

Planar Tetracoordinate Carbon Strips in Edge Decorated Graphene Nanoribbon

Menghao Wu, Yong Pei, and Xiao Cheng Zeng*

Department of Chemistry, Department of Physics and Astronomy, University of Nebraska—Lincoln, Lincoln, Nebraska, 68588

Received January 9, 2010; E-mail: xczen@phase2.unl.edu

The *spatial tetrahedral* coordination of saturated carbon has been a textbook concept since it was revealed independently by van't Hoff and Le Bel more than a century ago.¹ In 1970, Hoffmann and co-workers raised an intriguing question about the stability of the *planar tetracoordinate* carbon (ptC).² A few years later, the first theoretical prediction and experimental isolation of ptC systems were reported.³ Since then, exploration of unusual ptC systems has attracted considerable attention.^{4,5} Numerous ptC-containing molecules have been predicted via molecular orbital (MO) calculations.⁴ Some of these predicted ptC-containing molecules have been detected and even characterized in the laboratory.^{4k,5} Despite the fact that many ptC-containing molecules have been detected, the existence of ptC-containing units in condensed matter has not been observed. Only a few ptC-containing extended systems have been theoretically predicted.⁶ These extended systems are typically based on the arrangement of molecular ptC motifs such as CAI_4^{2-} , C_5^{2-} , or CB_4 .⁶ In this communication, we present *ab initio* calculation evidence of a *hitherto* unreported one-dimensional (1-D) ptC system, an infinite ptC strip embedded in an edge-decorated zigzag graphene nanoribbon (ZGNR).^{7a} The ZGNR can be carved out from a graphene, a single atomic layer of graphite.^{7b} The two edges of ZGNRs can be modified via chemical decoration. It was recently predicted that edge-decorated ZGNRs by chemical functional groups $-\text{NH}_2$, $-\text{NO}_2$, $-\text{F}$, or $-\text{OH}$ may become half metallic.⁸

We first show that a 1-D ZGNR can be a unique host system for the realization of an extended ptC structure due to its highly delocalized in-plane π -electrons and intrinsic rigid structure. In principle, the stabilization of a ptC unit requires satisfaction of both geometrical and electronic conditions, in addition to being the most energetically stable structure against any spatial conformation or atomic exchange between the central carbon and any peripheral noncarbon atom.^{4a} Because the structure of ZGNRs is mechanically robust, the atomic exchange between an edge carbon atom and a peripheral metal atom would likely result in higher-energy structures. Hence, only the geometrical and electronic requirements should be met to realize the ptC-containing ZGNR. In most cases, edge decoration of a ZGNR by functional groups (FGs) such as $-\text{H}$, $-\text{OH}$ results in binding of each edge carbon atom with only one FG, as represented by FG-ZGNR-FG . The edge carbon atoms have sp^2 hybridization. To achieve a ptC strip at an edge of a ZGNR, each anchoring ligand (L) must bind with two edge carbon atoms, as denoted by L-ZGNR-L .

We have examined a variety of ligands, including the organic groups such as $-\text{CH}$, $-\text{BH}$, $-\text{NH}$, and $-\text{B}$; as well metal elements including main-group metal atoms such as Li, Be, Na, Al; transition metal atoms such as Sc, Ti, Cr, Fe, Ni; and noble metals Cu, Ag, Au for edge decoration. For each system, we performed geometrical optimization without any symmetry constraints using a spin-polarized density functional theory (DFT) method. Specifically, the generalized gradient corrected (GGA) Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional and the double numerical plus polarization basis set (DNP), implemented in the Dmol³

package,⁹ were used. In addition, we examined several finite molecular model systems, for which we used DFT functionals including hybrid (B3LYP), meta-GGA (TPSS), and PBE, along with the 6-311++(2df,2dp) basis set implemented in the Gaussian 03 package.¹⁰ For both infinite 1-D and finite systems, the frequency calculations were done with the optimized structures.

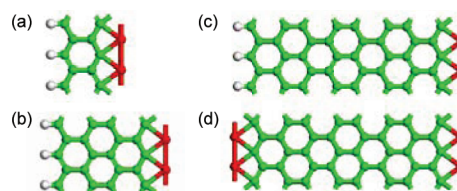


Figure 1. Optimized geometric structures of n -ZGNRs (only a unit cell is shown) with one (or two) edge(s) decorated by Cu. The width n is (a) 2, (b) 4, and (c) and (d) 8, respectively. Green, red, and white balls denote carbon, copper, and hydrogen atoms, respectively. The ZGNR with one edge decorated by Cu and another by H is denoted as H-ZGNR-Cu (a–c) and with both edges decorated by Cu is denoted as Cu-ZGNR-Cu in (d).

