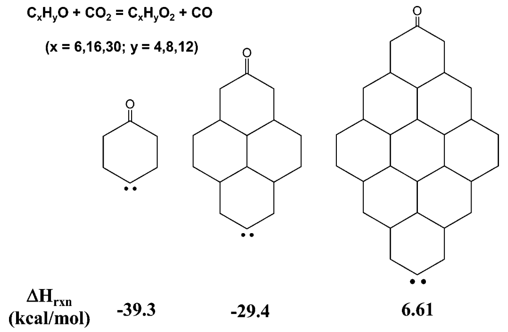

Figure 3. Theoretical analysis of the thermochemistry of dissociative oxygen chemisorption on singlet carbenes of increasing graphene size: B3LYP/6-31G(d)//B3LYP/6-31G(d).

Finally, we confirmed the intuitive expectation that the stability of the carbene and carbyne structures increases with increasing size of the graphene sheet, due to higher resonance energy contributions.[35] This is illustrated in Figure 3: the enthalpy of oxygen chemisorption on the carbene site not only becomes increasingly unfavorable but actually changes sign as the size of the graphene sheet increases from one to nine hexagons. (A more detailed analysis of this reaction is presented elsewhere.[36]) This supports our contention that the structures proposed in Figure 2 can be stable at ambient conditions.

Evidence from Carbon Surface Chemistry. The most common assumptions regarding edge chemistry, heretofore available in the literature, are both unrealistic:

(a) Complete saturation with H or other heteroatoms—thus forming aromatic (Ar) surface functionalities such as Ar−H,[37] Ar−COOH, Ar−OH, or Ar═O groups (see Figure 2)—is not consistent with the abundant experimental evidence revealed

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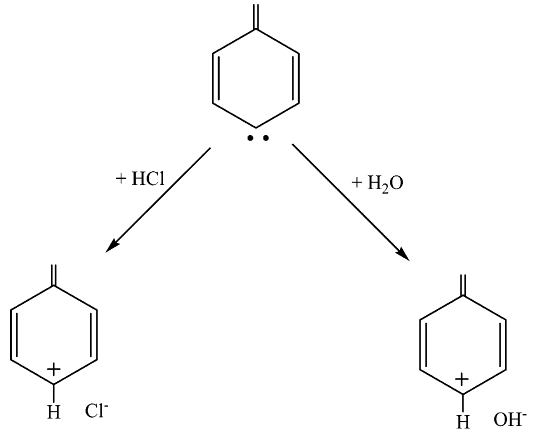
by the chemical analysis of many carbon materials. An incisive analysis, based on comparison between elemental composition and X-ray diffraction (XRD) results, was performed recently by Tomita and co-workers.[38,39] Three different anthracites, whose molar H/C ratios were measured to be 0.08, 0.13, and 0.18, were calculated to have mean graphene sizes of 3.7, 2.8, and 2.1 nm, respectively, whereas XRD analysis—confirmed by transmission electron microscopy—gave consistently lower values: 2.2, 2.0, and 1.7 nm. The authors attributed this discrepancy "to the fact that these techniques are based on different theoretical and mathematical assumptions;" however, an alternative (and straightforward!) explanation, which is consistent with the proposal presented in Figure 2, is the following: not all graphene edge sites are saturated with H, as assumed in their calculation.

(b) At the other extreme, the existence of completely unsaturated edges, as in "unadulterated" σ free radicals, is not consistent with the high reactivity of such sites[40] and the strong affinity of carbon materials for oxygen, with O_2 chemisorption known to occur readily at ambient conditions; at the same time, however, there is evidence[41,42] for the presence of oxygen-free carbon (edge) sites in room-temperature air after exposure of, for example, activated carbons to inert-gas heat treatment. This nascent site deactivation phenomenon is well documented in the carbon reactivity literature, as discussed below.

Yet another heretofore puzzling experimental fact can be explained by invoking carbene sites at zigzag edges. Carbon basicity, with isoelectric points well in excess of pH = 7, is known[14] to persist even in the absence of basic, heteroatom-containing functionalities (e.g., pyrones or chromenes). One candidate for basic oxygen-free sites that readily adsorb acids is the electron donor/acceptor (EDA) complex formed by the delocalized π electron system with (e.g., hydronium) cations in solution;[43,44] its relative contribution has yet to be demonstrated for carbon materials.[15,45] Another, and a very straightforward one at that, is the carbene site,[46] as illustrated below.



