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Families of carbon nanotubes: Graphyne-based nanotubes

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New families of carbon single-walled nanotubes are proposed and their electronic structures are investigated. These nanotubes, called graphynes, result from the elongation of covalent interconnections of graphite-based nanotubes by the introduction of *yne* groups. Analogously to ordinary nanotubes, armchair, zigzag, and chiral graphyne nanotubes are possible. We here predict the electronic properties of these unusual nanotubes using tight-binding and *ab initio* density functional methods. Of the three graphyne nanotube families analyzed here, two provide metallic behavior for armchair tubes and either metallic or semiconducting behavior for zigzag nanotubes. A diameter- and chirality-independent band gap is predicted for the other investigated graphyne family, as well as an oscillatory dependence of the effective mass on nanotube diameter.

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I. INTRODUCTION

The early report of graphite-based carbon nanotubes (CNT's) by Iijima[1] generated an enormous amount of research activity. New and exciting phenomena have been observed,[2] including field emission,[3] quantum conductance,[4] superconductivity,[5] higher thermal conductivity than diamond,[6] and constant-force nanosprings[7] as well as proposals of CNT-based nanodevices.[8,9] Depending upon structure, the nanotubes are either metallic or semiconducting, which is a feature that has been intensively investigated and exploited in prototype devices.[2]

Alternative structures containing heteroatoms (N, B, etc.) in the nanotubes, as well as various carbon-free nanofibers, have been recently synthesized.[2] While previous work has focused on graphitic nanotubes, we believe that other types of pure carbon nanotubes are feasible using different accessible hybridization states of carbon. One possibility that has been overlooked in the literature is to use graphyne sheets as the structural motif for carbon nanotubes. Graphyne is an allotropic form of carbon proposed by Baughman, Eckhardt, and Kertesz[10] in 1987, which has recently become the focus of new investigations.[11–13] Graphyne is the name for the lowest-energy member of a family of carbon phases consisting of planar molecular sheets containing only sp and sp^2 carbon atoms. The presence of acetylenic groups in these structures introduces a rich variety of optical and electronic properties that are quite different from those of ordinary carbon nanotubes.

As there are many different types of graphynes,[10] various new families of pure carbon nanotubes can be generated that have different electronic and structural characteristics. Just as a sheet of graphite (graphene) can be rolled to form different types of CNT's, armchair, zigzag, or chiral, various graphyne-based nanotubes (GNT's) are similarly possible (Fig. 1). In addition, the usual (n,m) nomenclature used to describe CNT's can be preserved.

In this paper, we report electronic properties for three families of graphynes (as both infinite planar sheets and nanotubes) using tight-binding (TB) and *ab initio* density functional methods. While one of these nanotube families behaves like CNT's, unusual characteristics are predicted for the others. Among these characteristics are a fractional rule for metallic zigzag nanotubes and a band gap independent from diameter and chirality values.

II. METHODOLOGY

A single-walled CNT can be considered heuristically as formed by rolling a graphene sheet to make a seamless cylinder.[2,14] In the same way we can imagine GNT's as formed by rolling graphyne sheets to form quite different seamless cylinders. Figure 1 represents this process for graphene [Fig. 1(a)] and for two types of graphyne sheets [Figs. 1(b) and 1(c)]. Figure 2 shows three-dimensional

