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A notable phenomenon is described involving the polarization of valence electrons that operates in the edge regions of graphene materials, including compact polyaromatic hydrocarbon (PAH) molecules, because of the mismatch between interior and perimeter chemical bonds. The topology of hexagonal-shaped zigzag-edged systems, with alternating perimeter CC bond lengths, enhances the effect, making recognition easier, compared to graphene ribbons where it is weak. The phenomenon is delineated in \textit{ab initio} density-functional theory calculations of the electronic structure of a 4 nm diameter hexagonal zigzag-edged molecule C_{486}H_{54}, chosen because it is a representative of larger ones. Using CC bond length as a surrogate measure, we map the polarization of valence electrons from the perimeter to the center. In a pattern that mimics the bonding, the polarization of the two outermost sets of edge bonds (transverse along rows and radial connecting nested rows of carbon atoms) is impressed on the graphene interior bonds with amplitude that decreases rapidly from the perimeter to the center. All bonds display a decaying oscillation with radial bonds longer than transverse bonds at the same location. This difference leads to a characteristic quinoidal pattern of CC bonds linking the zigzag hexagonal edges joined at each apex. The phenomenon and its analysis are applicable to geometries periodic or not, substituent modified edges and interior.

Graphene sheets and large compact polyaromatic hydrocarbon (PAH) molecules offer the possibility of manufacturable nanoscale electronic devices and even computers on molecules. Three events have fueled these developments. Berger et al.\textsuperscript{1} demonstrated epitaxial growth of graphene monolayers and multilayers on silicon carbide. Novoselov et al.\textsuperscript{2} peeled micron-sized graphene sheets from graphite crystals. Wu et al.\textsuperscript{3} synthesized the large hexagonal molecule C_{222}H_{42}, demonstrating how the gap between molecules and flakes can be bridged from the small side. Exploitation of graphene materials for nanoelectronic applications requires a deep understanding of how edge topology impacts the geometric and electronic structures. In two dimensions (2D) there is no screening of long-range interactions and whereas the sigma CC bonding network is highly localized, the pi-bonding system is not so constrained. Witness the ability of the pi systems to couple spins on adjacent and distant edges.\textsuperscript{4}\textendash\textsuperscript{7} There has been much less effort in understanding the geometry.

We demonstrate an unusual effect, whereby the pi system of the edge atoms impresses on the interior, row by row, an electronic polarization characteristic of the edge topology. This polarization decays rapidly with distance from the perimeter into the interior so that after about four rows the latter has the properties of infinite graphene. Though the phenomenon is quite general, it is most clearly seen in large hexagonal-shaped graphene molecules with zigzag edges. Accordingly we examine one of these systems in detail and delay until later comment on general systems and the underlying physics.

We have determined the electronic and geometric structures of the singlet antiferromagnetic spin ground state, singlet spin paired, and lowest triplet state of C_{486}H_{54}, the $m$ = 9 member of a series of hexagonal-shaped PAHs with zigzag edges and general formula C_{6m+2}H_{2m} ($m$ = 2,\ldots,10). The geometries are all very similar, so we use only the singlet spin paired data in the figures. Based on trends along the entire series, the molecule C_{486}H_{54} has a graphene central zone, an established perimeter and is the first in the series to have a singlet ground state with an antiferromagnetic spin distribution on a hexagonally sectored bipartite lattice. The model for the interior is an infinite graphene. A suitable model for the perimeter does not exist. Useful comparisons are planar D_{6h} annulene C_{102}H_{102} that has almost uniform CC bonding along the chain and the linear D_{2h} acene nonacene C_{36}H_{32} that has decreasing bond alternation from each end, tending to uniform bonding in the middle of the molecule.