Evidence from Electronic Properties. Our carbene/carbyne proposal is consistent with the pioneering, albeit heretofore largely ignored, studies and intuitive argument of Mrozowski: "The peripheral carbon valences do not seem to be present where they are expected; consequently, the peripheral carbon atoms have changed their state into a different hybridized state which does not show the activity of an unsaturated valence".[47] (A notable exception is the study by Shibayama et al.,[3] in which the authors do discuss this explanation, but they rule it out on the basis of the arguably false premise that "almost all σ-dangling bonds are terminated by foreign species".) Throughout the 1950s and 1960s, the then emerging technique of electron spin resonance (ESR) held promise to set such arguments on at least a semiquantitative footing, but for reasons briefly analyzed below, it failed to do so. In fact, the deluge of ESR studies of carbon materials in that period arguably produced more confusion than clarification; it culminated in the seminal, though undeservedly forgotten, discussion in print between Mrozowski and Ingram,[48] whose "diametrically opposite" arguments have not been reconciled to this date. While Mrozowski believed "that the [paramagnetic] resonance observed is due to localized σ electrons of the broken carbon bonds formed in the process of heat-treatment", while "some electrons from the π-states jump into these σ-orbitals and pair off with the original σ electrons, thus forming lone electronic pairs on the periphery of the molecules and leaving conducting holes in the π-band behind," Ingram "[could] not see how the unpaired electrons of the carbon can remain in purely σ-orbitals as these would have no means of stabilization and be highly reactive." Ingram did offer a "compromise": "Would it not be more correct to consider the actual position as involving configurational interaction between the π- and σ-orbitals, and speak of the free-radical electrons as being initially formed by breakage of a σ-bond, and then stabilized by admixture of a certain amount of π-bond character? As the ring clusters grow in size and approach the more defined graphite structure, one might expect the radical electrons to have their σ-character paired off, leaving holes in the π-band as suggested." Indeed, the carbene and carbyne structures proposed here are thought to offer just such $\sigma-\pi$ configurational interaction.

As discussed in the next section, Walker (as well as other investigators after him) had used the same concept—he called it the "in-plane σ pair" but never explicitly mentioned it in print[49]—to explain important carbon reactivity phenomena. Furthermore, in a pioneering and largely neglected study[50,51]

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Walker and co-workers documented the recently rediscovered[52−56] and indeed fascinating[57] changes in the thermoelectric power (TEP) of carbons, both curved and flat. On the basis of our proposal about graphene edge chemistry, this phenomenon—together with the highly publicized[58] sensitivity of carbon nanotubes to atmospheric oxygen[59]—has a straightforward explanation. We do support a "simple interpretation of the rather large positive high-temperature TEP [that] indicates hole-like carriers".[52] However, this result is *not* surprising, even though "metallic tubes ... are predicted to have electron−hole symmetry ... and thus a TEP close to zero".[52] As clearly shown by Tietjen,[50,51] upon oxygen accumulation on the graphene edge sites, as well as π electron localization at carbene sites, the TEP becomes less and less negative and eventually positive. Chemisorbed oxygen—e.g., in the form of electron-withdrawing Ar−COOH groups or π-electron-localizing quinone groups which facilitate carbene formation (see Figure 3)—is responsible for the increasing creation of excess holes within the graphene sheets (conduction band). It is interesting to note, in agreement with this interpretation, that Inokuchi[60] reported a consistent and sometimes dramatic decrease in electrical resistivity between a series of PAH molecules (e.g., violanthrene) and their quinone counterparts (e.g., violanthrone).

It remains to be seen whether our carbene/carbyne proposal, with its profound electronic structure implications, can also account for the reactivity differences between armchair and zigzag sites.[61] Since the pioneering studies of Thomas,[62] these differences have been known and occasionally discussed, but both the facts and the explanations have been elusive. For example, Kawai et al.[63] recently commented that the "zigzag edge is less stable and more reactive" but offered no additional evidence for this seemingly obvious conclusion. Some of the relevant issues are discussed in the next two sections, and they are related to the well-documented differences in broken resonance.[64−69] In the present study, we used computational chemistry to strengthen our argument for the existence of "unconventional radical sites"[64] at graphene edges (see below). These have indeed been the "subject of occasional speculation in the older carbon literature".[64] However, contrary to the argument by Stein in his pioneering HMO studies—that they involve "stabilization by *delocalization*"[64] (emphasis added)—our proposal implies that such stabilization is achieved by virtue of *localization* of itinerant π electrons through $\sigma-\pi$ coupling and formation of carbenes ("in-plane σ pairs") and carbynes. It is of course not surprising that Stein had not "found [any] basis for [the existence of such] sites":[64] HMO theory does not consider σ electrons at all.

Evidence from Carbon Reactivity. Our carbene/carbyne proposal explains the well documented concept of nascent site deactivation, as follows. After the thermal decomposition of the carbon precursor or heat treatment ("annealing" or surface cleaning, typically in inert atmosphere), the free radicals formed as a consequence of pyrolytic bond cleavage (e.g., evolution of H_2O, CO_2, CO, CH_4, etc.) are stabilized in one of two ways: (a) formation of a graphene sheet with free edges terminated as shown in Figures 1 and 2, (b) saturation of residual reactive sites upon exposure to ambient conditions, e.g., by O_2 chemisorption. (The three-dimensional connectivity of the graphene sheets will be discussed in an upcoming publication.) The extent to which this deactivation process occurs is responsible for important phenomena in operations as varied as "reactive" milling of graphite,[70] O_2-enhanced NO reduction by carbon,[71] or coal hydrogasification. This last phenomenon is particularly dramatic:[72] if coal pyrolysis and char gasification are temporally and/or spatially separated, the subsequent char gasification is a very sluggish reaction, and under typical conditions the extent of carbon conversion is quite modest (say, <50%, and essentially all of it due to pyrolysis alone); if they are not separated and pyrolysis is carried out in the reactive H_2 atmosphere, the char is much more reactive—its edge sites are not given the opportunity to form carbenes or carbynes—so under comparable conditions the extent of carbon conversion is much higher, and even close to 100% at sufficiently high H_2 pressure.