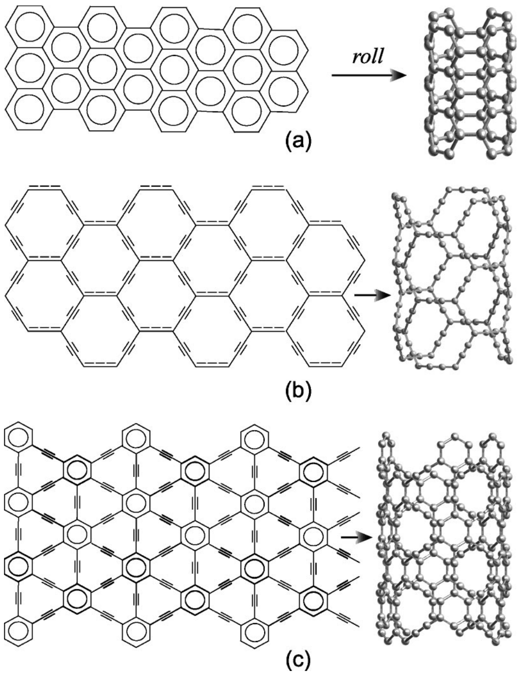

FIG. 1. The structural relationships between carbon sheets and single-wall carbon nanotubes for sheets of (a) graphene (a graphite sheet), (b) α-graphyne, and (c) γ-graphyne. Depending upon the axis used for rolling the carbon sheet to make a seamless cylinder, the nanotube is armchair [(a) and (b), right], zigzag [(c), right], or chiral.

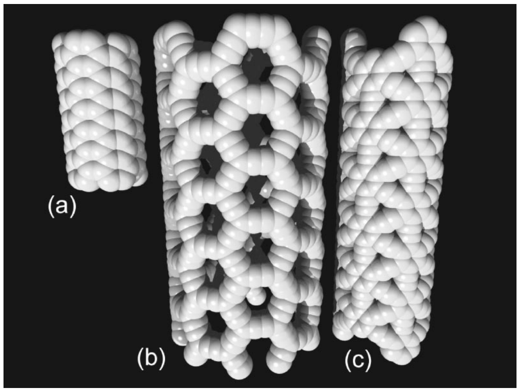

FIG. 2. Three-dimensional view of (a) a conventional armchair nanotube (CNT) based on a graphene sheet, (b) an armchair nanotube (α-GNT) based on an α-graphyne sheet, and (c) a zigzag nanotube (γ-GNT) based on a γ-graphyne sheet (Fig. 1). The increase in nanotube sidewall porosity in going from a CNT to a γ-GNT and an α-GNT is evident. The same van der Waals radius was used for all structures.

views of the tube structures shown in Fig. 1. We can see in this figure the first important difference between CNT's and GNT's: the graphyne nanotubes have porous sidewalls. This is an interesting aspect, since this porosity should facilitate materials transport through the nanotube sidewalls, which could be important for materials storage and electrochemical charging processes. In fact, selected dopants could even reside in the pore volume of the nanotube walls.

Three types of graphyne sheets, having the same space group as graphene ($p6m$), are considered in this paper. The first one, which we named α-graphyne, was chosen since it is most analogous to graphene. The graphene and α-graphyne chemical structures are shown in Fig. 3. The second type of graphyne, β-graphyne, is represented in Fig. 4(a). Its structure is a modification of the α-graphyne where the hexagons are covalently interconnected by double bonds. Therefore, comparison of these two families provides a good way to analyze the effects of structure on electronic structure. The last family analyzed here [Fig. 4(b)], named γ-graphyne, was chosen since it is the lowest-energy member of the graphyne family and it is the most likely to be synthesized.

We have used two approaches for evaluating the band structures of these sheets and nanotubes. Tight-binding calculations were carried out using the methodology of Saito *et al.*[15] and Wallace.[16] Following the Wallace[16] methodology for TB calculations, each carbon atom is described by one $2p_z$ orbital with first-neighbor interactions. The molecular orbital energy and hopping integral values were calculated in the extended Hückel theory framework,[17] using the parametrization proposed by Clementi and Raimondi.[18] The overlap integrals were calculated using the approach of Mulliken *et al.*[19] The TB approach used here overestimates energies (band gaps, for instance) but good qualitative agreement with *ab initio* results have been observed.

We have also performed *ab initio* density functional (DFT) calculations for the graphyne sheets using the SIESTA code[20] in the generalized gradient approximation, with a Perdew-Burke-Ernzerhof exchange-correlation functional.[21] The interactions between the valence electrons and ionic cores are described through fully nonlocal norm-conserving Troullier-Martins pseudopotentials.[22] A double-ζ basis set with polarization orbitals was used with core radii of 2.2 and 2.6 Å for $2s$ and $2p$ basis orbitals, respectively.