For the organic group ($-\text{CH}$, $-\text{BH}$, $-\text{NH}$, or $-\text{B}$) modified ZGNRs, the most stable structures all have their edge carbon atoms in sp^2 hybridization. In the case of metal atom decorated ZGNRs, the metal atoms form a stable 1-D metal wire at each edge of the ZGNRs. However, the geometric optimization and frequency calculations suggest that none forms perfectly planar L-ZGNR-L like systems except the Cu-decorated ZGNR. The most stable structure of Al- and Ni-decorated ZGNRs favors the L-ZGNR-L like structure with each metal atom binding to a single carbon atom. For other metal decorations (cf. Figure S1 in the Supporting Information (SI)), all metal atoms form irregular out-of-plane structures.

Hereafter, we focus on edge decorated ZGNRs by Cu, which give rise to one or two stable ptC strips denoted as either $\text{H-}n\text{-ZGNR-Cu}$ or $\text{Cu-}n\text{-ZGNR-Cu}$ (see Figure 1), where n is the width of the ZGNR. These ptC-containing planar structures are highly stable, regardless of the width of the ZGNRs. An independent geometric optimization and frequency calculation for the Cu-8-ZGNR-Cu system, using the Vienna *ab initio* simulation package (VASP)¹¹ with a 500 eV plane-wave energy cutoff and a $10 \times 1 \times 1$ k -point mesh, was also carried out. No imaginary frequencies were found, in agreement with the Dmol³ results. The stability of Cu-ZGNR-Cu systems is also reflected by relatively large binding energy (E_b) of a Cu atom to the edge of the ZGNRs. The computed E_b is 3.66 eV per Cu atom, notably greater than the cohesive energy (3.36 eV/atom) of the bulk Cu solid. Although such a binding energy is still much smaller than that of nonmetal functional groups such as $-\text{H}$ (5.09 eV) and $-\text{OH}$ (5.26 eV), the E_b can increase up to 4.22 eV/atom when two H-ZGNR-Cu systems fuse together at the edges as shown in Figure S2. Moreover, our calculations of binding energies per Cu atom with Cu atoms located on various positions indicate the binding of Cu atoms at the edge leads to the most stable structure (cf. Figure S3). We also examined the thermal stability of the ptC strip at the

edge of the ZGNR using the Born–Oppenheimer quantum molecular dynamics (MD) simulation (see the method details in the SI). Snapshot images of the equilibrium structure at the end of each MD simulation on the H-4-ZGNR>Cu system at 1200 and 1700 K, respectively (each for 5 ps), are shown in Figure S4, which suggest that the ptC structure can still be intact for 5 ps even at 1700 K. The high thermal stability of ptC structures was also reported in previous work.^{6d,12}

The perfectly planar structure of ptC strips at the edge of the Cu<ZGNR>Cu system stems from both steric and electronic stabilization. As shown in SI Table S1, the sum of van der Waals radii (2.80 Å) and covalent radii (2.64 Å) of two Cu atoms, as well as the Cu–Cu bond length (2.55 Å) in the bulk, all match the neighboring C–C distance (2.48 Å) very well along the edge direction. Hence little mechanical strain is incurred upon the edge decoration of the ZGNR by Cu atoms. In addition, the electronic stabilization may be imparted by both aromatic delocalization and the σ -donation from the electropositive groups.^{4a} The $2p_z$ orbital of the edge ptC is significantly delocalized in the ZGNR due to in-planar π -electrons. Furthermore, significant charge transfer from Cu to the ptC is found. Based on the Hirshfeld charge analysis, the ptC atom carries a -0.11 |e| negative charge, and the Cu atom has a positive charge (0.15 |e|) (cf. Table S2). In contrast, the interior C atoms of the ZGNR are nearly charge neutral. Figure 2a shows the deformation electronic density¹² of the Cu<8-ZGNR>Cu system. One can see that the edge ptC atoms form multicenter electron-deficient covalent bonds (blue regions in Figure 2a) with Cu atoms. The highest occupied electronic state (HOES) and the lowest unoccupied electronic state (LUES) at the gamma (Γ) point are displayed in Figure 2b and 2c, respectively. The HOES is mainly contributed by the $2p_z$ atomic orbitals of the ptC atoms. The LUES clearly shows multicenter bonding between ptC and Cu atoms, as well as a highly delocalized σ -orbital among peripheral Cu–Cu atoms. The electronic band structure and density of states of the Cu<8-ZGNR>Cu system are shown in Figure S5, which suggest that Cu<8-ZGNR>Cu is a spin-nonpolarized semiconductor with a band gap of ~ 0.42 eV. The Hirshfeld spin analysis reveals significant spin distribution to the edge ptC atoms (cf. Table S2). The two ptC strips are antiferromagnetically coupled with each other, even though the edge Cu atoms do not exhibit significant magnetism.