Additional implications of our proposal for the reactivity behavior of carbon materials are yet to be reconciled, and they are the subject of our current research. Thus, for example, triplet carbenes have been reported[73] to "react rapidly with oxygen," while "the singlet carbenes react slowly, if at all." On the other hand, Tomioka[30] has argued that the triplet state "is a less reactive and selective reagent." Mendez et al.[74] reported a "good

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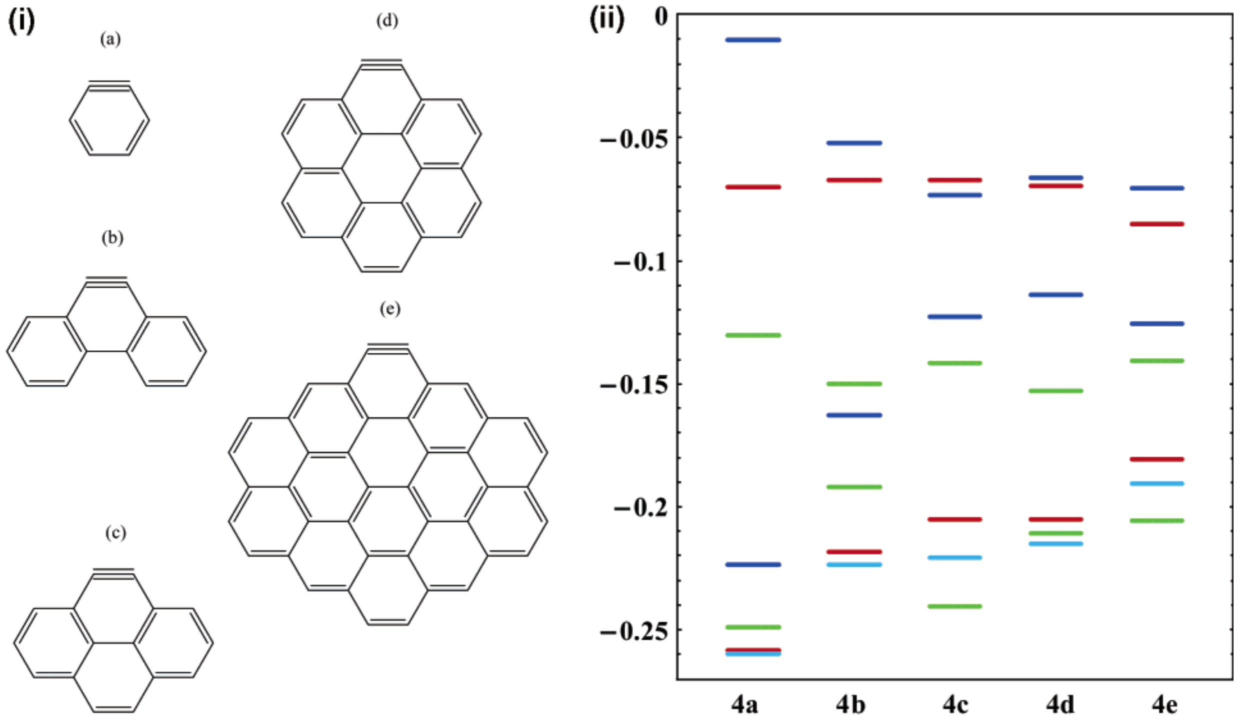

Figure 4. Representative carbyne structures in a flat graphene sheet of carbon materials: (i) geometries; (ii) HOMO−LUMO gaps: red, $M = 1$; dark blue, $M = 3$ (α); light blue, HOMO-1 (α or β); green, $M = 3$ (β). Both here and in Figures 5−7 the units of the ordinate are hartrees (1 hartree = 27.2116 eV).

correlation ... between the singlet−triplet energy gap and the condensed softness for electrophilic attack at the triplet carbene carbon, which reflects the level of carbene stability upon electron donation." Kawai et al.[63] have also found theoretical evidence for "[s]trong edge reconstruction of H-free armchair ribbons forming triple bonds." Intriguingly, however, they concluded that "H-free zigzag ribbons ... have both the edge state and the dangling bond state."

Evidence from Quantum Chemistry. Figure 4 shows representative carbyne-containing structures, along with their calculated HOMO and LUMO energy levels. Figures 5−7 show representative carbene-containing structures and their HOMO−LUMO gaps. These structures were selected to explore the effects of graphene size and shape and the presence of heteroatoms on the stability of the edges. Table 2 summarizes the results for the total energies and the singlet/triplet transitions. The geometries of the optimized structures, as well as their electron density distributions, are all reasonable, and they will be discussed separately. The likelihood of formation of these structures depends on the size and condensation patterns of the graphenes. It is interesting to note that geometry optimization in the absence of all-H termination was greatly facilitated by introduction of semiquinone oxygen (see Figure 5)—in agreement with the stability of 4-oxocyclohexa-2,5-dienylidene[75]—an event that is likely to occur during ambient exposure to air of a freshly prepared carbon.