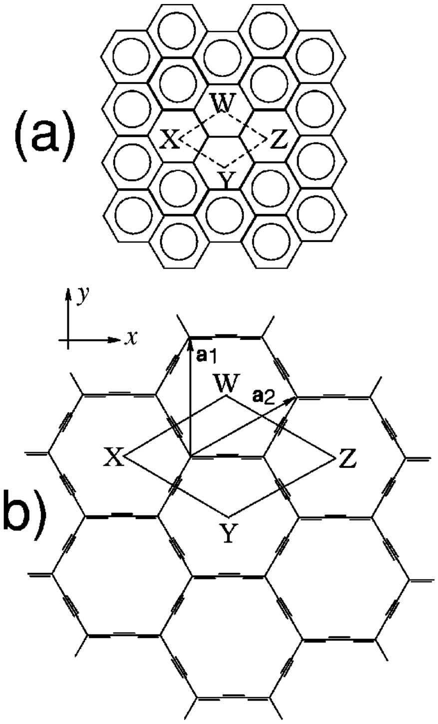

FIG. 3. Schematic chemical structure and unit cell representation for (a) graphene and (b) α-graphyne sheets (Ref. 10). The lattice vectors are given by $\mathbf{a}_1 = a\hat{y}$ and $\mathbf{a}_2 = a(\sqrt{3}\hat{x}/2 + \hat{y}/2)$. The construction of the unit cell *XYZW* in (b) is straightforwardly obtained from its equivalent in (a). The α-graphyne unit cell has eight atoms. This unit cell pertains both for the pictured bonding structure and for the case where all linkages in the structure become equivalent as a result of resonance.

Although the TB approach is quite simple, comparison of predictions of the TB and DFT methods shows that the main electronic features of graphyne-related structures (sheets and tubes) are reliably predicted using this method. Also, the TB approach has the major advantage that the geometrical transformation of a flat sheet into cylinders (nanotubes) can be easily simulated using the "slicing" process.[2] This process obtains the band structure of a nanotube through application of constraints predicted for the analogous planar sheet structure. This approach is not feasible using DFT methods. Thus, the GNT band structure was derived from the calculated band structure of the corresponding planar sheet using the TB approach.

III. RESULTS AND DISCUSSIONS

A. α-graphyne tubes

The geometry optimization of the α-graphyne structure was carried out using SIESTA.[20] The final geometry obtained is a perfect hexagon with the following distribution of bond

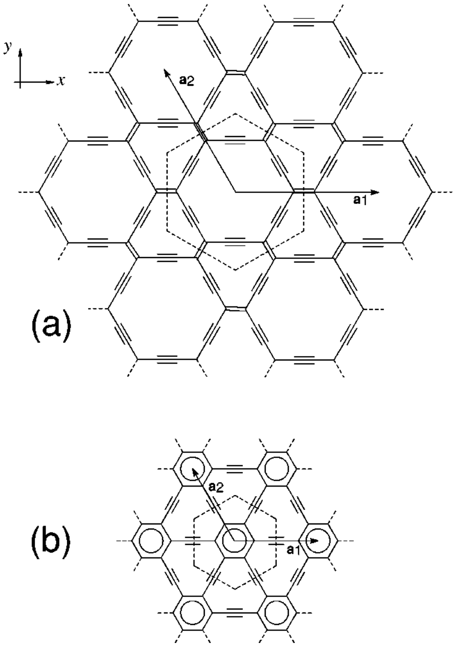

FIG. 4. Schematic chemical structure and unit cell representation for (a) β-graphyne and (b) γ-graphyne sheets (Ref. 10). The lattice vectors are given by $\mathbf{a}_1 = a\hat{x}$ and $\mathbf{a}_2 = a(-\hat{x}/2 + \sqrt{3}\hat{y}/2)$. The unit cell of β-graphyne (γ-graphyne) sheet has 18 (12) atoms.

lengths for each side: 1.4, 1.244, and 1.4 Å. The corresponding lattice parameter obtained is $a = 4.04\times\sqrt{3}$ Å. Because of this equivalence of the sides of the hexagons, α-graphyne is analogous to graphene, which facilitates comparison between α-GNT's and CNT's.