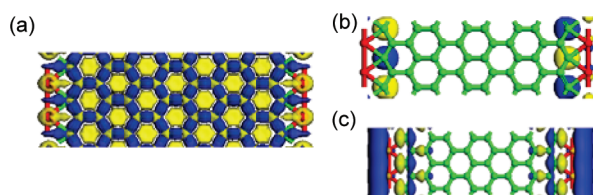


Figure 2. Iso-surface (0.05 e/au) of the deformation electronic density of Cu<8-ZGNR>Cu. Blue and yellow color represent electron-rich and -deficient region, respectively. The (b) highest occupied electronic state and (c) lowest unoccupied electronic state of the Cu<ZGNR>Cu at Γ point.

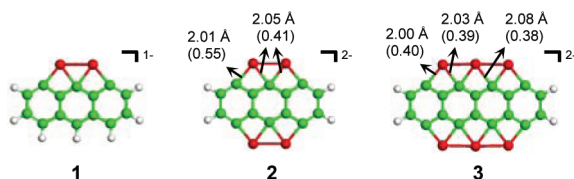


Figure 3. Structures and WBI (in parentheses) of molecular anions 1–3, where green, red, and white balls denote C, Cu, and H atoms, respectively.

To gain more insight into the bonding nature of ptC in Cu<ZGNR>Cu, we investigated three planar molecular systems 1–3 (see Figure 3). Since the number of Cu atoms in 1–3 is one less than that of edge carbon atoms at each edge, an extra electron is added for each Cu-decorated edge in order to mimic 1:1 ratio of Cu vs. ptC atoms in infinite ZGNRs. The anions 1–3 are all stable local minima (the lowest frequencies are listed in Table S3; a snapshot of each structure at the end of 5 ps quantum MD

simulation at 1000 K is shown in Figure S6). In the dianion 2 and 3, both sides of the molecules exhibit ptC centers. The Wiberg bond index (WBI) analysis and natural population analysis (NPA) were undertaken for 1–3 based on natural bonding orbital (NBO) calculation. As shown in Figure 3, the Cu–C bonds are weaker with the increasing number of ptC centers from 2 to 3, reflected by the smaller WBIs of Cu–C bonds in 3. However, the total WBI for the ptC is maintained at ~ 4.0 in 1–3. The NPA analysis suggests that Cu atoms are positively charged while the ptC is negatively charged, consistent with the Hirshfeld analysis for the periodic Cu<ZGNR>Cu system. In addition, the main features of the HOMO and LUMO of 3 are consistent with the HOES and LUES of the periodic system (cf Figure S7 for the HOMO and LUMO of 3). The natural electron configuration for the ptC centers in 3 is $2s^{0.98}2p_x^{1.02}2p_y^{1.02}2p_z^{1.2}$, suggesting that the stability of the ptC stems mainly from the delocalization of $2p_z$ electrons of ptC atoms, rather than from the σ -donation^{5b} from Cu atoms. In summary, the stability of multicenter ptC strips stems from both the highly delocalized π orbital of the ZGNR and nearly perfect match between Cu–Cu bonding geometries and the unpassivated carbon atoms at the ZGNR edges.

Acknowledgment. This work was supported by grants from the Office of Naval Research (N00014-05-1-0432), NSF (CMMI-0709333), and Nebraska Research Initiative and by the University of Nebraska Holland Computing Center.