The results for the singlet/triplet transitions are of primary interest. Abundant literature is available on this issue: $\Delta E_{\mathrm{S/T}}$ calculation has been used as a test of theory level adequacy[76−79] and also for reliable predictions.[73,79] Of greatest significance in the present study is the fact that the carbene structures all have a triplet ground state (with the exception of those containing basal-plane nitrogen), whereas the carbyne structures all have a singlet ground state. This is in agreement with the results of Aloshyna et al.,[25] who predicted that all their postulated carbenes have triplet ground states. The obvious implications for the magnetic properties of such structures[80,81] are discussed below. The predicted stability of the carbyne ground states is seen to be greater than that of the carbene ground states. The true zigzag sites, those that have basal-plane neighbors (structures 5e,f) are seen to have a smaller gap than the sites whose neighbors are edge sites themselves. It will be interesting to confirm the apparent absence of a monotonic trend with increasing graphene size; if anything, there appears to exist a maximum in the value of the singlet−triplet gap at intermediate sizes (series 4b−e).

Incorporation of heteroatoms into the carbon structure is a well-documented strategy to tailor electronic, electrochemical, and surface reactivity properties. The results in Figure 7 suggest that boron substitution produces a reduction of the S/T gap and that the triplet is the ground state. Pyridinic nitrogen is predicted to have a similar effect, whereas the presence of substitutional

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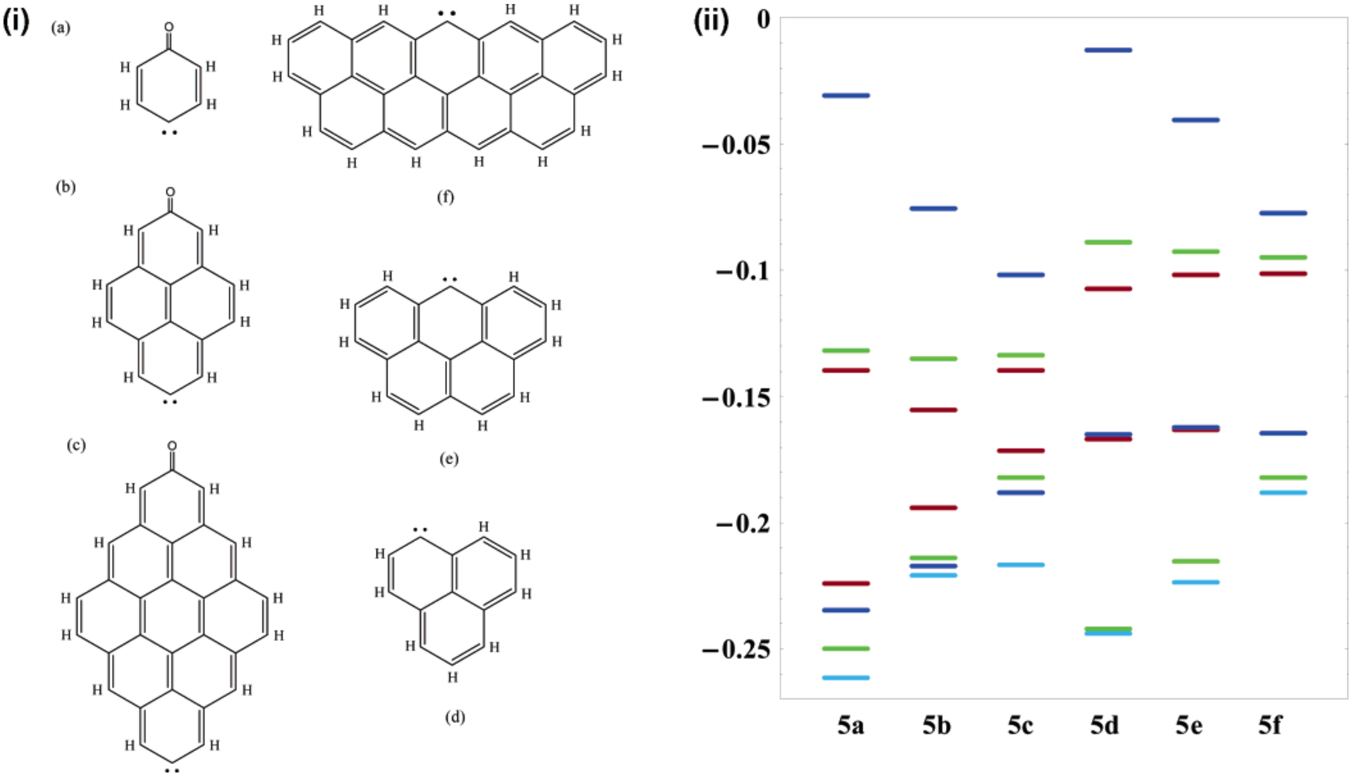

Figure 5. Representative carbene structures in a flat graphene sheet of carbon materials: (i) geometries; (ii) HOMO−LUMO gaps: red, M = 1; dark blue, M = 3 (α); light blue, HOMO-1 (α or *β*); green, M = 3 (*β*). Note that the 5e and 5f HOMO values for M = 1 and M = 3 (α) are almost coincident.