The construction of zigzag and armchair α-GNT's is done analogously to the case of CNT's. Defining the chiral vector as $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 = (n,m)$ (n,m integers), zigzag and armchair tubes are generated from $(n,0)$ and (n,n) chiral vectors [Fig. 3(b)], respectively.

Figure 5 shows the band structure for the graphene and α-graphyne sheets obtained from DFT calculations, which are qualitatively similar. Hence, we can expect similar behavior for nanotubes of α-graphyne and graphite.

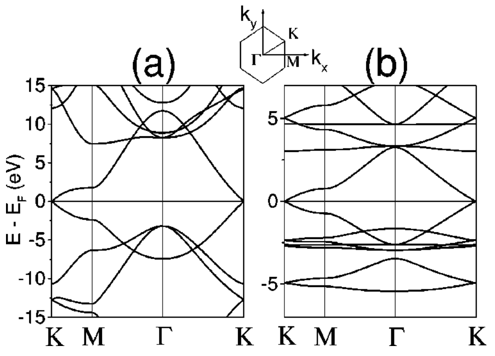

FIG. 5. Band structure of (a) graphene ($a = 1.42$ Å) and (b) α-graphyne sheets obtained from DFT calculations. The Brillouin zone is also shown. E_F is the Fermi energy.

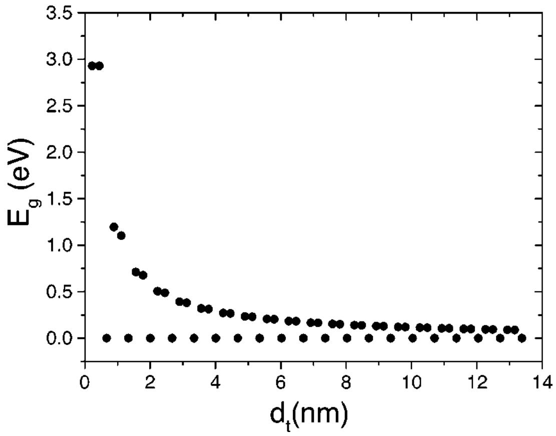

FIG. 6. Band-gap variation for zigzag α-GNT's obtained from TB calculations.

In order to derive α-GNT properties, we have also evaluated the band structure for a α-graphyne sheet using TB calculations and the previously described geometry. From these results we have extracted the α-GNT's band structures. We predict metallic behavior for all armchair α-GNT's and either metallic or semiconducting behaviors for zigzag α-GNT's. Furthermore, the same rule applies for determining which zigzag CNT's and GNT's are metallic; i.e., the nanotubes are metallic only when n is a multiple of 3. This aspect can be observed in Fig. 6 from the band-gap E_g variation with the tube diameter $d_t = na/\pi$. The expected gap decrease with increasing GNT diameter is evident, as well as the oscillatory behavior of band gap with increasing values of n.

B. β-graphyne tubes

A perfect hexagon was assumed for the β-graphyne sheet with bond lengths of 1.43, 1.2, and 1.34 Å for the single, triple, and double bonds [Fig. 4(a)], respectively.[10] The corresponding lattice parameter is $a = 9.46$ Å. Zigzag β-GNT's are defined by $(2m,m)$ and armchair ones by $(n,0)$ combinations.