The calculations used \textit{ab initio} plane-wave-based density-functional theory (DFT) methodology, with projector augmented wave potentials\textsuperscript{8}\textendash\textsuperscript{10} and the spin polarized generalized gradient approximation with the exchange-correlation energy functional parametrized by Perdew et al.\textsuperscript{11} All valence electrons were included. The plane-wave energy cutoff was 400 eV. Calculations were done in a periodic tetragonal cell with $6.0 \times 6.0 \times 1.5$ nm\textsuperscript{3} edges. Atoms in different cells were more than 1.5 nm apart. Brillouin-zone integrations were done at the gamma point. Geometry optimization was done with atoms constrained to a plane until forces acting on any ion were less than 3.4 \textmu\text{eV}/\text{pm}. Room-temperature graphite has $a$ = 245.6 pm and CC=141.8 pm. Our calculations of periodic graphene yielded $a$ = 246.7 pm and bond CC=142.4 pm. These, similar to the previous ones,\textsuperscript{12} slightly exceed the experimental values.

Prior calculations showed that in PAHs the CC bond length is directly proportional to the maximum isometric surface charge (MISC) density on the stick bond joining carbon atoms.\textsuperscript{13} In a new set including acetylene, ethylene, ethane, benzene, pyrene, and coronene, a plot MISC vs CC length was almost linear in the range 120–153 pm. Using the CC bond length as a surrogate measure, we analyzed the isometric surfaces of the total valence charge density and obtained a description of the two zones, interior and perimeter, their separation by long radial CC bonds and the polarization of the interior valence charge patterned after the topology of the outermost set of transverse and radial bonds (notation: trans-
FIG. 1. (Color online) The main panel A shows a converged geometry of the (+,+) quadrant of molecule \(C_{48}H_{54}\) with stick bonds and an overlay of an isometric surface of the total charge density (\(\rho=2.02e/\text{Å}^3\)), together with the labeling of CC bonds used in text. Labels r1, r2,..., r9 on the left side indicate some of the nested hexagonal rows of carbon atoms. Panel B is a detail of the right side vertical edge. Inset panel Q shows an idealized quinoid ring in standard organic notation.

FIG. 2. (Color online) Plots of bond length (\(\text{Å}pm\)) vs row label for all CC bonds in the (+,+) quadrant of the molecule. The coordinate is the row number, integers (1, 2,..., 9) for the transverse and half odd integers (1.5, 2.5,..., 8.5) for the radial bonds. The inset panel shows the variation in length of transverse bonds along rows r9 and r8.
Radial bonds have a different trend, they exhibit little dispersion within their row, and all jump in length as the perimeter is approached. The radial bonds in the row 8.5 are the longest in the molecule. Radial bond variations along each row \( \{n.5 \text{ with } n=1,2, \ldots, 8\} \) are shown in Fig. 3. The row numbers are shown as half integer labels on the LHS of each curve. The curves show that there is little variation along a given row. The coordinate denotes the position along the row. In the direction of the center of the molecule, succeeding rows have one bond less. Accordingly in Fig. 3 each curve is centered on coordinate axis position 9, presenting an interdigitated set of points consistent with their spatial position in the molecule (see Fig. 1). The central point in the lowest curve marks the radial bond \( r1.5(b) \) on row \( r1.5 \) in Fig. 1. The curves have the property of being shape similar, meaning their shape is independent of the number of data points. The radial bonds, mostly constant within the row, decrease the most between the \( r8.5 \) and \( r7.5 \). Thereafter they converge quickly to the central value. This change in bond length with row can be fitted to a polynomial function. The near constancy of the radial bonds on a particular row is an important feature that provides the long bond sides of the quinoidal structures present within the real estate of each apex.