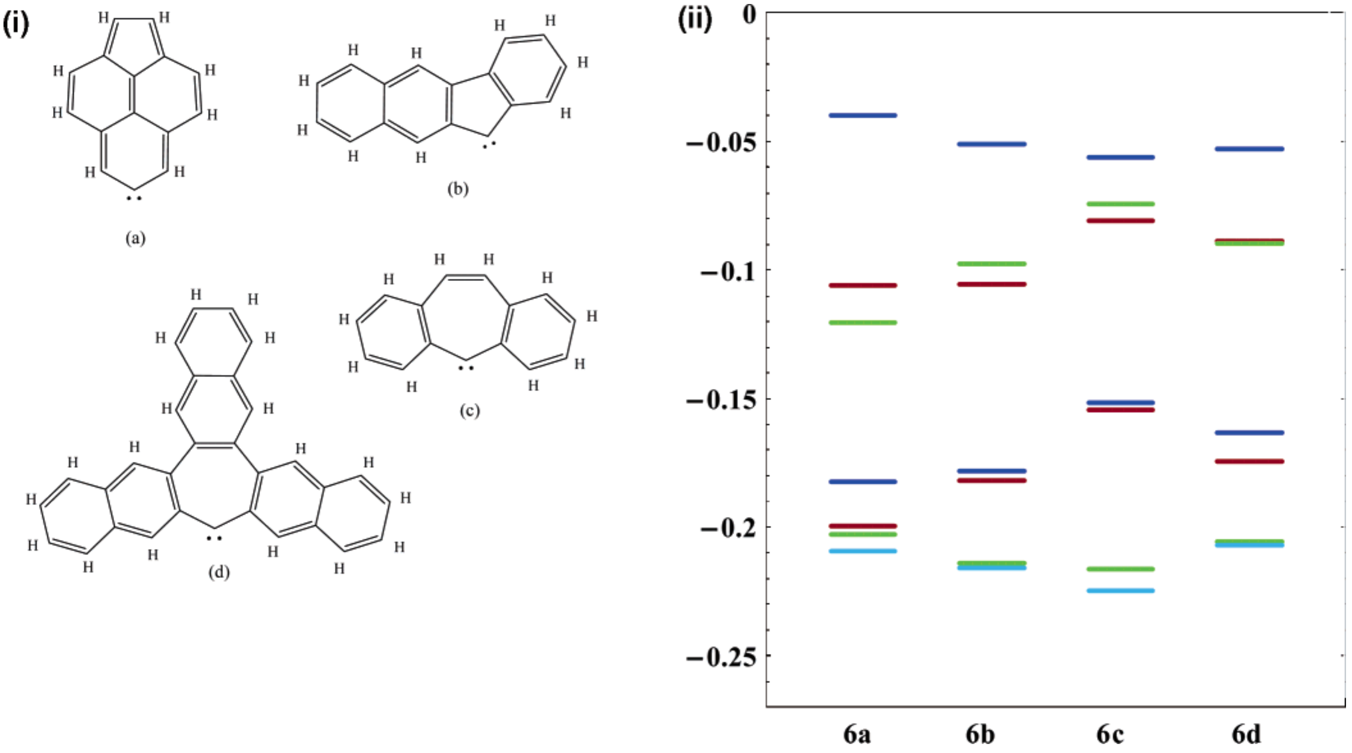

Figure 6. Representative carbene structures in a graphene sheet incorporating curvature: (i) geometries; (ii) HOMO−LUMO gaps: red, M = 1; dark blue, M = 3 (α); light blue, HOMO-1 (α or *β*); green, M = 3 (*β*).

(or "quaternary") nitrogen—which is known not to occur in graphitic carbons but is presumably possible in more disordered materials—results in a singlet ground state.

The effect of the presence of pentagons or heptagons, which introduces curvature, is seen (Figure 6) to be particularly effective in producing narrow-gap, triplet-ground-state structures. In their absence, the zigzag single-wall carbon nanotube (SWCNT) shown in Figure 8a, does have a triplet ground state but is predicted to have a wide S/T gap. The armchair SWCNT shown in Figure 8b also has a very wide gap but is predicted to have a singlet ground state, in agreement with the results for the flat sp^2 structures.