Figure 7 shows the band structure calculated for a β-graphyne sheet using the DFT method. The point of band crossing predicted for a β-graphyne sheet occurs on a differ-

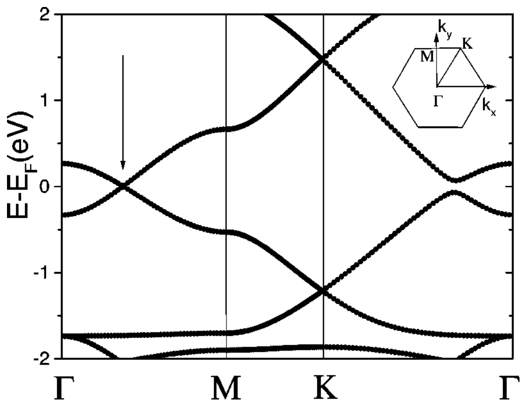

FIG. 7. Band structure of the β-graphyne sheet obtained from DFT calculations. The arrow indicates the point ($\vec{k}^*$) where the band crossing occurs.

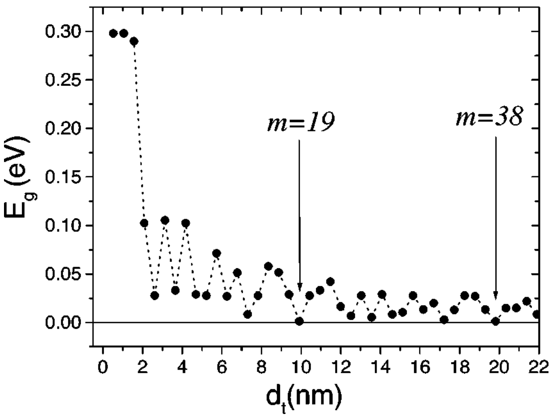

FIG. 8. Tube diameter dependence of the zigzag β-GNT's band gap obtained from TB calculations. The arrows indicate the m values where metallic behavior is expected. The dotted line just connects the points.

ent position than for α-graphyne and, consequently, the rule for metallic behavior is altered. This point for the β-graphyne sheet is $\vec{k}^* = \lambda \pi / a\hat{y}$ ($\lambda \cong 0.487$ from TB calculations and $\lambda \cong 0.425$ from DFT calculations). From the band structure of the sheet (Fig. 7), all armchair β-GNT's are predicted to be metallic. This is due to the occurrence of $\vec{k}^*$ in the ΓM direction, which is always reached by the selected k points through the armchair GNT quantization rule.

On the other hand, the occurrence of metallic or semiconducting behavior for zigzag β-GNT's is not a simple function of diameter. The rule for obtaining metallic zigzag GNT's can be derived by equaling $\vec{k}^*$ to the zigzag β-GNT quantization rule, i.e.,

$$k_y^* = \frac{2\pi}{\sqrt{3}a}\frac{l_m}{m}, \quad l_m = 1,2,3,\ldots,2m, \tag{1}$$

which leads to (for λ_{DFT})

$$m \cong 2.72l, \quad l = 1,2,3,\ldots\ldots \tag{2}$$

In other words, a fractional number rule predicts metallic behavior for the zigzag β-GNT's, which is satisfied for l values that make m integer. This rule, different from the multiple of 3 rule for CNT's and α-GNT's, has not been previously observed or predicted for any carbon nanotube type (either pure carbon or containing heteroatoms). Figure 8 illustrates the calculated behavior, which includes a nonuniform band-gap decrease with increasing diameter. The first predicted "metallic" nanotube is the (38,19) β-GNT ($l = 7$). However, due to the rapid diameter increase with increasing m (due to the large unit cell of the sheet), metallic behavior is expected to occur before $m = 38$ (the second expected metallic zigzag β-GNT) for finite temperatures.

C. γ-graphyne tubes

The electronic properties of the γ-graphyne sheet has been investigated by Narita *et al.*[11] using *ab initio* methods and the local density approximation (LDA). They obtained a band gap of 0.52 eV, which is below the 1.2 value predicted by Baughman, Eckhardt, and Kertesz.[10] For comparison, and to obtain the γ-GNT band structures, we also calculated the band structure for a γ-graphyne sheet.