Supporting Information Available: Charge analysis, electronic state, band structure, density of states, vibrational frequencies, Cu adsorption on ZGNR, snapshot of MD simulation, and complete ref 10 are presented. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Kekulé, A. *Justus Liebigs Ann. Chem.* **1857**, 104, 129. (b) van't Hoff, J. H. *Arch. Neerl. Sci. Exactes Nat.* **1874**, 445. (c) Le Bel, J. A. *Bull. Soc. Chim. Fr.* **1874**, 22, 337.
- (2) Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, 92, 4992.
- (3) (a) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, 98, 5419. (b) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, 99, 7886.
- (4) (a) Schleyer, P. v. R.; Boldyrev, A. I. *J. Chem. Soc., Chem. Commun.* **1991**, 113, 1536. (b) Rasmussen, D. R.; Radom, L. *Angew. Chem., Int. Ed.* **1999**, 38, 2876. (c) Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1998**, 120, 7967. (d) Merino, G.; Méndez-Rojas, M. A.; Vela, A. *J. Am. Chem. Soc.* **2003**, 125, 5026. (e) Wang, Z.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2001**, 123, 994. (f) Pei, Y.; Zeng, X. C. *J. Am. Chem. Soc.* **2008**, 130, 2580. (g) Wu, Y.-B.; Lu, H.-G.; Li, S.-D.; Wang, Z.-X. *J. Phys. Chem. A* **2009**, 113, 3395. (h) Erhardt, S.; Frenking, G.; Chen, Z.; Schleyer, P. v. R. *Angew. Chem., Int. Ed.* **2005**, 44, 1078. (i) Keese, R. *Chem. Rev.* **2006**, 106, 4787. (j) Jemmis, E. D.; Subramanian, G.; Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1997**, 119, 9504. (k) Rotger, D.; Erker, G. *Angew. Chem., Int. Ed.* **1997**, 36, 812. (l) Merino, G.; Méndez-Rojas, M. A.; Vela, A.; Heine, T. *J. Comput. Chem.* **2007**, 28, 362.
- (5) (a) Li, X.; Zhang, H.-F.; Wang, L. S.; Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1999**, 121, 6033. (b) Wang, L. S.; Boldyrev, A. I.; Li, X.; Simons, J. *J. Am. Chem. Soc.* **2000**, 122, 7681. (c) Li, X.; Zhang, H.-F.; Wang, L. S.; Geske, G. D.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2000**, 39, 3630. (d) Siebert, W.; Gunale, A. *Chem. Soc. Rev.* **1999**, 28, 367.
- (6) (a) Pancharatna, P. D.; Méndez-Rojas, M. A.; Merino, G.; Vela, A.; Hoffmann, R. *J. Am. Chem. Soc.* **2004**, 126, 15309. (b) Yang, L.-M.; Ding, Y.-H.; Sun, C.-C. *J. Am. Chem. Soc.* **2007**, 129, 658. (c) Geske, G. D.; Boldyrev, A. I. *Inorg. Chem.* **2002**, 41, 2795. (d) Wu, X.; Pei, Y.; Zeng, X. C. *Nano Lett.* **2009**, 9, 1577.
- (7) (a) Son, Y. W.; Cohen, M. L.; Louie, S. G. *Phys. Rev. Lett.* **2006**, 97, 216803. (b) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Firsov, A. A. *Science* **2004**, 306, 66.
- (8) (a) Kan, E. J.; Li, Z.; Yang, J. L.; Hou, J. G. *J. Am. Chem. Soc.* **2008**, 130, 4224. (b) Wu, M.; Wu, X.; Gao, Y.; Zeng, X. C. *Appl. Phys. Lett.* **2009**, 94, 22311. (c) Wu, M.; Wu, X.; Zeng, X. C. *J. Phys. Chem. C* **2010**, 114, 3937.
- (9) DMol³: Delley, B. *J. Chem. Phys.* **1990**, 92, 508; **2003**, 113, 7756. DMol³ 4.1 and 4.3 are available from Accelrys, San Diego.
- (10) Frisch, M. J. et al. *Gaussian 03*, rev. E.02; Gaussian, Inc.: Wallingford, CT, 2004.
- (11) Kresse, G.; Furthmuller, J. *Phys. Rev. B* **1996**, 54, 11169.
- (12) (a) Perez, N.; Heine, T.; Barthel, R.; Seifert, G.; Vela, A.; Méndez-Rojas, M. A.; Merino, G. *Org. Lett.* **2005**, 7, 1509. (b) Wu, Y.-B.; Jiang, J.-L.; Zhang, R.-W.; Wang, Z.-X. *Chem.–Eur. J.* **2010**, 16, 1271.

JA100206