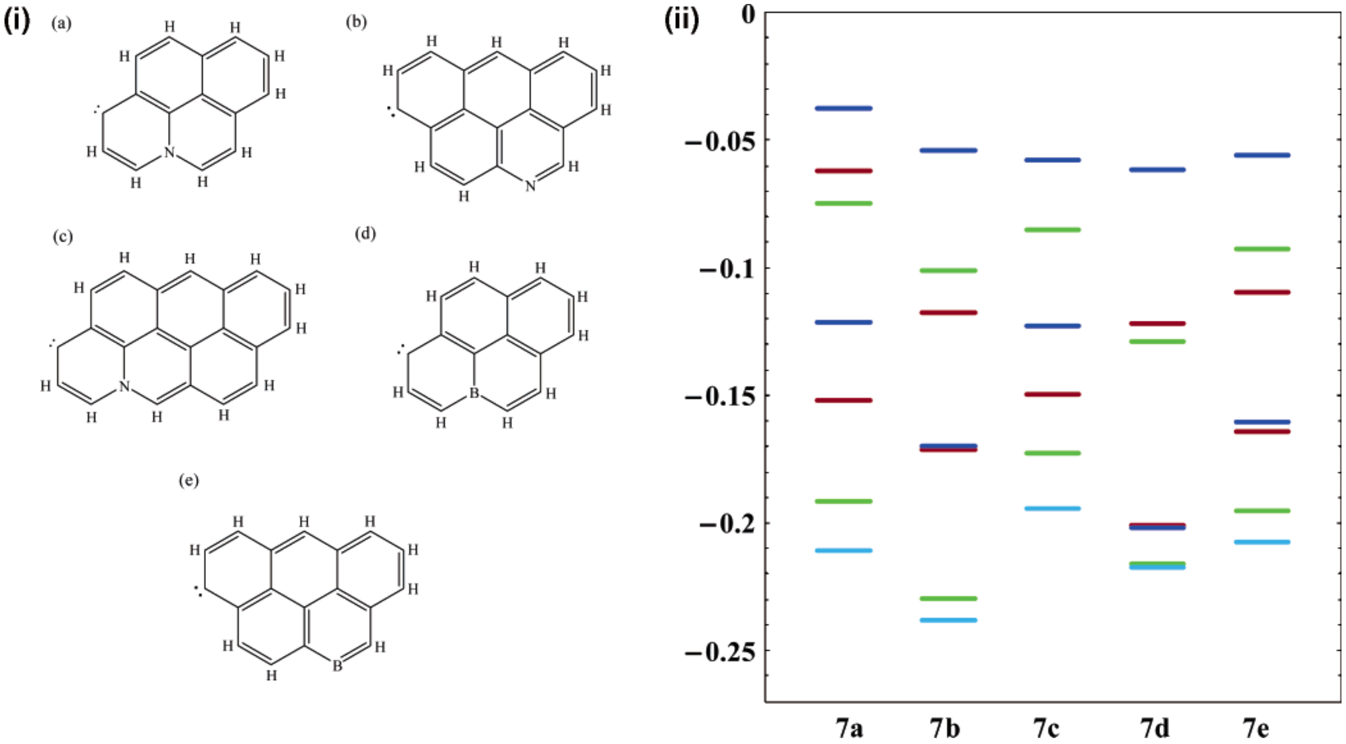

Figure 7. Representative carbene structures in a graphene sheet incorporating basal-plane boron or nitrogen: (i) geometries; (ii) HOMO−LUMO gaps: red, $M = 1$; dark blue, $M = 3$ (α); light blue, HOMO-1 (α or β); green, $M = 3$ (β). Note that the 7c LUMO values for $M = 1$ and $M = 3$ (β) are almost coincident.

Table 2. Singlet and Triplet Energies of Model Graphene Structures

structure	energy, hartrees		$\Delta E_{S/T}$[b] (kcal/mol)
	$M = 3$[a]	$M = 1$	
4a	−230.8629979	−230.9099478	29.5
4b	−538.1329680	−538.2048047	45.1
4c	−614.3568331	−614.4400081	52.2
4d	−920.4706815	−920.5627761	57.8
4e	−1608.9703514	−1609.0257799	34.8
5a	−306.1426265	−306.1155223	−17.0
5b	−689.6642188	−689.6209323	−27.2
5c	−1225.6416476	−1225.6109670	−19.3
5d	−500.1246276	−500.1050780	−12.3
5e	−730.0085488	−729.9978606	−6.7
5f	−1189.7597561	−1189.7495996	−6.4
6a	−576.3192659	−576.3073662	−7.5
6b	−653.7439559	−653.7372791	−4.2
6c	−577.5175631	−577.5093381	−5.2
6d	−1192.0868659	−1192.0813099	−3.5
7a	−631.6739937	−631.6983377	15.3
7b	−746.0451536	−746.0225463	−14.2
7c	−861.5454247	−861.5659361	12.9
7d	−601.8018451	−601.7803051	−13.5
7e	−716.0837710	−716.0640041	−12.4
8a	−2056.0763682	−2055.7722934	−190.8
8b	−1840.7821083	−1840.8973354	72.3

[a] Except for structures 8a and 8b where $M = 19$ and $M = 5$, respectively.
[b] Note: Negative values of $\Delta E_{S/T}$ indicate triplet ground state.

It should be mentioned that the zero-point correction[82] was not applied in the calculation of the S/T gaps. The emphasis here is on relative rather than absolute $\Delta E_{S/T}$ values, although the latter are considered to be in reasonable agreement with literature values; thus, for example, Wenthold et al.[24] obtained experimentally 37.5 kcal/mol for *o*-benzyne, vs 29.5 kcal/mol shown in Table 2.