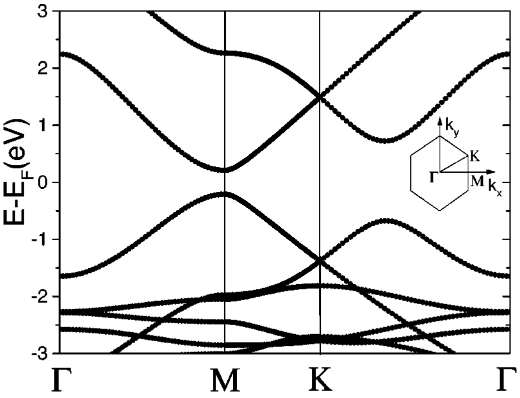

FIG. 9. Band structure of the γ-graphyne sheet obtained from DFT calculations.

Perfect hexagons were assumed with the bond lengths obtained from geometry optimization by Narita *et al.*[11] [1.42, 1.40, and 1.22 Å for $C(sp^2)-C(sp^2)$, $C(sp^2)-C(sp)$, and $C(sp)\equiv C(sp)$ bonds, respectively, and $a = 6.86$ Å]. These values are consistent with those obtained in Ref. 10 using the modified neglect of differential overlap quantum chemical method. Figure 9 presents the DFT results for a sheet of γ-graphyne. Using this method the band gap is predicted to be 0.42 eV at the M point. LDA calculations, using a Ceperley-Alder exchange-correlation functional, have also been carried out (not presented here) and provide a predicted $E_g = 0.39$ eV. The TB calculations predict $E_g = 1.3$ eV.

Like β-GNT's, zigzag γ-GNT's are defined by $(2m,m)$ and armchair ones by $(n,0)$ combinations (Fig. 4). In Fig. 10 we show the band structure of some γ-GNT's obtained from TB calculations. These bands represent the behavior of all armchair and zigzag γ-GNT's. The n odd and even armchair nanotubes will have the same qualitative behavior of the pre-

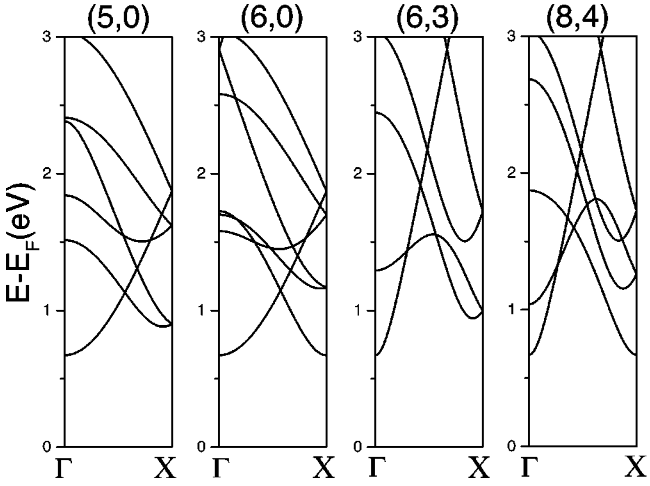

FIG. 10. Band structure of four γ-GNT's obtained from TB calculations. X points for armchair and zigzag γ-GNT's correspond to $k = \pm \pi / \sqrt{3}a$ and $k = \pm \pi / a$, respectively.

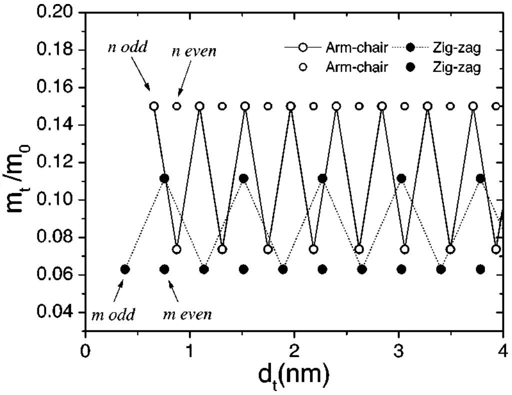

FIG. 11. Dependence of the tube effective mass m_t^* on the tube diameter (d_t) for γ-GNT's. These effective masses correspond to the Γ and X points of the Fig. 10. The numerical values plotted here were determined using $0.15m_0$ for the $\Gamma \rightarrow M$ and $0.063m_0$ for the $M \rightarrow K$ direction, which are from Narita *et al.* (Ref. 11). m_0 is the electron mass.