Figure 4 shows smooth curves drawn through data points for transverse bonds on each row from row \( r9 \) (perimeter) to row \( r1 \) (center). Note that in the middle of each row the transverse bonds converge from below on the bond length of the central row \( r1 \). This is opposite to the radial bonds, which converge from above and contributory factor to the bond-length oscillation seen in Fig. 2. Consider the transverse bonds of the perimeter row. In Fig. 1 these have the labels \( r9(q1) \) (mid row) to \( r9(q9) \) (apex) to \( r9(q26) \) (apex). Starting from the apex (Fig. 1, \( q9 \) or \( q26 \), CC \( \sim 136 \) pm), the bonds display a decreasing alternation toward a more uniform value in the middle of the edge, where CC \( \sim 141 \) pm. Although the main panel shows all the curves, only the easily distinguished ones in rows \( r9, r8, r7, \) and \( r1 \) are labeled. Curves for rows \( r6, r5, \) and \( r4 \) are shown separately in the middle set and curves for rows \( r3, r2, \) and \( r1 \) in the bottom set. The middle and lower data sets are shown displaced downward and have greatly expanded bond-length scales. The set of curves for the transverse bonds have a self-similar shape in the sense that each succeeding curve resembles the next longest row with the row end oscillations removed. Taken together these radial and transverse bond variations permit a detailed look at the range and distance dependence of the interior-perimeter interaction. Starting from the shortest bonds the curves serve to focus attention on the strong bond alternation along the perimeter. Their pattern, with the large apex oscillation and more uniform midedge value, resembles that found for the linear acene nonacene \( C_{38}H_{22} \), except for an offset due to the two cross-linking bonds at each end of the acene molecule.

The mechanism causing the polarization can be understood using the ideas underlying the Koster-Slater theory of impurity levels applied to edges. The difference between perimeter and interior atoms provides an interaction which localizes levels at the top of the valence band. The charge density of this collection of highest occupied molecular orbital (HOMO) levels is spread in a decaying fashion onto the neighboring interior rows, causing bond lengths to change. The topology of the perimeter controls the polarization pattern and which part of an interior row is most affected. Partial charge densities of the Kohn-Sham levels verify the localization and range of the polarization. By analogy with the Rashba effect in doped molecular crystals, other phenomena of a collective or cooperative nature may be manifested in graphenes.

The geometry of the representative hexagonal zigzag-edged molecule \( C_{48}H_{54} \) is the result of competing effects, the central region strives to adopt the geometry of infinite graphene and the zigzag perimeter in isolation strives for a uniformly conjugated geometry permitting pi-electron delocalization. The interaction between the interior and perimeter
results in CC bonds joining perimeter row (r9) to the penulti-
timate row (r8.5) getting long (but well short of single CC
= 153 pm), facilitating some separation of perimeter from
the interior. This elongation acts to reduce the polarizing
interaction of the perimeter across the radial row r8.5 bonds.
The net result is an imprinting from the edge onto the interior
of an electronic polarization which is manifest as self-similar
bond variations in the interior rows. In a hexagonal-shaped
zigzag system a direct consequence of these interactions is
the appearance of a pattern of linked quinoidal C6 rings ex-
tending out on either side of each apex.

For periodic zigzag-edged graphene strips the phenom-

enon is weak, present mostly in the radial bonds because
bonds with a projection on the periodic direction are con-
strained. Figure 5 shows the dependence of the CC bond
length (pm) for a simple zigzag nanoribbon that is 15 rings
wide (y axis) and one ring periodic along the x direction.
The periodic cell formula was C32H2. The change in transverse
bonds is about half or less of the radial bonds, and deviations
from the ribbon center occur only near the perimeter. Unit-
cell periodic width was set to the graphene distance corre-
sponding to CC = 142.4 pm. In the nanoribbons the occur-
rence of edge states localized in the density of states near the
Fermi level was recognized early on,16 but not the general
nature of the phenomenon as described here.

In large crenelated (arm chair) edged graphene molecules
the MISC polarization effect was observed17 within the apex
region as a regular C6 ring with six equilength radiating CC
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These results for the apexes of finite-sized molecules can
be generalized to periodic systems with protrusions, defects,
substituted, or derivatized edges and interior. In graphene
systems with ragged edges, defects, or substituents, there
will be a polarization distortion from the affected region im-
pressed on the interior bonds or surroundings. Its form will
be characteristic of the electronic and geometric structures of
the irregularity. Available scanning tunnel microscope (STM)
images of ragged graphene edges already hint at some of
these effects.19 Complex even rough geometries can be ana-
alyzed using the basic ideas presented here. The design of
graphene devices and study of graphene growth and
combustion20 will benefit from the understanding of edge vs
interior provided by this Brief Report.

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