The HOMO−LUMO gap is also of interest because it is known to be an index of both kinetic stability and electrical conductivity. The values shown are in the range 0.9−5.8 eV, of the same order of magnitude as, or less than, those obtained for the corresponding PAH molecules (see Table 1). In most cases, the HOMO−LUMO gap is smaller for the singlet state than for the triplet state. A notable exception are the armchair-edge carbyne structures shown in Figure 4, as well as the armchair-edge SWCNT (Figure 8b); here the highest singly occupied molecular orbital (SOMO) levels for the triplet states (marked in dark blue) are seen to be higher than the HOMO levels for the singlets (marked in red). The same trend is observed in Figure 7; triplet is predicted to be the ground state when its highest SOMO level lies very close to singlet's HOMO. The latter trend is also seen in Figure 5, with several SOMOs being even lower than the corresponding HOMOs. In the presence of pentagons or heptagons, the trends are not as straightforward (Figure 6); in structures 6a and 6d, even though triplet is the predicted ground state, the highest SOMO lies above the HOMO.

In a recent study[31] of triplet vs singlet states of CH_2 and SiH_2, an argument was presented that ground-state prediction involves more than an analysis of the HOMO−LUMO gap. Here we have confirmed the fact[83] that the triplet CH_2 has a narrower gap between the two highest SOMOs (23.1 kcal/mol) than the triplet SiH_2 (42.1 kcal/mol), and the latter thus has a singlet ground state. The same argument holds in our case (e.g., singlets

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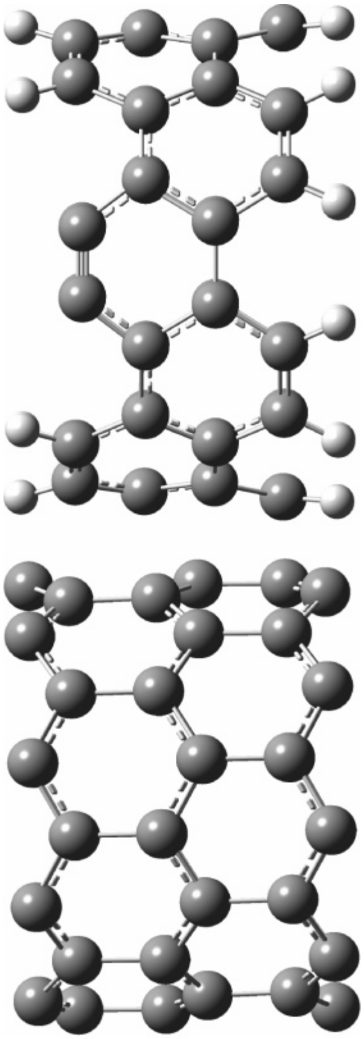

Figure 8. Optimized geometries of open, edge-stabilized single-wall carbon nanotubes (see Table 2): (a) zigzag, C_{54}; (b) armchair, $C_{48}H_{20}$.

4c, 4d, and 4e have a very high such SOMO gap, while triplets 5a−c, 5f, 6a, 6b, 6d, 7d, and 7e have a much lower one), but there are some obvious exceptions (e.g., singlet 4a and triplet 5d). More detailed studies will be needed to evaluate the importance of factors other than the frontier electrons[31] and further rationalize the predictions summarized in Table 2.

Implications for Magnetic Properties. The intriguing paramagnetic properties of carbon materials have been scrutinized since the early 1950s, but as mentioned previously, these prolific and largely unmined studies have not produced conclusive results[84] because of inadequate understanding of carbon surface chemistry at the time and also because it has been (and still is!) quite a challenge to distinguish the resonance effects of itinerant π electrons, of stable nonalternant π or σ radicals,[40] and particularly so, of the ubiquitous physisorbed or chemisorbed molecules of the paramagnetic oxygen. More recent studies are no less confusing and, above all, have not shown consistency with what is now known about carbon surface chemistry. Thus, for example, Tanaka et al.[85] argued that “the spins giving the broad peak are ... apt to correlate in a kind of ferromagnetic fashion”, whereas the “rather mobile π electrons give the narrow peak”, and they tentatively concluded that “the spins responsible for the superparamagnetic or, even more, occasional ferromagnetic behavior and for the broad ESR peak are of sp^3-type (that is, σ-type) radicals in the product structure originating from the dangling bonds reflecting the partially remaining adamantane structure” (after thermal CVD at 1000 °C); they also noted that “pyrolytic carbon prepared from adamantane shows completely different magnetic features compared with other pyrolytic products prepared at 200−220 °C that have been revealed to have a triplet state ... on the average.”

The exciting ferromagnetic properties of some carbon materials—now well documented and with little doubt that they are intrinsic[86−89] and not due to the presence of ferromagnetic impurities—have been even more mysterious. There is now much interest in reproducible preparation of magnetic carbons (see, for example, the November 2004 issue of *Physics World*[90]), and our carbene/carbyne proposal is thought to provide a clearer target, not only for flat sp^2 carbons but for the curved ones as well. Indeed, structural analyses of “polymerized” C_{60} revealed “very broad Bragg peaks” indicative of “highly disordered graphite-like phase”.[87] This is consistent with the presence of carbene structures at the (mostly flat) edges. It also gives a much more concrete form to, chemically speaking, rather vague arguments that do appear to point in the same direction. Thus, for example, Makarova concluded that “this effect is caused by induced disorder with a partial change of hybridization from the sp^2 type to the sp^3 type”.[8] Han et al.[86] also argued that the theoretical results of Ovchinnikov and Shamovsky[91] “indicate that a mixture of sp^2−sp^3 carbon atoms may lead to a ferromagnetic state with a magnetization larger than pure Fe.” They have also reported that “not the disorder alone but the proton (hydrogen) inclusion is substantial to induce ferromagnetism by bombardment.” Chan et al.[87] have also noted the important role of hydrogen. Obviously, from the representative structures shown in Figures 4−6, hydrogen availability during pyrolysis and its ultimate content in the carbon is expected to influence the ratio of carbene-to-carbyne structures. If carbenes are dominant, ferromagnetic carbons will be formed.