sented (5,0) and (6,0) nanotubes, respectively. Thus, n odd armchair γ-GNT's will have the band gap at $k=0$ (Γ point) and n even armchair γ-GNT's will have the band gap at Γ and X points. The same results are predicted for the zigzag γ-GNT's. Chiral γ-GNT's (not presented here) also present the same band gap but with different patterns. Moreover, the band-gap value is the same for all γ-GNT's, showing a diameter independence characteristic. This new predicted property arises because the selected tube k values (by the slicing technique) always reach the M point (energy minimum value) on the sheet band structure.

Since the γ-GNT's present either one or two k points associated with band gaps, important nanotube properties depend upon tube type. One of these characteristics is the effective mass and its dependence on nanotube diameter for the armchair and zigzag tubes represented in Fig. 11. Differences in effective mass can lead to different optical and electronic transport properties for the various γ-GNT's. Furthermore, preliminary studies[23] have shown that the dimensional changes resulting from charge injection are different when one or two k points are responsible for the electronic behavior of the nanotubes.

The stability of forms of graphyne and methods of synthesis are key remaining issues. γ-graphyne is more attractive for synthesis efforts than is β-graphyne, since it has lower energy and much higher expected stability. The molecules shown in Fig. 12 have been synthesized, as well as more complex molecules that contain the carbon bonding arrangement of γ-graphyne.[24,25] Since conversion of either planar γ-graphyne or a graphyne nanotube to graphite and a ordinary single-walled carbon nanotube, respectively, would require the rupture of at least one carbon bond for every six carbons, high stability is suggested. High stability is also found for known molecules that contain fragments of the graphyne structure. Pioneering synthesis efforts in different laboratories have already produced large fragments of a graphyne sheet.[26–31] Hence, there are reasons to believe that the synthesis of large sheets of graphyne may be soon achieved.

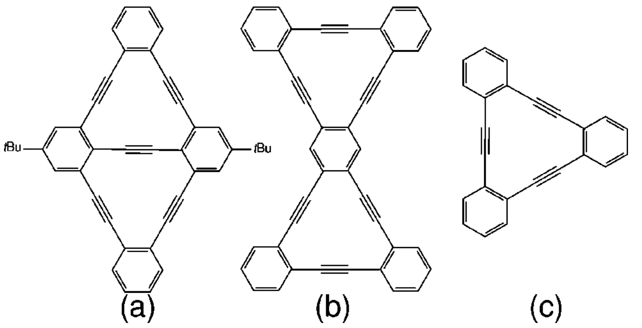

FIG. 12. Synthesized subunits of a γ-graphyne sheet (Ref. 25).

In addition to having interesting electronic and electrochemical properties, γ-graphynes are expected to have interesting third-order nonlinear optical properties,[13] similarly to recently observed for structurally related dendrimeric supermolecules.[32–34]

IV. CONCLUSIONS

In summary, the proposed new families of single-walled carbon nanotubes show even richer variation in electronic properties than do ordinary single-wall nanotubes. α-GNT's present electronic properties similar to the usual carbon nanotubes. On the other hand, armchair β-GNT's are metallic while zigzag ones present either metallic or semiconducting behavior depending on a fractional rule for the tube indice m. A band gap (0.4–0.5 eV) that is independent of nanotube diameter is predicted for γ-GNT's. The holes in graphyne-based nanotubes shells can enable unprecedented shell doping, as well as rapid materials transport through the nanotube sidewalls. Reflecting interest in these unusual properties, we are now trying to make GNT's, so that the fascinating predicted properties can be experimentally investigated.

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