Such ferromagnetism of the zigzag sites also makes more understandable the following observations and (again chemically ambiguous) arguments of Makarova:[8] “One of the specific features of the graphite electronic structure with zigzag edges is the presence of flat energy bands near the Fermi level. A consideration of the effects of electron−electron interactions in the context of the Hubbard model shows that there can be a

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spontaneous magnetic ordering in nanographite. In the case of the zigzag-type strips, a ferrimagnetic structure is possible; the appearance of magnetic ordering is controlled by the magnitude of the surface deformation caused by electron−phonon interaction."

The possibility that nonfullerene (i.e., edge-site-containing) structures may be responsible for ferromagnetic behavior has also been mentioned by Narozhnyi et al.[92] because they noted (but did not show) XRD evidence for the presence of "amorphous carbon" in their ("polymerized") fullerenes obtained by treatment at high pressure and high temperature, whereas rhombohedral fullerenes treated at 700 °C and below exhibited no ferromagnetism.

A related "physical" interpretation of magnetism in carbons is the Fujita/Klein argument:[81,93] spin polarization leading to a "sharp peak in the density of states at the Fermi level"[94] is a consequence of electron localization at zigzag edges, and this induces "lattice distortion due to the electron−phonon interaction and/or magnetic polarization due to the electron/electron interaction".[93] This electron localization phenomenon had earlier been documented by Stein and Brown:[64,95] "[f]or the armchair-edge structure, electron densities are rather evenly distributed over the structure, while for the zigzag-edge series, densities are concentrated at the edges".[64] But its consequences for the "chemical" structure and the behavior of carbon materials had not been clarified.

More than a decade ago, Araki and Yoshino[96] postulated that chars (nongraphitizable carbons) derived from pyrolysis of triphenoxytriazine exhibit ferromagnetic behavior because of "parallel spins of the nitrogen and/or oxygen radicals in those structures." Here we invoke essentially the same argument, but the parallel spins are postulated to be on the carbon rather than on the heteroatoms (which are not as abundant in common carbonaceous solids), and they are postulated to reside on stabilized carbon zigzag edges rather than on the periphery of highly reactive molecules such as 2,6,10-tri-*tert*-butyltriangulene for which a triplet ground state is also expected.[97] We argue therefore that the representative structures shown in Figures 4−7 should be added to the list of candidates for molecular magnets offered by Blundell and Pratt[98] (see their Figure 1). Furthermore, the "holy grail" of molecular magnets, which may make quantum computers[99] a reality, is illustrated in Figure 8a. Such a short, open, carbene-stabilized zigzag single-wall nanotube is predicted to have a saturation magnetization of several hundred emu/g, comparable to 200 for α-Fe. (It would be interesting to see whether the (nano)graphene ribbons[66,67,94,100] could achieve even higher magnetization values.) Its calculated properties are summarized in Table 2 and are compared with the analogous armchair SWCNT (Figure 8b). These results are consistent with those shown previously for the flat graphenes.

4. Conclusions

The chemical nature of the edges of a graphene layer in sp^2-hybridized carbon materials, which has been largely ignored since the pioneering and incisive analysis by Coulson, appears remarkably consistent with carbene and carbyne structures at H-free zigzag and armchair sites. One consequence of this proposal is that the often invoked[86,89,101] "mixture of sp^2- and sp^3-hybridized states" as the origin of ferromagnetism[89] simply reflects the formation of carbene structures at zigzag sites, as intuitively suggested by Coulson half a century ago. We consider it unlikely, given the well-documented affinity of carbon materials for oxygen, that "the existence of dehydrogenated [graphitic] ribbons [will be] verified experimentally"[63] and that the "dangling bonds" survive exposure to room-temperature air intact. Zigzag-terminated carbons are thus proposed to be the ultimate (and the elusive) polycarbenes.[102] It will be interesting to confirm that this "holy grail of modern [synthetic] polymer research"[103] has been within our grasp, in nature.

These chemical features of carbon materials, if controlled to achieve optimized degrees of $\sigma-\pi$ coupling, offer promising solutions for molecular electronics and organic ferromagnets. To paraphrase Makarova,[8] our conclusion is that high-temperature ferromagnetism in carbon should indeed be expected, because the triplet state is energetically more favorable at the carbene edges, and these are arguably dominant in some carbons. As a corollary, preparation of zigzag-only nanotubes offers exciting opportunities for magnetic carbon materials (e.g., quantum computing). Indeed, there is no need "to introduce triplet carbene units on a polynuclear aromatic system":[104] carbon materials themselves are certainly "stable enough to be assembled into crystalline structures".[98]

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Supporting Information Available: Tables of coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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